THESIS ON MECHANICAL ENGINEERING E84

Thermoreactive Polymer Composite with High Particulate Filler Content

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PRESS

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Declaration:
I hereby declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been previously submitted for a doctoral or equivalent academic degree.

/Aare Aruniit/

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AARE ARUNIIT

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KIRJASTUS

Design is so simple, that's why it is so complicated.

- Paul Rand

CONTENTS

LIST OF PUBLICATIONS

The present dissertation is based on the following papers, which are referred in the text by their Roman numerals:

I Aruniit, A.; Kers, J.; Tall, K. (2011). Influence of filler proportion on mechanical and physical properties of particulate composite. *Agronomy Research*, 5(1), 23-29.

II Aruniit, A.; Kers, J.; Majak, J.; Krumme, A.; Tall, K. (2012). Influence of hollow glass microspheres on the mechanical and physical properties and cost of particle reinforced polymer composites. *Proceedings of the Estonian Academy of Sciences*, 61(3), 160-165.

III Aruniit, A.; Kers, J.; Krumme, A.; Poltimäe, T.; Tall, K. (2012). Preliminary Study of the Influence of Post Curing Parameters to the Particle Reinforced Composite's Mechanical and Physical Properties. *Materials Science*, 18(3), 256-261.

IV Aruniit, A.; Antonov, M.; Kers, J.; Krumme, A. (2014). Determination of Resistance to Wear of Particulate Composite. *Key Engineering Materials*, 604, 188-191.

V Aruniit, A.; Kers, J.; Krumme, A.; Peetsalu, P. (2014). Particle size and proportion influence to impact properties of particulate polymer composite. – *Proceedings of the 9th International Conference of DAAAM Baltic Industrial Engineering: 24-26 April 2014, Tallinn, Estonia.* (forthcoming)

The content of the thesis has been presented at the following conferences

1. International Scientific Conference "Biosystems Engineering 2011", 12-13 May 2011, Tartu, Estonia.
2. 18th International Conference on Composite Materials (ICCM 18), 21-26 August 2011, South Korea.
3. Baltic Polymer Symposium 2011 (BPS 2011), 21-24 September 2011, Pärnu, Estonia.
4. 20th International Baltic Conference "Materials Engineering 2011", 27-28 October 2011, Kaunas, Lithuania.
5. 15th European Conference on Composite Materials (ECCM 15), 24-28 June 2012, Venice, Italy.
6. Baltic Polymer Symposium 2012 (BPS 2012), 19-22 September 2012, Liepaja, Latvia.
7. 19th International Conference on Composite Materials (ICCM 19), 28 July - 2 August 2013, Montreal, Canada.
8. 22nd International Baltic Conference of Engineering Materials & Tribology (BALTMATTRIB 2013), 14-15 November 2013, Riga, Latvia.
9. 9th International DAAAM Baltic Conference – Industrial Engineering, 24-26 April, Tallinn, Estonia.

FOREWORD

The thesis presents a synergistic study of a polymer composite and its production technology. The research was a cooperation of three parties – the author, Tallinn University of Technology and Wellspa LLC. The author is employed as Technical and Development Manager at the company. The project was realized through the DoRa 3 program "Research cooperation between universities and businesses" that combines doctoral studies and a position at a company or an R&D institution in Estonia.

Balteco Ltd has been developing and manufacturing bathtubs and spa equipment since 1990. At the moment it is the biggest company in its field in Northern Europe. Wellspa LLC is a subsidiary of Balteco that manufactures jacuzzis and wellness capsules. In 2009 a new production line was installed and Wellspa started the production of engineered stone bathware. However, machinery without know-how is of no use. This led to this research project.

The motivation of the company is to offer a product that fulfils customers' expectations and market it at a competitive price. The author aims to glean new knowledge and a more complete perspective of academia. TUT strengthens its ties with the industry and helps to develop a knowledge-based economy together with efficient production technologies.

INTRODUCTION

Composite materials are taking over in all industries. This is due to the search for more efficient solutions. The search is driven by cost, design and environmental considerations. The same applies to interior decoration products and materials.

By combining mineral powders with polymers a composite material is formed that opens up new opportunities. The engineered stone can be casted into shapes and is easily machinable. Polymer gives ductility and mineral adds hardness.

Engineered stone is mostly sold as sheet material and used for making counter tops and in interior-exterior decoration. In addition, it is casted into shapes and due to its lower density and better mechanical properties used as a substitute for concrete. Engineered stone is fabricated with vacuum assisted extruders. The pore free dispersion is casted onto conveyer for making sheets or into moulds to form shapes.

In bathware sector engineered stone products have gained considerable attention and market share in recent years. The material provides freedom of design, sturdiness, and longevity compared to alternatives. Nevertheless, as the material is in the introduction phase of the life cycle there is room for improvement.

The **object** of the research is a particulate polymer composite material that is suitable for casting shaped products of uniform structure and composition throughout the thickness.

The objectives of the research are:

- The main objective is to design the material targeting economically viable and low density composition that assures good mechanical, functional, and technological properties.
- The first sub-objective is to examine the physical-mechanical properties and economical aspects of the proposed composition with experimental methods and numerical modelling.
- The second sub-objective is to evaluate and improve the functional properties like stain, wear, and impact resistance of the attained material.
- The third sub-objective is to develop an efficient production process and assure constant quality of the chosen material composition.

The research activities included:

- Optimisation of the filler and matrix proportion.
- Study of low density fillers and hard reinforcing particles.
- Study of the influence of composition and curing conditions to the polymerisation of the composite material.
- Study of the effect of surface roughness to staining.
- Study of tribological and thermo-mechanical properties.
- Study of the crack propagation mechanisms.

- Study of the influence of the post-curing process to the properties of the composite material.
- Study of the morphology of the filler.
- Study of particle aggregation and sedimentation.

The research is mainly based on experimental work to achieve the objectives outlined above. The complexity of failure mechanisms and the influence of environmental and fabrication variables limit the use of virtual testing and analytical modelling techniques. Experiments are often more sound due to prompt feedback and lower cost.

Fillers are traditionally utilised in thermoplastic resins. In addition, the interest of many scientists is the reinforcement of high-performance thermoreactive resins like epoxy with 2-5 wt% of nano-particles. The commodity thermoreactive resins and established fillers are overlooked. On the other hand, these materials are used in new applications and the industry is looking for innovative solutions. The **novelty** of this research is the study of a thermoreactive composite with filler content exceeding 60 wt%.

The thesis presents the results of 4 years of co-development and the current knowledge on particle reinforced polymer composites. The work has resulted in a new combination of matrix, reinforcement and additives with better material and technological properties. This not only improves the products and competitiveness of one company but can also be expanded to contribute to the quality and price of other products. Moreover, the acquired practical skills and methodology are applicable with other novel particulate composites. The acquired know-how within both industry and research contributes to developing innovative, knowledge-intensive and globally competitive polymer composite products in Estonia.

The structure of the thesis differs from the traditional approach. It is divided into four chapters that cover the four objectives. As the thesis combines different disciplines, the chosen structure gives in the author's opinion a more fluent overview and is easier to follow for a non-academic reader.

ABBREVIATIONS AND SYMBOLS

Abbreviations:
ATH – aluminium trihydrate
COF – coefficient of friction
DSC – differential scanning calorimetry
FEM – finite element modelling
HGM – hollow glass microspheres
MEKP – methyl ethyl ketone peroxide.
NPC – not post-cured
PI – polyimide
PTFE – polytetrafluoroethylene
PA – polyamide
PEEK – polyether ether ketone
RT – room temperature (23 °C)
SEM – scanning electron microscopy
TDS – technical data sheet
UHMWPE – ultra high molecular weight polyethylene
vol% – volume fraction
wt% – mass fraction

Symbols:
$C_{\%}$ – percent of cure
D – maximum particle size in each particle size-fraction
d_{50} – average particle size
D_{max} – max desired particle size
d_p – particle diameter
D_s – inter-particle spacing
F_n – normal force
G_c – fracture toughness
G_m – fracture toughness of matrix
H – indentation hardness
k – proportionality constant
k_p – constant (function of the particle vol%)
L – line tension
m_a – specimen weight in air
m_f – specimen weight in fluid
R – materials resistance to crack extension
R-curve – a plot of R against crack extension
S – constant (depends on interface adhesion)
T – temperature
t – time
T_g – glass transition temperature
V – volume worn per unit sliding distance
V_p – particle volume fraction

W_s – weight per cent of each fraction
ε – elongation to break
μ – coefficient of friction
ρ_{bulk} – bulk density
ρ_f – density of the fluid
$\rho_{specific}$ – specific density
σ – strength
σ_c – composite strength
σ_m – matrix strength
σ_u – ultimate tensile strength
σ^* – limit value of stress
φ – porosity
ΔH_{cured} – heat of cure of post-cured sample
$\Delta H_{uncured}$ – heat of cure of room temperature cured sample
$\bar{x}$ – vector of design variables
x_i^* – upper bounds of the design variables
x_{i*} – lower bounds of the design variables

1. DESIGN OF THE MATERIAL

The first assignment was to understand the concept of particulate polymer composite and formulate the needs of consumer and requirements of production in order to choose the main components. Second task was to propose a preliminary composition of the composite material.

The design of the material is an iterative process. The composition is altered as new knowledge is gained. Each of the following paragraphs contributes to the design of the material.

1.1 Essence of particulate polymer composite

Polymer composites consist of two or more components and two or more phases – one being a polymer matrix and the other reinforcement. Additives may be continuous like long fibres that run through the entire product or discontinuous like short fibres or particles. Polymer composites reinforced with the former are often referred to as high-performance composites and the latter as low-performance composites. Based on the nature of the reinforcement the same materials are also known as macrocomposites and microcomposites or in case the dispersed fibres or particles are in the nano scale, nanocomposites. [1]

In case of particulate polymer composites (alternatively particle reinforced composites) the reinforcement is in the form of particles. The term "reinforcement" is appropriate if the particles are used to enhance the mechanical properties of the composite (the particle wt% is usually < 20%). In case the particles have cost reduction purpose and are used at 40-60wt% level it is more appropriate to name the particles as filler. In addition to the main particulate phase particulate additives are used to enhance specific properties (electrical, hardness etc.). These materials form a secondary phase and they amount usually under 5 wt%.

Reinforcing particles can be natural or synthetic, organic or inorganic solid material. Particles may have irregular, acicular, flaky or spherical shape. When used in bulk particles are referred to as filler. The demonstrative characteristics of filler are the particle size, the particle size distribution, the particle shape, the way in which the particles pack together, particles surface area and surface treatment. The particles used in polymer composites are in microscale (micrometer to millimeter size) or nanoscale. Particulate filler loadings are usually 5-40% by weight in thermoplastics. Katz [2] predicts that compounds with 75 parts of filler per 100 parts of resin could be common. Particulate fillers are used for a variety of reasons: for cost reduction, to enhance mechanical properties and appearance, to modify electrical or thermal properties or to adjust rheology and shrinkage. The use of fillers took off during the oil crisis in the 1970s although they have been in use since the early days of phenolic plastics [2]. There is an endless list of possible particulate fillers because almost anything in the form of solid particles could be added to a polymer matrix. Based on Table 1.1 the current market leaders by volume are: 1) carbon black,

2) $CaCO_3$ 3) silica, 4) $Al(OH)_3$ 5) talc, and 6) kaolin [3]. Each filler has its own unique set of features and applications.

Synthetic polymers are divided into thermoreactives and thermoplastics. Thermoreactives account for 15% of worldwide polymer production [4]. Most widely used thermoreactive resins are unsaturated polyesters, phenolics, formaldehydes, polyurethanes and epoxies [4]. Thermoreactive resins are generally low-viscosity liquids. Thermoreactives usually have higher mechanical properties than thermoplastics because of cross-linking and they tolerate higher temperatures. At the same time, they are more brittle and manufacturing technologies are less efficient. It has been said that due to their brittleness many thermoreactive resins would be practically useless without fillers or fibres [1].

1.1.1 Engineered stone

Part of the thermoreactive resins reinforced with discontinuous phase is used for casting applications. These include construction (polymer concrete), decoration (decorative figures, flex trim mouldings) and furniture (countertops, bathware).

In the industry of bathware and interior products a major distinction is made in whether the casted particulate polymer composite has a surface coating (gel-coat) or not. The material that has a gel-coat is commercially called *Cultured Marble* and the material without it is known as *Solid Surface*. The latter is the focus of the current thesis. It is also called *artificial stone* due to the resemblance by look and feel to natural minerals.

The main matrix resins used for casting the non-gel coated composite are unsaturated polyester, acrylic or modified unsaturated polyester resin. The discontinuous reinforcement varies as well and is often the subject of differentiation for manufacturers. The most frequently used reinforcement is aluminium hydroxide. Other popular choices are quartz and wollastonite.

The material under study in the current thesis is composed of aluminium hydroxide and unsaturated polyester resin. The material is used for producing bathware like bathtubs, washbasins, shower trays and steam cabins. This sets the requirements and constraints to the composition of the material. In order to fulfil functional expectations the material must have high surface hardness in order to be scratch and wear resistant, chemically inert to be stain resistant, stiff to provide sturdy footing, temperature resistant to withstand steam and boiling water, stable to weathering by water and UV, impact resistant to withstand accidentally dropped objects and fungal resistant. On the other hand, the composition must provide proper rheological properties for casting large shaped products, machinability and cost efficiency. These are proper challenges for any research.

1.2 Unsaturated polyester resin

The purpose of the matrix is to bind together the reinforcement, to protect it from environmental effects and to transfer load to the reinforcement [5].

Unsaturated polyesters have a history of 80 years. First patents were registered in the 1930's. The invention is ascribed to Carleton Ellis. He discovered that the addition of reactive monomers like styrene leads to fast copolymerisation. The added benefit of styrene is the reduced viscosity of the polymer that makes it easier to handle and use. Commercial production started in 1941 when the resin was used together with glass fibre reinforcement to build radomes. [6]

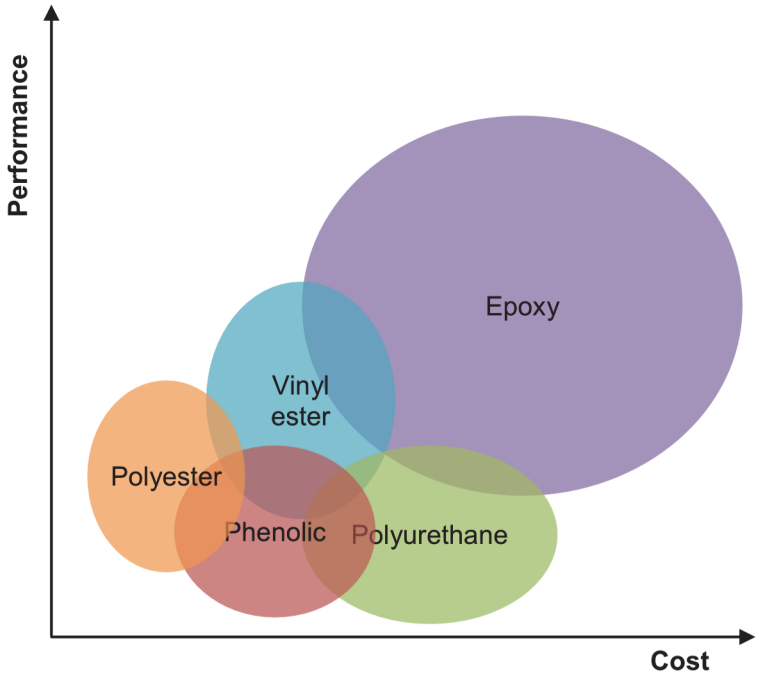

Figure 1.1 The performance and cost comparison of main thermoreactive resins (redrawn from [7])

The global unsaturated polyester market was valued at € 460 billion in 2012 and is expected to rise to € 736 billion in 2019. The expected compound annual growth rate in the period 2013-2019 is 7.5%. In terms of volume, the market demand in 2012 was 4305 kilotons. From the overall global thermoreactive resins market polyester had a 66% market share in 2007 ahead of epoxy (23%) and others (11%). The leader in demand for unsaturated polyester resin is the building and construction industry (utility poles, bridges, swimming pools, bathtubs etc.) that is driven by urbanisation in China and India. Other players in the market are pipe and tank industries which supply mainly to the chemical industry and the third big user of unsaturated polyester resin is the electrical and

electronics industry (PCB, rods, electrical housing etc.). The *artificial stone* market is also named as one of the growth areas and a place for new opportunities for resin producers in the upcoming years. In 2012 the biggest demand was in the Asia-Pacific region followed by North America and Europe. [8, 7]

Behind the popularity of unsaturated polyesters are their simple processing, easily variable properties and good performance to cost ratio (Figure 1.1).

Ester forms through the reaction of an acid with an alcohol. The reaction of a difunctional acid (diacid) and a difunctional alcohol (glycol) produces a linear polyester (thermoplastic polyester). To produce unsaturated polyesters (thermoreactive polyester) part of the saturated diacid is replaced with an unsaturated diacid. There are reactive double bonds (unsaturation) throughout the polymer chain, which will cross link with other polymer chains during the polymerisation reaction. The cross links prevent the plastic from returning to liquid form. Different polyesters are produced by varying diacids and glycols.

$$HO\left(\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-R'-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-R'-O\right)_n H$$

Figure 1.2 Polyester chain with reactive carbon-carbon double bonds (unsaturated bonds) [5]

Unsaturated polyesters are divided into classes based on the acid – orthophthalic, isophthalic, terephthalic, chlorendic, dicyclopentadiene and bisphenol-fumarate resins [5].

The resin used in current research is an unsaturated polyester based on isophthalic acid and neopentyl glycol. It is meant for casting applications where no gel-coat is used. It behaves like a gel-coat and due to this will not fade in a water environment.

The degree of unsaturation has a considerable impact to the mechanical properties and the reactivity of curing. Unsaturation is adjusted by mixing saturated and unsaturated dicarboxylic acid.

Isophthalic acid based unsaturated polyesters are considered to have greater strength, toughness, flexibility and heat resistance than orthophthalic resins [5]. The advantage lies in the structure – a carbon atom of the benzene ring separates the acid groups. This produces a polymer with higher linearity and molecular weight in the esterification process.

The choice of the glycol also has a major effect on the properties of the polyester. A resin containing neopentyl glycol has good alkali, water and overall chemical resistance. Lack of these properties is common to ether glycol based polyesters because the ester linkages are prone to hydrolysis. By increasing the size of the glycol one decreases the free ester links.

Unsaturated polyester resins are produced by dissolving the polycondensation product (unsaturated polyester) in a monomer. The most common monomer is styrene, but methyl methacrylate, α-methyl styrene and vinyl toluene are also used, frequently in combination with styrene [9]. The

choice of monomer affects the properties of the polymer. Styrene is prone to oxidative degradation and is therefore mixed with methyl methacrylate [10]. The copolymerisation of the polyester with styrene-methyl methacrylate combination improves gloss and colour-retention and UV-resistance [11]. The polymer and monomer both have carbon-carbon double bonds and a polymerisation reaction between these leads to cross-linking of the polymer.

1.2.1 Unsaturated polyester polymerisation

The polymerisation of unsaturated polyester resins is initiated with organic peroxides. The peroxide decomposition and thus polymerisation initiation takes place at temperatures above 100°C or at room temperature in conjunction with a cobalt naphthenate or octoate [12].

A common "initiator" is methyl ethyl ketone peroxide. There are a variety of MEKPs in order to achieve desired the gel time, exothermic temperature and other process parameters. Peroxide content is usually 0.8 - 2.5% by weight based on resin [13]. Cobalt wt% is 0.5 - 4.0 wt%. Resin systems are often pre-accelerated and only the catalyst is added on-site [12].

1.3 Aluminium hydroxide

The main duty of the reinforcement is to carry the load. Discontinuous reinforcement usually enhances the stiffness and the hardness of the composite while the toughness can be improved or decreased depending on the volume fracture and nature of the discontinuous reinforcement.

Although there are a myriad of possible fillers the market is dominated by less than 10 different materials (Table 1.1). Elastomers are the biggest group of materials utilising fillers, thermoplastics account for 35% and thermoreactives merely 15% [3]. US consumption of fine particle and surface treated $Al(OH)_3$ was 41700 tonnes in 2003. It is expected to increase 6% per year [14].

Table 1.1 Market share of fillers in order of volume in 2011 (data from [3])

Filler	Millions of Tons	Billions of Euros
Carbon black	4.5	3.96
Natural $CaCO_3$	2.3	0.17
Precipitated $CaCO_3$	0.2	0.12
Precipitated silica	0.3	0.3
$Al(OH)_3$	**0.3**	**0.17**
Talc	0.3	0.14
Kaolin	0.2	0.03
Others	0.8	0.12
Total	8.9	5.01

Fillers are generally chemically inert [3]. Because of this filler chemistry has a rather limited influence on the properties of the composite.

According to DeArmitt [3] there are 4 fundamental aspects that govern the properties of a particle reinforced polymer composite:

1. filler concentration,
2. particle size and size distribution of the filler,
3. filler dispersion,
4. particle shape and aspect ratio.

Effective adhesion together with improved stress transfer and environmental durability between the matrix and the reinforcement is achieved with coupling agents.

Aluminium hydroxide has the chemical formula $Al(OH)_3$. It is also known as aluminium trihydrate ($Al_3O_2*3H_2O$) or "hydrated alumina". The popular abbreviation ATH is also derived from the former name. The term "hydrate" became part of the abbreviation because of the endothermic dehydration in fire [1]. Aluminium hydroxide is found in nature as the mineral gibbsite.

Aluminium hydroxide came into wider use in the 1960's as a flame-retardant to substitute the heavy metal or halogen containing flame retardants. If temperature rises to 220°C then 35% of $Al(OH)_3$ is released in the form of steam. This restricts the access of oxygen to the burning polymer. Today it is the largest volume flame retardant used in the world, representing 43% of entire global consumption [1].

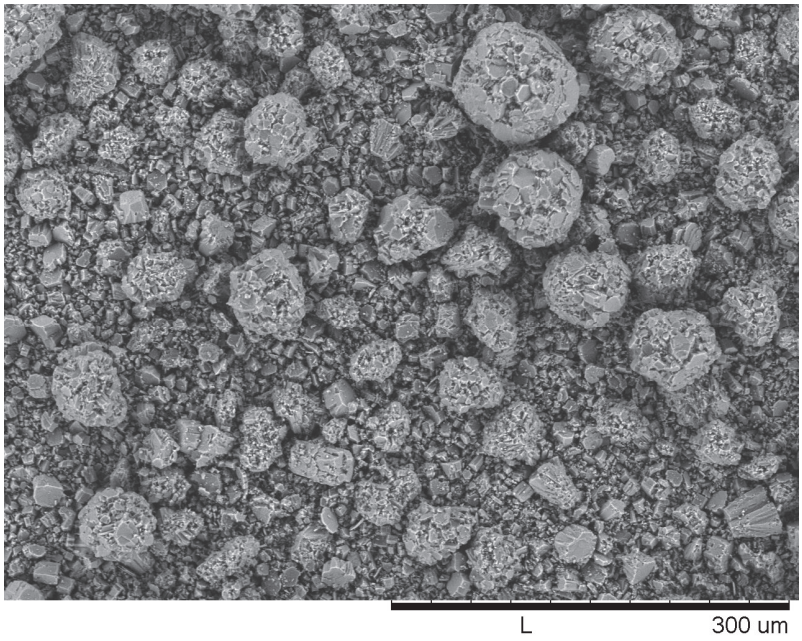

Figure 1.3 Aluminium hydroxide

Aluminium hydroxide is chemically inert and noncorrosive. It is insoluble in water, non-toxic and odourless. $Al(OH)_3$ has low thermal conductivity. Its natural colour is white. Due to the dominance of white colour in the bathware

industry it suits well. Since the surface of $Al(OH)_3$ has a low sorptive capacity it has low resin demand.

ATH hardness on the Mohs' hardness scale is 2.5 - 3. This is more than the hardness of the polymer so the addition of ATH improves the hardness of the composite. At the same time, the hardness is not extreme so no special tools are needed for fabrication as is the case with quartz that has Mohs' hardness index of 7. The specific density of aluminium hydroxide is 2.40 g/cm^3. Bulk density depends from the particle size and size distribution: d_{50} 7 μm bulk density is 0.95 g/cm^3 and d_{50} 35 μm is 1.10 g/cm^3.

Aluminium hydroxide is produced in a variety of particle sizes and size distributions using grinding or precipitation process. Mechanically ground $Al(OH)_3$ has a wide particle size distribution and a better packing fraction [1]. This leads to less dusting, better mixing, higher filler loading and lower viscosity of the dispersion. On the other hand, a precipitation process gives hexagonal platelet morphology and narrow size distribution.

1.3.1 Summary of main components

Unsaturated polyester resin together with aluminium hydroxide has a good potential to be used as the material for fabricating bathware. In order to maximise the cost reduction effect the filler content should be maximised. As preliminary tests showed the maximum mass fraction of ATH is in the vicinity of 65%. This is the desired filler content. Nevertheless, the proposed composition has to be validated by testing mechanical and functional properties of the material. To be able to observe the effect of the filler it is varied from 50-65 wt% in the tests.

2. MECHANICAL PROPERTIES

After conceptual design the mechanical and physical properties of the proposed composition were tested. The main driver to increase filler proportion is cost reduction. Nevertheless, the material has to correspond to the requirements set by its application. The research aims to verify the feasibility of the high filler content concept and map the mechanisms that govern the strength and stiffness in order to improve the composition.

2.1 Filler content effect to properties

The material design proposes to use 65 wt% of filler in order to lower costs, following paragraph analysis if it is feasible from the point of view of mechanical properties. To investigate how the mass fraction (wt%) of particulate reinforcement influences the physical and mechanical properties and cost of the composite a variety of tests and analyses were carried out. The results have been published in [**Paper I**].

2.1.1 Literature overview on filler effect to properties

Julson et al. [15] bring forth decreased cost, increased stiffness, reduced energy consumption and shorter cycle time as the advantages of fillers. Even though the flexural modulus is increased, the flexural strength is reduced due to the unfavourable geometry of particulate fillers [1]. The modulus of composites with a rigid matrix (like thermoreactive polyester) depends upon the modulus of fillers and filler content [1].

Although some theories suggest that particle morphology does not play a role in stiffness of composites, experimental data shows that finer particles and size distribution at the finer end increase modulus of composites. This is related to greater particle surface area and energy of finer particles and good packing density [16].

Nielsen has named “the strength of the adhesive bond between different phases, the type of dispersion and the amount of particle agglomeration” [17] as the prominent factors affecting the properties of a particle reinforced composite.

Kim et al. [18] studied composites with different particulate fillers and with varying filler content 40 - 80 wt%. They found that the flexural strength and modulus are influenced by filler morphology and mass fraction. Composites with round particles exhibited higher flexural strength and modulus than composites with irregularly shaped particles. Composites with the highest filler content had the highest flexural modulus, hardness and flexural strength.

Foroutan et al. [19] studied the effect of micro- and nano-scale Al_2O_3 particles on the mechanical properties of polymers. They observed an increase in flexural strength from 45 to 50 wt% of filler and a decline afterwards. They attributed the decrease of flexural strength to poor particle-matrix interaction. Hence, increase of filler mass fraction increases weak links. Nevertheless, flexural modulus and Vickers micro-hardness improved with greater filler

content. They explain it with the restricted motion of the polymer due to filler particles.

Alsharif et al. [20] suggest that increased filler mass fraction leads to particle aggregation and poorer particle-matrix adhesion. This causes a decline in flexural strength. Nevertheless, this does not apply to all the mechanical properties. They observed improvement in hardness and flexural modulus. Experimental results of Chaowasakoo et al. [21] who studied fly ash-epoxy composite agree with Alsharif et al. and they also point out the effect of filler aggregation.

In addition to the aforementioned authors other researchers also observed improvement of hardness when particles were incorporated into the composite [22, 23, 24]. Raju et al. [23] mention as a downside that silica particles increase the density of the composite. Urabe et al. [22] studied the effect of particle size (0.45, 0.96 and 1.46 particles). Hardness of the composite increased regardless of particle size, although 0.96 μm showed better results than the others. D'Almeida et al. [24] suggest that finer particles increase the probability that an external indenter will come across a particle. They show that useful increase in hardness is achieved with filler volume fractions over 30%.

2.1.2 Experimental design of mechanical properties testing

Unsaturated polyester resin specified in paragraph 1.2 and ATH with d_{50} 35 μm was used. Initial cure of specimens was done at room temperature (23 ± 2 °C). That was followed by post cure at 40 °C for 12 h. The flexural properties of the material were determined by a 3 point bending test as specified in ISO 178 Plastics – Determination of flexural properties. Hardness was measured by GYZJ 934-1 Barcol impressor according to ASTM D2583. The density of the material was determined by the Archimedes-method. A kit of analytical scale and a weighing jig was used for weighing specimens in air and fluid. The density was determined by the equation:

$$\rho = \frac{m_a \times \rho_f}{m_a - m_f}, \qquad \textbf{(2.1)}$$

where m_a is specimen weight in air, m_f is specimen weight in fluid and ρ_f is density of the fluid. [**Paper I**]

Table 2.1 Composition of mechanical test specimens (adapted from [Paper I])

Material	K-1 (wt%)	K-2 (wt%)	K-3 (wt%)
Resin	45	40	35
Filler	55	60	65
Initiator	1	1	1

The composition of the test specimens is presented in Table 2.1. Specific info about the experimental setup can be found in [**Paper I**].

2.1.3 Results and discussion of flexural properties

The mechanism of fracture was brittle as can be seen from the stress-strain curve (Figure 2.1) and the fracture surface. There was practically no plastic deformation before breakage.

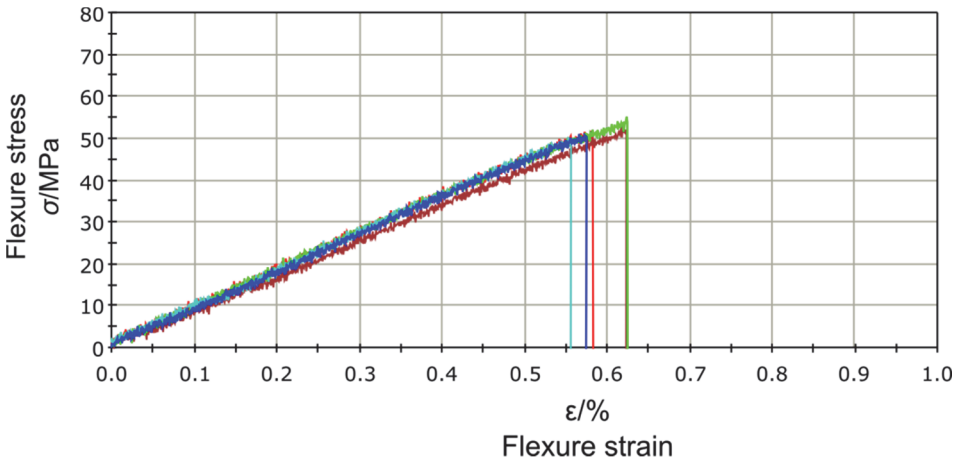

Figure 2.1 Stress-strain curve of flexure specimen

The results of flexure, indentation hardness and density tests are gathered in Table 2.2. The table also contains properties of neat resin. It is easy to follow the increase in rigidity with the incorporation of the particles.

Table 2.2 Mechanical and physical properties of test specimens (adapted from [Paper I])

	Neat resin	K-1	K-2	K-3
Filler wt%	0	55	60	65
Flexural strength (MPa)	140*	61 ± 3	60 ± 6	57 ± 7
Flexural modulus (GPa)	3.6*	6.5 ± 1.2	7.2 ± 0.9	10.0 ± 2.1
Indentation hardness (Barcol scale)	40 - 45*	50 ± 1.7	51 ± 0.9	53 ± 0.6
Density (g/cm^3)	1.10*	1.64	1.69	1.77

*Taken from manufacturers TDS

Foroutan et al. [19] display identical stress-strain curves. The increase of flexural modulus and decrease of flexural strength that is accompanied with higher filler content correspond to the findings of Alsharif et al. [20] and Kim et al. [18].

The increase of flexural modulus together with filler wt% increase can be attributed to the rigidity of filler particles. As the mass fraction increases the filler properties prevail.

The flexural strength decreases due to insufficient plasticity of the composite. Table 2.2 shows that neat resin has a much higher plasticity than the composite.

We assume that the particle-matrix adhesion is good and particles are more rigid than the matrix. If the space between particles is greater than the particle size then when force is applied the matrix in-between the particles deforms plastically before breaking and the breaking occurs in the matrix.

When filler forms half or more of the composite there is no plastic deformation due to an insufficient amount of matrix. The breakage does not take place in the matrix. The two possible weak links are particle-matrix interface and particle itself. Usually the particle is the hardest nut to crack and the composites strength depends from the bond between particle and matrix.

The particle-matrix bond can be enhanced with coupling agents. The ATH used in current research is treated with silane. It is likely due to this that the reduction in flexural strength is much smaller than the increase of flexural modulus (6.5% vs. 53%).

2.1.4 Results and discussion of indentation hardness

Indentation hardness illustrates ability of materials to withstand plastic deformation [10]. The indentation hardness of the composite is greater than the hardness of the neat resin as can be seen from Table 2.2. With filler wt% increase the hardness increases. On the Mohs' scale of mineral hardness ATH hardness is 3. Resin hardness on the Barcol scale is 40. An approximate conversion to the Brinell scale (10 mm ball 500 kg load) of both components was made. On the Brinell scale ATH hardness is 90 and resin hardness is 25. The filler has clearly higher modulus than the polymer. The results confirm the proposed relation between filler modulus, filler concentration and composites hardness in case of rigid matrix.

The same trend is evident in the results of Foroutan et al. [19] who measured the Vickers micro-hardness of polymer composite containing 45 - 60 wt% of Al_2O_3 μm-size filler. We can add here also all the other researchers who were mentioned in the literature overview.

2.1.5 Results and discussion of cost

Part of the study was to evaluate the effect of filler content to cost. When filler mass fraction increases the net value is reduced. With a 10% increase the net value is reduced by 7.5% as depicted on Figure 2.2.

A negative aspect that accompanies filler mass fraction increase is the increase of density. Heavier products raise transportation costs and in some instances custom duties.

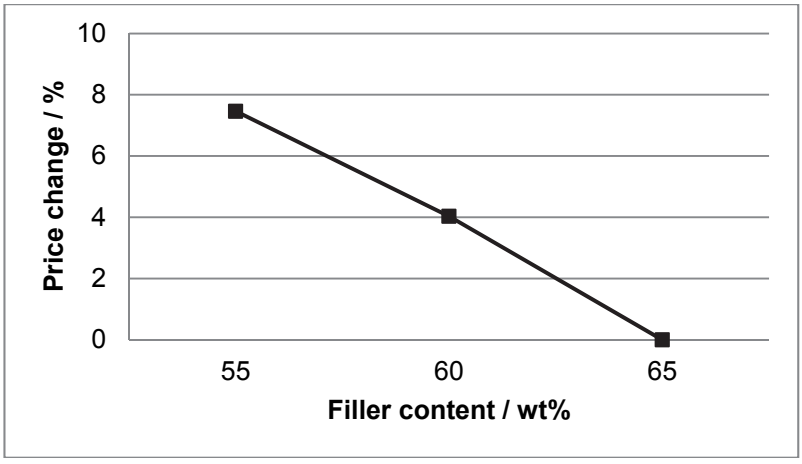

Figure 2.2 Price reduction with filler content increase

2.1.6 Summary of filler content effect

The experimental results of filler content effect to mechanical and physical properties correspond to the ones reported in literature. Filler wt% increase improves indentation hardness and flexural modulus but reduces flexural strength.

The latter suggests that filler in high concentration causes brittleness. It is an unwanted property in bathware. The effect is studied more closely in [**Paper V**] that deals with impact properties of the composite. As was indicated in literature in conjunction with flexural properties if at the same time high filler content and good mechanical properties are desirable then decisive factors are filler particle size and particle size distribution.

High flexural modulus guarantees a sturdy product. Indentation hardness is expected to reflect the scratch and wear resistance of a material. This assumption was tested in [**Paper IV**] and [25]. In case of polymer composites the mechanism is not that straightforward. Filler content and hardness have a linear relation but wear of the composite does not correlate to that.

All in all, the high filler content proved to be viable. The calculations proved that filler reduces cost of the material. The downside is an increase in density. The following paragraph looks into ways to overcome this deficiency.

2.2 Density reduction of the composite

Paper II looks into ways of reducing the density of the particulate composite material and subsequently evaluates its mechanical properties. Mass reduction of the product means easier handling, reduced transportation costs and in some instances also reduced customs duty. Nevertheless, the mechanical properties cannot be compromised. Moreover, the economic gain has to be calculated.

2.2.1 Literature overview on low density fillers

One way to reduce the density of the composite is to replace part of $Al(OH)_3$ with some low density filler. There are many alternatives.

Cenospheres could be one possible lightweight reinforcement. These are hollow inert microspheres that are found in the fly ash of thermal power plants. Cenospheres have Mohs' hardness index 5 - 6 and density of 0.40 - 0.60 g/cm^3 [26]. They are composed mainly from silica and alumina and have a dark grey to white colour. Cenospheres could be used for weight and cost reduction due to their low density [27]. Due to their high hardness they also have potential for improving tribological properties [28, 29].

Besides cenospheres, low density thermoplastic or thermoreactives' chips could be used. The plastic particles decrease the density. Thermoplastics like PMMA and ABS have a density of 1.20 g/cm^3 and the density of unsaturated polyester or acrylic resin chips is 1.10 g/cm^3. Thermoplastic particles are produced by recycling used plastic products [30]. They are milled into the desired particle size 0.16 - 2.50 mm with disintegrator technology [31]. Thermoreactives' chips are available commercially and also often have an aesthetic function. An alternative to commercially available chips could be recycling of manufacturing scrap material.

A common option is microscopic hollow soda-lime-borosilicate spheres. These hollow glass microspheres (HGM) are used in thermoplastics, adhesives, putties, concrete etc. They are used to reduced density, cost and shrinkage or to adjust rheological properties, improve thermal shock resistance and machinability [32]. Due to their round shape the microspheres have excellent packing density and low viscous drag [33]. The common loading is 5 - 10% but thermoplastics are loaded up to 25% [14].

Hollow glass microspheres were chosen for the experiment due to the reason that they are white coloured (matches with the composite), they are widely used in the plastics industry, there is assurance that they are compatible with UP resin and have good adhesion with the matrix, they are commercially available in wide assortment [14]. The chosen spheres had the following properties: (a) true density 0.20 g/cm^3 (b) particle size d_{50} 55 μm (c) target crash strength 3.4 MPa (d) white colour.

2.2.2 Literature overview on HGM effect to mechanical properties

Hollow glass micro-spheres have many favourable effects: reduced weight, dimensional stability, improved stiffness and impact resistance [14].

The spherical shape provides uniform stress distribution unlike the irregular shape of mineral fillers. This should also reduce the stress concentration sites in the matrix and thus improve fracture toughness. Hollow spheres are expected to improve impact resistance. [2]

Hollow glass microspheres have many favourable properties. However, there are also drawbacks. Liang [34] observed tensile strength and impact strength decrease of a thermoplastic composite with increasing volume fraction of hollow glass microspheres.

Kim et al. [35] studied the effect of HGM on an epoxy matrix. They varied the volume fraction of microspheres up to 0.65 and measured flexural and impact properties. The increase of microspheres reduced flexural strength and fracture toughness but marginally improved the flexural modulus at high volume fractions. They concluded that HGM crush strength is too low. Fracture took place in the spheres not in the matrix.

Kishore et al. [36] explored the effect of HGM size distribution and volume fraction to compressive strength and modulus of epoxy matrix composite. They observed a decrease in both properties as the volume fraction of HGM increased. A composite with narrow size distribution HGM exhibited higher compressive strength. In case of a low volume fraction of HGM the epoxy matrix deformed but with a high amount of filler the HGM crushed.

From test data of Baumeister et al. [33] it is visible that HGM reduce tensile and flexural strength of composites. While Baumeister et al. studied a highly loaded epoxy composite (65 - 78 vol%) then Park at al. [37] exmined the effect of 1 - 2 wt% of HGM. They observed an improvement in fracture toughness and contributed this to the improved interfacial interaction.

Gupta et al. [38] explored the idea of improving the tensile properties of HGM-epoxy syntactic foam by increasing the wall thickness of the micro-balloon. Thicker walls improved the tensile modulus of the composite. Nevertheless, all synthetic foams containing 30 - 60 vol% of HGM showed 60 - 80% decrease in tensile strength compared to neat resin. Brittle fracture was evident from the stress-strain curves. In syntactic foams the matrix acts as the load bearing phase.

Literature reference to the effect of HGM to indentation hardness was not found.

2.2.3 Experimental design of testing and optimisation

The material was composed from unsaturated polyester resin specified in paragraph 1.2 and ATH with d_{50} 35 µm. The material was first cured at room temperature (23 ± 2 °C) and then post-cured at 40 °C for 12 h. Tensile tests were performed according to ISO 527 standard. The indentation hardness of the material was measured with GYZJ 934-1 Barcol impressor according to ASTM D 2583. The density of the material was determined by the Archimedes-method. A multi-criteria optimisation problem was formulated based on the physical and mechanical properties of the material. The solution was obtained by applying the Pareto optimality concept. [**Paper II**]

Table 2.3 Composition of HGM test specimens

Material	H-1 (wt%)	H-2 (wt%)	H-3 (wt%)	H-4 (wt%)
Resin	40	40	40	40
ATH	60	54	51	48
HGM	0	6	9	12

The composition of the test specimens is presented in Table 2.3. Specific info about the experimental setup can be found in [**Paper II**].

2.2.4 Results and discussion of HGM effect to properties

The tensile strength of the composite decreases as the HGM wt% was raised (Figure 2.3).

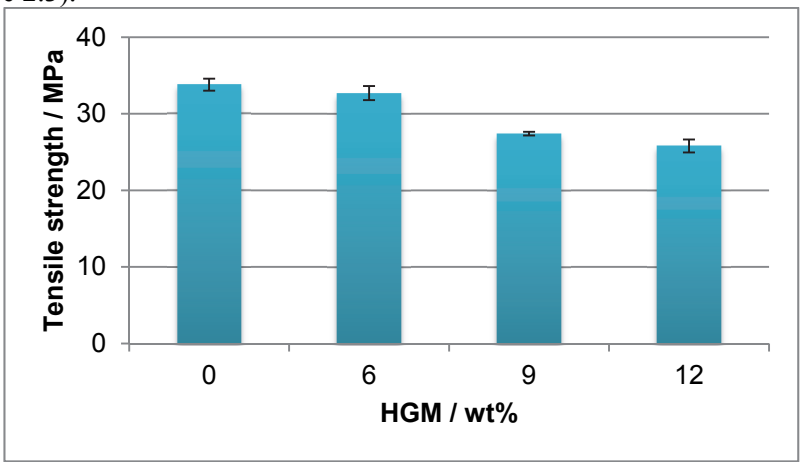

Figure 2.3 HGM effect to tensile strength

This corresponds to the results reported in literature [33, 34, 38]. As tests in [**Paper I**] showed, filler reduces the plasticity of the composite. In cases of high filler loading the strength properties of the composite depend on the particle-matrix adhesion and particle modulus. Hollow glass microspheres have good adhesion but lower rigidity than ATH or polyester. Therefore they form weak spots in the composite and the fracture is caused by the breaking of the micro-balloons. The crushing of HGM was observed by Kishore et al. [36] and Gupta et al. [38].

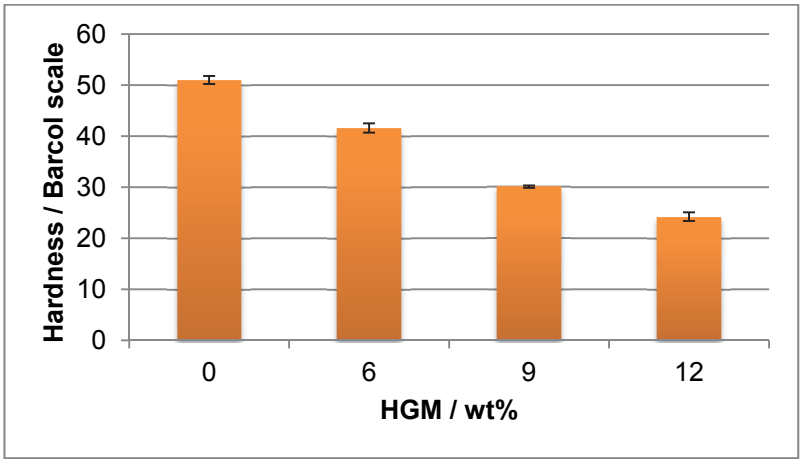

Figure 2.4 HGM effect to indentation hardness

Similarly to tensile strength also indentation hardness decreased as more HGM were included (Figure 2.4). Moreover, the decline was much steeper. Part of the decline is explained by the reduction of ATH mass fraction in the composite when it is replaced by HGM. Nevertheless, it is clear that the largest part of the hardness loss can be attributed to the low crush strength of HGM.

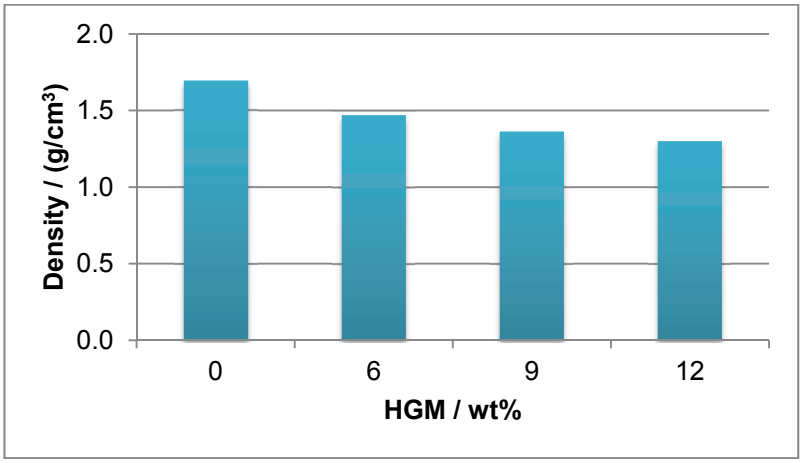

Figure 2.5 HGM effect to density

The positive effect of HGM is density reduction. Although, the density decrease it is not as steep as the loss of mechanical properties as can be seen from Figure 2.5. Other proposed positive effects like improved dimensional stability and stiffness are not an issue because ATH already fulfils that function. Contrary to handbooks [2, 14] Liang et al. and Kim et al. also observed a decrease of impact properties with the inclusion of HGM [34, 35].

2.2.5 Results and discussion of HGM effect to cost

The raw materials have different densities and costs. Hollow glass micro-spheres have a lower density than aluminium hydroxide (true density 0.20 g/cm^3 vs. 2.41 g/cm^3) but cost 7 times more. This has to be taken into account in cost calculations. Katz [2] states: "The relative cost/benefit of the hollow spheres must be determined based on the volumetric displacement of the resin or other raw materials". As can be seen from Figure 2.6 the volume of HGM did not make up for the price.

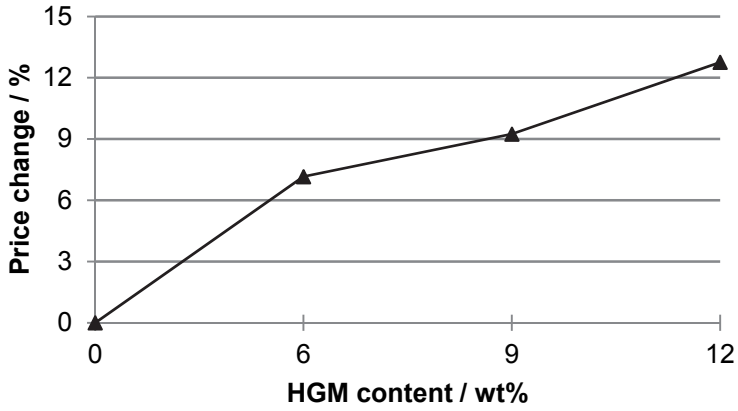

Figure 2.6 Effect of HGM to cost

2.2.6 Multi-criteria optimisation of composites properties

The goal of the study was to find a cost effective material composition that has low density with sufficient mechanical properties. The work included multi-criteria optimisation of the set objectives based on experimental data. Surrogate models are frequently used for this task. In **Paper II**, the response surfaces of the physical and mechanical characteristics were modelled with artificial neural networks. The objective was to maximise tensile strength and surface hardness and minimise density. The solution to the posed task is in the form of a 2D Pareto front that was constructed based on the Pareto optimality methodology [39][40].

The multi-criteria optimisation problem can be formulated flowingly:

$$f(\bar{x}) = \min(f_1(\bar{x}), f_2(\bar{x})), \tag{2.2}$$

subjected to linear constraints:

$$x_i \le x_i^*, \quad -x_i \le x_{i*}, \quad i = 1,...,n, \tag{2.3}$$

and non-linear constraints:

$$\sigma(\bar{x}) \le \sigma^*. \tag{2.4}$$

Mechanical characteristics are designated as f_1, density is f_2 and $\bar{x}$ is the vector of design variables. In (2.3) x_i^* and x_{i*} stand for the upper and lower bounds of the design variables, respectively. The non-linear constraints (2.4) is imposed on stress σ and requires that it does not exceed the given limit value σ^*.

It can be seen from Figure 2.7, that the relation between the two objectives is described by a Pareto curve consisting of two linear parts (can be approximated as linear). Reducing of the material density function from 0.76 down to 0.43

leads to a proportional decrease of the combined function (from tensile strength and surface hardness), further reduction of the material density function leads to a much faster reduction of the combined function. The optimal solution for the posed optimization problem can be selected as the intersection point of two linear parts of the Pareto curve, but not necessarily.

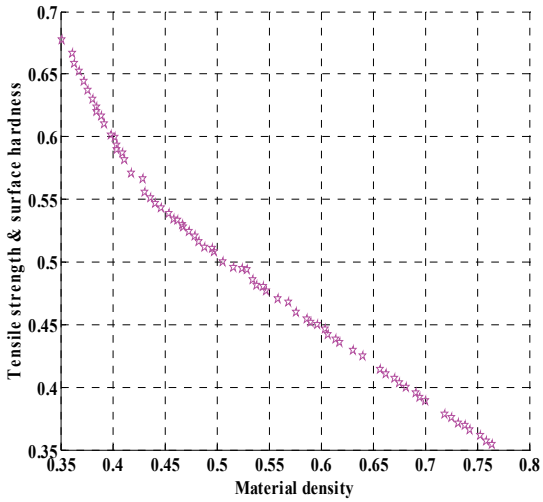

Figure 2.7 Pareto front

2.2.7 Summary of HGM effect to composite

Density reduction is desirable because it reduces transportation costs and customs duties. The hollow glass microspheres were chosen as a secondary filler in order to reduce the density of the composite. Although, the HGM proved their ability to reduce mass they failed in all the other aspects. The mechanical properties decreased drastically and the cost went up. All in all, the hollow glass microspheres turned out to be impractical.

3. FUNCTIONAL PROPERTIES

The current study defines the stain, wear and impact resistance as the functional properties of the composite material. These are the interpretations of consumer requests. People do not set requirements to specific mechanical or chemical properties they express their expectations in a more general manner. These three properties define the bathware that is easy to maintenance, longeval and practical. The following paragraphs study the mechanisms that influence these properties and look into ways of improving them.

3.1 Stain resistance

3.1.1 Literature overview on stain resistance factors

The term stain is used here as a distinguishable change in materials colour or gloss caused by another material.

First of all, staining can be caused by deposition of a substance onto the surface. The substance can be of a biological or non-biological type [41]. There are 3 main types of organisms that cause biological soiling and change in the appearance of the substrate surface: 1) bacteria, 2) microscopic algae, and 3) fungi [41]. Due to the fact that this type of polymer composite does not support microbial growth it is not considered in the current study [42].

The non-biological type of soiling is caused by pollutants in air or by physical interaction of materials [41, 43]. Due to surface roughness the substance is trapped. An example is soot from industry or exhaust gases. These substances are hydrophobic so they are hard to wash away with water [43].

The second reason for staining is chemical interaction between materials. The usual type of bonds form: 1) ionic bond, 2) hydrogen bond, 3) Van der Waals forces, 4) covalent bond, and 5) hydrophobic interaction [44]. If the polymer is not fully cured covalent bonds can form with external substances. Study in [**Paper III**] showed that ethanol is able to constitute secondary bonds even with a highly cross-linked polymer.

Lu et al. [45] studied polymer composites that are used as dental restorative materials and found that discoloration increased with an increase in surface roughness and the process was accelerated by time. The surface roughness is increased by wear processes [46].

Dondi et al. [47] studied the effect of microstructural defects of materials (i.e. pores) and defects caused by polishing (cracking, crazing). They found that staining is proportional to the amount of defects.

Cured polyesters are generally resistant to organic solvents but react with chlorinated hydrocarbons (chloroform), esters (ethylacetate) and ketones (acetone). Strong alkalis degrade the polymer through hydrolytic reaction with ester groups. Polyester is resistant to most organic and inorganic acids [10].

3.1.2 Experimental design of stain resistance tests

The staining, cleaning and evaluation procedure was carried out according to ISO 19712 – 3 Method B. The test specimens were left on the surface of the material for a period of 16 h. The surface was treated with 15 different staining agents.

Preliminary cure of the composite was done at room temperature (23 °C ±2 °C) for 12 h. That was followed by post-cure at (40 °C ±2 °C) for 16 h. The parameters were chosen based on [**Paper III**] and practical observations in production.

Five different test slabs were cast to test the influence of composition and related phenomenon (Table 3.1). The mass fractions were chosen based on [**Paper I**] and literature.

Table 3.1 Composition of staining test specimens [48]

Material	MA-1 (wt%)	MA-2 (wt%)	MA-3 (wt%)	MA-4 (wt%)	MA-5 (wt%)
Resin	45	35	35	35	35
Filler	55	65	65	65	65
Initiator	1	1	1	2	2
Accelerator	0	0	1	0	1

In order to determine the influence of surface treatment and surface roughness to the stain resistance all the slabs were prepared with 4 different surface finishes (Figure 3.1). The first quarter of the slab was untreated mould surface. The second quarter was polished. The third quarter was sanded with P1500 sandpaper and the final quarter was sanded with P240 sandpaper. The abrasive grit was chosen based on needs in production. [48]

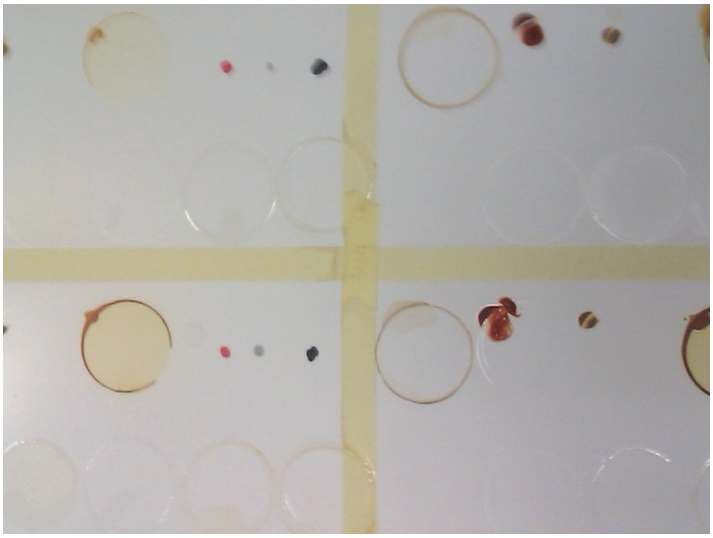

Figure 3.1 Fraction of staining test slab

3.1.3 Results and discussion of composition variation

The first assumption was that ATH causes staining. The proposed mechanism was sorption of staining agents. In order to validate this, composites with 65 wt% and 55 wt% of ATH were tested. The rating according to ISO 19712 gave equal results. Side-by-side comparison did not distinguish either any notable difference. Based on this one can stick to the claim that ATH has a low sorptive capacity and thus does not cause staining through sorption of staining agents.

The second assumption was that resin causes staining. The proposed mechanism was chemical interaction between the polymer and the staining agent. It was expected that higher cross-link density and thus chemical inertness would increase the stain resistance. The effect was partly proven in [**Paper III**] where it was shown that post-curing will increase cross-link density and a highly cross-linked polymer is less vulnerable to external chemical aggression. Here it was tested if initiator (organic peroxide) and accelerator (cobalt naphthenate metal salt solution) concentrations above a minimum level affect the cross-link density and chemical inertness.

In order to evaluate the effect of peroxide concentration composite with 1 wt% of peroxide as the minimum recommended by resin manufacturer and 2 wt% were tested. There was a clear improvement in stain resistance with higher peroxide concentration. Peroxide initiates the polymerisation process by forming reactive radicals. A certain amount of radicals is necessary to form covalent bonds between all carbon atoms and reach complete cure (terms “all” and “complete” are used with reservation). Based on these tests the concentration of peroxide recommended by the resin manufacturer is insufficient to achieve complete cure. High cross-link density and stain resistance was achieved with 2 wt% of peroxide. Nevertheless, this does not mean that the properties could be endlessly improved. There is a certain limit to peroxide concentration above which the peroxide inhibits polymerisation. Moreover, higher peroxide concentration speeds up the polymerisation and is thus a limiting variable in the production.

Reactive radicals form when peroxide (initiator) decomposes. This redox reaction is started by cobalt naphthenate metal salt (accelerator) in the current resin system. Peroxide also decomposes by means of heat if temperatures exceed 100 °C. The exothermic temperature of neat resin was tested and it reached 150 °C. This is sufficient to decompose the remaining peroxide that has not reacted with cobalt naphthenate metal salt. Nevertheless, measurements in production showed that filler reduces the exothermic temperature to 60 - 70 °C. The meaning of the latter is that the redox reaction is fully on the shoulders of the accelerator. Based on this and the previous section there are two prerequisites for good cure: 1) adequate peroxide concentration to bond all carbon atoms, and 2) adequate accelerator concentration for complete redox reaction of peroxide.

The resin system is pre-accelerated. The objective was to test if the accelerator concentration in the resin is sufficient for complete decomposition

of the peroxide. A composition with 1 wt% of initiator and 1 wt% of accelerator was prepared. The material showed remarkable improvement in stain resistance compared to test specimen where solely 1 wt% of initiator was used. This shows that the pre-mixed accelerator concentration in the resin is not sufficient to decompose all the initiator. The last statement is applicable in current application where a high concentration of filler reduces the exothermic temperature so it does not exceed the initiators decomposition temperature. If we compare current results to the tests where initiator concentration was varied we can conclude that the poor results were the consequence of inadequate initiator decomposition not deficiency of the initiator. Material with 1 wt% of initiator and 1 wt% of accelerator had better stain resistance than material with solely 2 wt% of initiator.

Ethanol proved to be an effective cleaner of coffee and ketchup stains. Bleach on the other hand removed tea, citric acid, mustard and pencil marks.

3.1.4 Results and discussion of surface roughness

The second goal was to study the hypothesis that mechanical processing of a materials surface degrades stain resistance. It was proposed that during casting, resin forms a thin film on the outer surface of the material. The thickness of the film corresponds to particle size [16]. This film covers pores and evens out smaller asperities. It was assumed that mechanical processing would remove this film and open up pores. In addition, mechanical processing would increase surface roughness. This would cause trapping of solid particles of staining agents to surface bumps.

The surface of the product has an uneven gloss when it comes from the mould. The surface has to be machined to give it an even appearance. In order to investigate the presence of pores a quarter of the test slab was preserved as it came from the mould. Another quarter of the slab was polished – the least aggressive mechanical processing method (maximum material removal 0.2 mm). No degradation in stain resistance is evident if the two surfaces are compared. On the contrary, polishing improves cleanability. This suggests that the material does not contain pores and the resin film layer does not have a role in stain resistance. Moreover, this is the first evidence that surface roughness reduction reduces staining.

The remaining two quarters of the test slabs were sanded with P1500 and P240 grit aluminium oxide abrasive paper. The mechanical processing proved to decrease the stain resistance. The surface that was treated with the coarser abrasive showed more severe staining. This indicates that surface roughness has a clear influence to materials stain resistance.

The production process of current polymer composite is different from production of porcelain tiles. The resin-filler dispersion is mixed in a vacuum. This material is not porous and contains a very small amount of trapped air. The porosity does not have such an effect on stain resistance as it has to porcelain as was pointed out by Dondi et al. [47].

The down side of finer surface treatment is that it is easier to spot any changes in colour or gloss. A matt surface covers the defects better.

3.1.5 Summary of stain resistance factors

The tests showed that the stain resistance of the polymer composite is related to the cross-link density of the polymer and surface roughness. Due to the low exothermic temperatures of the highly filled polymer the curing relies on adequate dosing of initiator and accelerator. Low surface roughness is achieved with finer abrasive finishing and polishing.

3.2 Wear resistance

Environmental consciousness includes long service life and durability. Materials that need frequent maintenance or products that need replacement are uneconomical and burdensome to the environment. Tribological properties are a vital part of material durability.

Wear is the modification of the surfaces of interacting materials. Wear is not a material property but a characteristic of a tribological system. Wear is influenced by the interacting bodies, environmental conditions, intermediate material, load and motion. Wear types include: adhesive, abrasive, fatigue, corrosive and a combination of the latter. The wear type may change during the process due to frictional heating, wear debris or chemical film formation. [49]

3.2.1 Literature overview on polymer composites wear resistance

The tribology of polymers has three major influencers. Firstly, sliding contacts geometrics and kinematics. Secondly, mechanical properties of the polymer and their change with environmental conditions. Thirdly, the presence and properties of a third body. [50]

There are several wear resistant thermoplastics available like PI, PTFE, PA and PEEK. Thermoplastics are used due to their exceptional frictional properties [51]. Nevertheless, also thermoreactives like epoxy are used [52]. Both matrix types are combined with different reinforcements. The reinforcement can be ceramic or mineral particles, glass, aramid or basalt fibres [52, 53, 54]. These composites are used for producing roller bearings, gaskets, gearwheels, prosthesis and for coating parts that are subjected to wear.

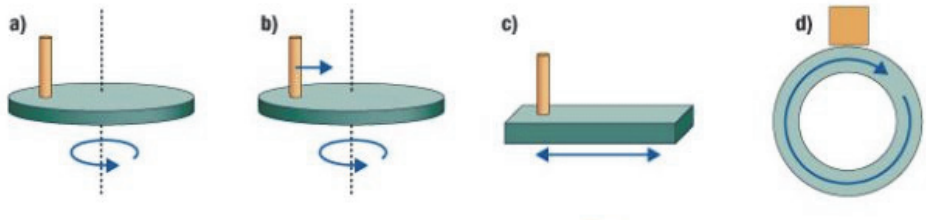

Figure 3.2 Experimental methods for wear testing: a) pin-on-disc with circular track; b) pin-on-disc with spiral track; c) pin-on-plate; d) block-on-ring [55]

A lot of effort goes into exploring the possibilities to improve wear resistance of thermoplastics with inclusion of low volume fraction (0 - 10%) of micro- and nanoscale particles [56, 57]. Common experimental techniques are pin-on-disc or block-on-ring configurations (Figure 3.2).

The incomplete coverage of wear behaviour of thermoreactive composites in literature motivated **[Paper IV]** and article [25] that explore the wear resistance of highly filled (> 50 wt%) thermoreactive composite and study 3-body abrasive wear conditions.

3.2.2 Literature overview on particle size effect to wear

Oleiwi studied the effect of particle size on wear rate with a polyester-silica composite using a pin-on-disc apparatus [58]. His findings suggest that smaller particles should give lower wear rate. Oleiwi theorises that coarser particles increase the pre-existing cracks and thus predispose crack propagation and crack linking. Other researchers suggest that finer particles improve the wear resistance because there is higher probability that the scratching asperity will meet the reinforcing particle [57]. Chauhan et al. [26] studied a vinyl ester composite reinforced with 2 - 10 wt% of micro and nano scale cenospheres. They observed that decrease in particle size decreased wear rate and COF.

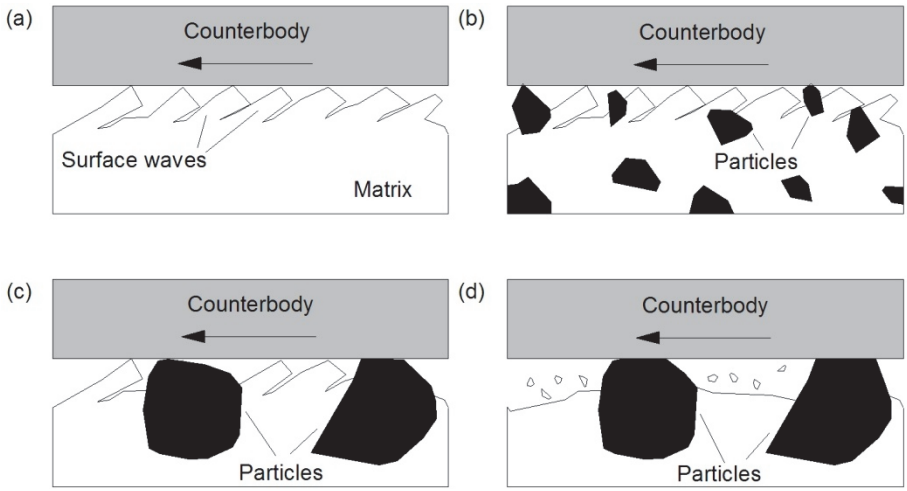

Figure 3.3 Illustration of the wear mechanisms in particulate composite: (a) crack wave formation at the surface of unreinforced matrix; (b) crack wave formation at the surface of composite containing small particles which are removed together with polymer debris; (c) wear of composite containing large particles which protect the polymer matrix from wear; (d) wear of particles by fracturing and small particle debris creation (redrawn from [59])

Durand et al. [59] on the other hand had diametrically opposite results. Namely, they found that mean particle size increase (7,5; 15; 20; 30; 45; 100 μm) reduced wear coefficient. They observed the same effect with a number of different particles (TiO_2, TiC, Al_2O_3, ZrO_2, SiC). They concluded: “particles

can provide effective wear protection to the matrix when the mean particle size is largely greater than the thickness of the material surface layer which is affected by the wear and gives rise to wear debris" [59] (Figure 3.3).

3.2.3 Literature overview on filler mass fraction effect to wear

Researchers have observed that at low speeds and contact forces the reinforcing particles protect the polymer matrix and effectively reduce the wear rate [60, 59]. Kanchanomai et al. [60] achieved 97% wear rate reduction with silica particles (68,5 wt%) in epoxy resin. Durand et al. [59] observed that there was a significant improvement in wear resistance up to 20 vol% of reinforcement. Higher volume fraction did not give any further improvement. Bijwe et al. [61] concluded, based on Ratner-Lancaster plots, that tensile strength and elongation to break have significant influence to composites abrasive wear behaviour. Ratner and Lancaster relate the wear rate of polymers in case of abrasive wear to quasi-static mechanical properties according to the following equation [62, 63]:

$$V = \mathrm{k}\left(\frac{\mu F_n}{\mathrm{H}\sigma_u \varepsilon}\right) \tag{3.1}$$

where

V – volume worn per unit sliding distance,
k – proportionality constant,
μ – coefficient of friction,
F_n – normal force,
H – indentation hardness,
σ_u – ultimate tensile strength,
ε – elongation to break.

The Ratner-Lancaster relation has been studied by several researches and a correlation has been found [26, 50, 64, 65, 66].

3.2.4 Experimental design of wear tests

[Paper IV] and article [25] use different methods to evaluate the wear. This corresponds to materials service conditions where wear modes vary. Experiments in article [25] were done with pin-on-plate configuration according to ASTM G132 that simulates 2-body abrasive wear. In [**Paper IV]** ASTM G65 dry sand/rubber wheel methodology was used to explore the 3-body wear behaviour of the composite. The latter is an uncommon method for plastics. Nevertheless, in service there is always some debris or contamination that affects the wear behaviour of the material. The results of the two methods are inconsistent and the findings of the 3-body abrasive wear surprising.

The study also included experimenting with test parameters like force, speed and duration because like Ma et al. [67] stated test parameters have a considerable effect on the wear rate and can produce unexpected results. Kanchanomai et al. [60] found the following relations between test parameters and wear when testing a highly filled epoxy-silica composite with pin-on-disc

method: (a) increased contact load increases volume loss at different sliding speeds (b) wear rate does not have a linear dependence on sliding speed, it is highest at medium speeds (c) at slow sliding speeds and temperatures ($< T_g$) the wear mechanism is abrasive wear or additional particle detachment and the process is time dependent (d) at high sliding speeds and temperatures ($> T_g$) the wear mechanism is abrasive wear and particle detachment and the process is temperature dependent.

The pin-on-plate methodology in article [25] assures a 2-body wear mechanism – the pin reciprocates on the plate and the plate shifts constantly so the pin is in contact with a clean abrasive surface. The speed and load was chosen so the temperature would not affect the results.

The majority of the research on polymer wear is done with a two-body configuration. Trezona and Hutchings point out that in service three-body wear is dominant because contaminating particles are practically inevitable [68]. Dry sand/rubber wheel methodology is widely used with metals and ceramics. Budinski used the same method for comparing different thermoplastics [51]. This method was also used in [**Paper IV]** to examine the influence of particle size and weight fraction to the composites' wear properties.

3.2.5 Results and discussion of 3-body wear tests

The results of the test are contradictory to the general understanding. The unreinforced polymer produced the lowest wear rate and with an increase of filler the wear rate increased. SEM images (Figure 3.4) revealed that this was not due to the difference in COF but because the abrasive quartz particles adhered to the test sample and formed a tribo-layer (Figure 3.5).

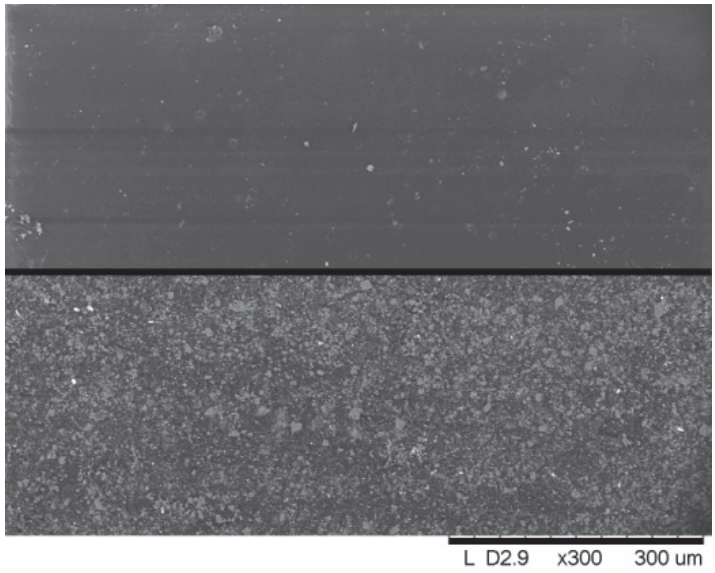

Figure 3.4 SEM images of neat resin sample (upper part of the image is unaffected area and lower part is wear track)

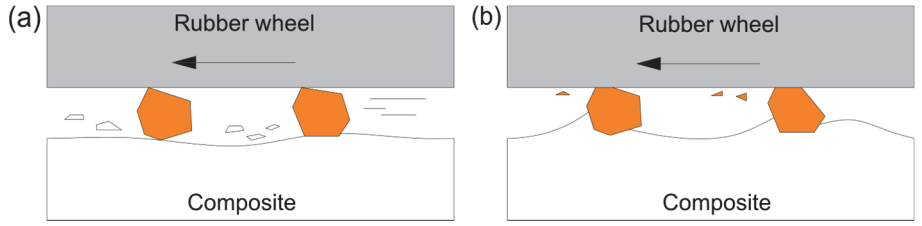

Figure 3.5 The abrasives particles adhere to the composites surface and form a tribo-layer that reduces wear

With more matrix there was more surface area for the quartz particles to adhere to. Due to the fact that SiO_2 has Mohs' hardness index 7 and $Al(OH)_3$ has 3 the adhered sand has a greater effect on the wear rate than the increase of filler's wt%.The process was not temperature dependent because the wear specimen was cooled.

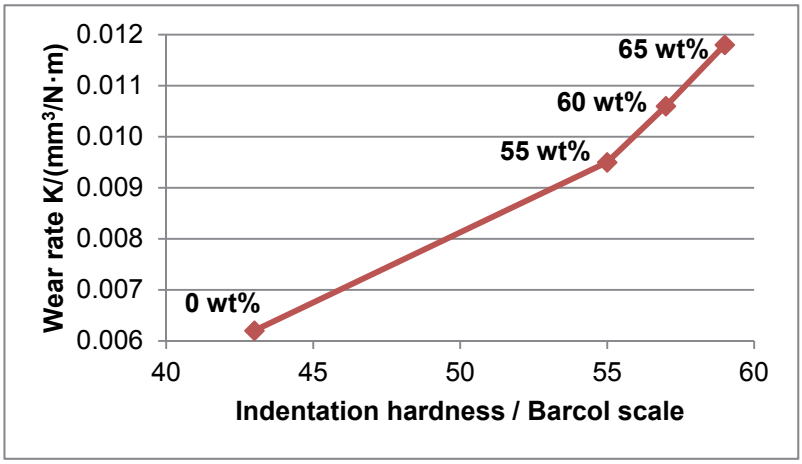

Figure 3.6 Wear rate relation to hardness in 3-body wear of composites with different filler mass fraction

Budinski observed similar contradictory results that he could not relate to quasi-static mechanical properties [51].

3.2.6 Results and discussion of polymer curing effect

Post curing of the composite has a positive effect on the wear resistance. A more cross-linked material has a lower wear rate. The wear rate is reduced by 24% if the material is post-cured 12 h at 60 °C compared to a room temperature cured sample. Cross-linking enhances the mechanical properties of the composite including hardness. The latter is considered to be the dominant variable in improving wear resistance.

Another demonstrative fact about the importance of the curing process is that test specimens with an unaccelerated resin-paste additive had 5% higher wear rate. The unsaturated polyester resin system needs both initiator and accelerator

for the curing process. The unaccelerated resin-paste formed an unpolymerized substance and by that lowered the mechanical properties of the material.

3.2.7 Results and discussion of filler hardness effect

Abrasive wear can be reduced by replacing the existing materials with harder alternatives [69]. Due to this hypothesis the tests also included a digression in the reinforcement type. Material specimens with quartz (SiO_2) and aluminium oxyhydroxide (AlO(OH)) were fabricated in order to evaluate their wear resistance. These mineral powders could be used as a third phase in the composite to further enhance the wear properties. SiO_2 has Mohs' hardness index of 7, density 2.65 g/cm^3 and d_{50} 80 μm. AlO(OH) Mohs' hardness index is 3,5 - 4, density 3,07 g/cm^3 and d_{50} 2 - 4 μm [70, 71]. Both have higher hardness but also density than $Al(OH)_3$. SiO_2 is beige and AlO(OH) white with slight beige undertone.

SiO_2 showed 96% lower wear rate and 43% higher hardness and AlO(OH) showed 20% lower wear rate and 17% higher hardness at 60 wt% compared to $Al(OH)_3$.

Based on the results there is ground for consideration of adding one of these fillers to the aluminium hydroxide in order to improve hardness and wear resistance. AlO(OH) is a more promising candidate due to the better colour match. The volume fraction of the third phase needs testing but could be around 5 - 10% as has been suggested to be effective to the properties [56, 72, 73].

3.2.8 Results and discussion of particle size effect

Even though, there is contradiction in the findings of different authors on the subject of particle size effect on wear resistance there is a common conclusion – the particle size does affect the wear performance of a material. The effect of particle size was under observation in [**Paper IV]**. There was no change in the wear rate with the change of the particle size. The results in [**Paper IV]** are most likely related to the 3-body abrasive wear methodology and the adhesion of the abrasive medium to the specimens.

3.2.9 Results and discussion of filler weight fraction effect

The effect of particle weight fraction was studied in both [**Paper IV]** and article [25].

In article [25] with the introduction of $Al(OH)_3$ the wear rate of the composite decreased compared to the neat resin. Material with 65 wt% of aluminium hydroxide had 10% lower wear rate than the neat resin. This is due to the difference in hardness of the matrix and the reinforcement. If the hardness difference was greater the wear rate reduction could be even more. Further loading did not give any additional reduction.

With pin-on-plate methodology the wear mechanism was abrasive wear. The fracture was generated through micro-cutting as the harder silicon carbide particles penetrated the softer composite's surface (P400 (35 μm) silicon

carbide abrasive paper was used as the abrasive surface). The process included some adhesion of the composite to the abrasive. The wear surfaces of the specimens were evenly furrowed and no detachment of aluminium hydroxide particles was observed. Due to the continuous shift of the abrasive surface the specimen was not affected by the wear debris.

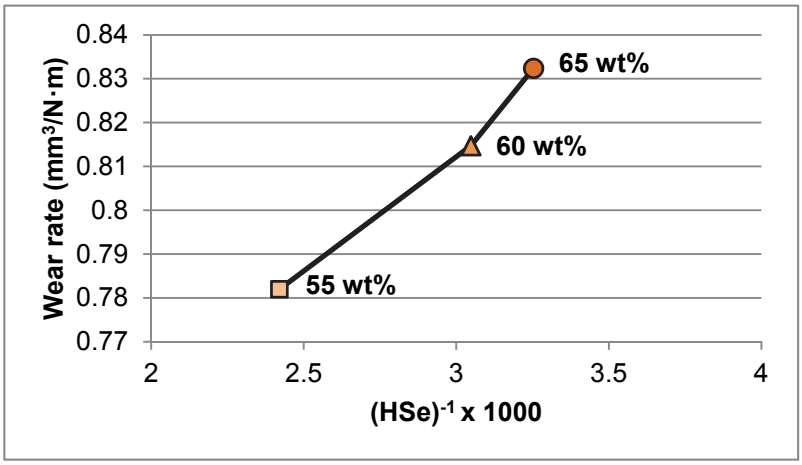

Figure 3.7 Ratner-Lancaster plot of the composites with different weight fraction

Figure 3.7 presents the Ratner-Lancaster plot based on the wear data from article [25] and mechanical properties from **Paper I.** This near linear relation confirms the correlation between bulk mechanical properties and abrasive wear in the composite.

3.2.10 Summary of wear resistance factors

The wear of polymer composites is a lot more complicated than the wear of metallic materials. The wear of the material is firstly affected by the wear mode – 2-body or 3-body wear. Secondly, the wear test conditions like speed and force play an important role. In current research it was observed that in 3-body wear the abrasive's particles adhere to the composites surface and change the game completely. In 2-body wear conditions aluminium hydroxide reinforces the polymer and reduces wear. If lower wear rate is desirable than high hardness additives like aluminium oxyhydroxide can be used.

3.3 Impact resistance

Composites combine different materials and create novel properties. Nevertheless, a composite is also a compromise – winning in one property means losing in another. It is the same case with particulate composites. As the tests in **Paper I** and **IV** showed filler mass fraction increase improves indentation hardness, stiffness and wear resistance. These are all awaited properties but as Foley et al [74] stated – since hardness and toughness are

inversely related, increased wear resistance is accompanied by reduced impact resistance. It was acknowledged during the tests in **Paper III** that post curing has an even greater effect to the decrease in toughness. The composite becomes impractically brittle when post cured at temperatures over 60°C. This led to a crossroads – toughness could not be sacrificed but other mechanical properties and low cost had to be maintained. One proposition was to use smaller fraction particles. As literature review in the following paragraph shows there is no consensus about how particle size or mass fraction influences toughness. This led to **Paper V** where the influence of these parameters and post curing to toughness was tested.

3.3.1 Literature overview on particle size effect

There are numerous studies on the subject of toughness of particle reinforced polymer composites. Fu et al. have gathered the proposed toughening mechanisms to the following list: 1) crack front bowing (or crack pinning), 2) particle bridging, 3) crack deflection by hard particles, 4) particle–matrix interface debonding, 5) bifurcation, 6) micro-cracking, 7) micro-shear banding, 8) breakage of particles, 9) crack-tip blunting, 10) diffused matrix shear yielding, etc [75, 76] (Figure 3.8).

Hard particles can have a weakening or toughening effect on the matrix. If they act as stress concentrators they are the weak link. On the other hand, they may deflect the crack front and slow down the crack growth [75].

Singh et al. suggest [77] the following: “In the case of ceramic and glass, the internal defect size and hence the intrinsic particle strength is a function of particle size,” meaning that as the particle size increases so does the number of defects. Thus smaller particles should provide greater toughness. At least, when particle breakage is present.

In the opinion of Li and Huang the toughening effect of smaller particles consists in creating larger number of “pins” for the same volume fraction [78].

Crack pinning is an effect where reinforcing particles pin down the crack. The crack is unable to halve the particles and is forced to bow. Bowing on the other hand requires additional energy. The concept does not apply in case of weak particles. The crack bowing mechanism explains the toughening effect of hard particles in a brittle thermoreactive matrix. From SEM images the crack pinning is distinguished by the “tails” behind the particles.

A precondition for crack pinning is that the particles are hard (high tensile strength, toughness) and there is good adhesion between the particle and the matrix. Otherwise the crack might halve the particle or transform into a crack between the particle and the matrix [78].

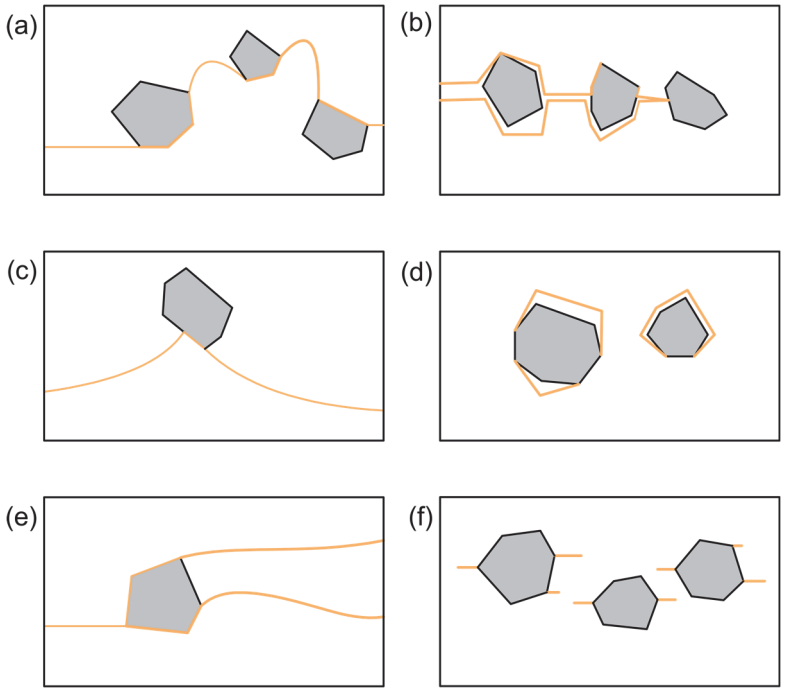

Figure 3.8 Toughening mechanisms: (a) crack pinning (b) particle bridging (c) crack path deflection (d) debonding (e) bifurcation (f) micro-cracking

Based on the observations that a crack front changes its shape when it meets inhomogeneity in a brittle matrix and the concept that it has line energy Lange proposed a model where he linked composites' fracture toughness (G_c) and line tension (L) [79]:

$$G_c = G_m + \frac{L}{D_s}, \tag{3.2}$$

$$D_s = \frac{2d_p(1-V_p)}{3V_p}, \tag{3.3}$$

where
G_m – fracture toughness of matrix,
D_s – inter-particle spacing,
d_p – particle diameter,
V_p – particle volume fraction,
L – line tension.

Lange's line tension concept was revised by Green et al. [80, 81, 82]. According to them the stress for crack growth, particle size and volume fraction can be interrelated:

$$L = L(V_p, d_p, D_s). \tag{3.4}$$

Nevertheless, as the models do not include variables like interfacial adhesion, strain rate or material properties they are of low practical value.

Hojo et al. [83, 75] had experimental results where particle size increase lowered the strength of a silica particle reinforced epoxy matrix. They formulated the following relation:

$$\sigma_c = \sigma_m + k_p(V_p)d_p^{-1/2}, \tag{3.5}$$

where
k_p – constant (function of the particle vol%),
σ_c – composite strength,
σ_m – matrix strength.

$$\sigma_c = \sigma_m + \frac{S}{D_s} \tag{3.6}$$

Formula (3.6) was proposed by Young and Beaumont [84]. They suggested a relation between composites' strength and particle distance. *S* represents a constant that depends on interface adhesion.

Formulas (3.5) and (3.6) predict that smaller particles increase the composite strength.

Another important toughening mechanism in composites is crack bridging [78, 85, 86, 87]. It is similar to the fibre pull out mechanism in fibre reinforced composites. If a crack tip passes a hard particle and is unable to break neither the particle nor the particle-matrix interface then there forms a particle "bridge" in the wake of the crack. The additional energy that goes into debonding and pulling these bridging particles out from the matrix improves the toughness.

Firstly, bridging is associated with geometrical interlocking of the irregularly shaped particles in the matrix [87]. Secondly, there is frictional traction in the particle-matrix interface during the grain pull-out [88, 89]. Bennison and Lawn believe that internal residual stress caused by thermal expansion mismatch controls the restraining stress of bridging [89].

A larger particle means a longer pull-out distance. Nevertheless, it would be more effective to introduce a higher number of bridging particles as the former reduces the strength of smaller particle sizes. [87]

There is consistent experimental data that smaller particle size increases strength (σ). Nevertheless, it is under dispute how the particle size influences the toughness through crack bridging. It is believed that sizes from 10 - 40 μm have a toughening effect and smaller or larger do not contribute to toughness through bridging.

Li and Huang suggest that small and large particles should be optimally mixed to maintain both toughness and strength as larger size aggregates are beneficial for the former, whereas smaller aggregates are good for strength [78].

Experimental studies with ceramics show that there is a strong relation between the microstructure and the *R-curve*. Namely, increase in grain size increases the toughness due to the bridging occurring behind the crack tip [87]. Resistance in materials to crack extension is commonly designated as *R*. The crack resistance curve is a plot of *R* against crack extension thus the *R-curve*.

Fu et al. [75] attribute the impact strength increase effect of smaller particles to the greater total surface area of the particles. They suggest that there is better stress transfer between the matrix and the reinforcement.

Katz [2] sees another side in the particle size. Inclusions (voids, fibres, particles, notches etc.) that differ in ductility from the matrix act as stress concentrators. An important parameter in this case is the maximum packing fraction of the filler. Poorly packed fillers disperse unevenly in the matrix and form more stress concentrators. Fillers with higher maximum packing fraction lower the impact strength less. Aluminium hydroxide is a rigid, high-modulus material and thus embrittles the matrix. A filler with coarser particles and thus better particle packing should decrease the toughness less than a finer filler.

There is little data available about impact properties of particulate composites with unsaturated polyester matrix. If we rule out the thermoplastics that are superior to thermoreactivess in toughness [75] we can compare our results with epoxy matrix particulate composites. The absolute values might differ but due to the similarity in fracture mechanisms the trends are comparable.

Radford and Lange studied the effect of different particle sizes and loadings of aluminium hydroxide to the fracture toughness (kJ/m^2) of an epoxy matrix [72, 90]. They compared particle sizes 1, 2, 5, 8 and 12 μm. With particle size increase the toughness improved.

3.3.2 Literature overview on filler content effect

The crack growth resistance of a polymer – filler interface is considerably lower than that of pure polymer which deforms plastically and absorbs part of the impact energy. The impact strength is proportional to the rate at which the crack grows. The crack does not halve the hard particles but propagates through the relatively weak particle – matrix interface that is ruled by the adhesion forces between the two. [91, 92]

Nie summarised the role of particle-matrix interface as follows: “For composites with weak interfacial bonding, the debonding is the major damage mode. For composites with strong interfacial bonding, the breakage of the agglomerate of particles is the major damage mode.” [93]

When Radford and Lange studied the effect of aluminium hydroxide loading to epoxy matrix fracture toughness they compared loadings 0.100, 0.215, 0.295 and 0.430. The toughness peaked at a particle volume fraction of 21.5% [72, 90].

The equations (3.2) and (3.3) predict a rise in fracture toughness with increased particle loading at a constant particle size. But as Lange and Radford themselves proved G_c is improved only to a certain maximum and will decrease with further loading of filler.

3.3.3 Experimental design of impact tests

The impact tests were conducted according to ISO 179 “Plastics – Determination of Charpy impact properties”. The indentation hardness of the

materials was measured with a GYZJ 934-1 Barcol Impressor. The indentation hardness tests were conducted according to ASTM D2583. Unsaturated polyester resin specified in paragraph 1.2 was used. ATH with d_{50} 35 µm, d_{50} 20 µm and d_{50} 7 µm was used. Initial cure of specimens was done at room temperature (23 ± 2 °C). That was followed by post cure at 40 °C for 12 h. In addition neat resin samples were fabricated from which half were not post-cured.

Table 3.2 Composition of impact test specimens

Material	IM-1	IM-2 NPC	IM-3	IM-4	IM-5	IM-6	IM-7
Resin (wt%)	100	100	50	40	35	40	40
ATH (wt%)	0	0	50	60	65	60	60
ATH (d_{50}/µm)	-	-	7	7	7	20	35

The composition of the test specimens is presented in Table 3.2. Specific info about the experimental setup can be found in [**Paper V**].

3.3.4 Results and discussion of particle size effect

It was expected that the decrease in fillers particle size would linearly increase the impact strength of the composite. When the influence of fraction size was examined no clear trend was found. Although the composite with the smallest 7 µm particles had the highest impact strength, the second best was composite with 35 µm particles not with 20 µm particles as can be seen from Figure 3.9.

The better performance of the 7 µm composite could be attributed to the higher specific surface area and thus better stress transfer. According to laser granulometry tests the specific surface area of 7 µm ATH is 14 900 cm^2/cm^3 but 35 µm ATH has 9900 cm^2/cm^3.

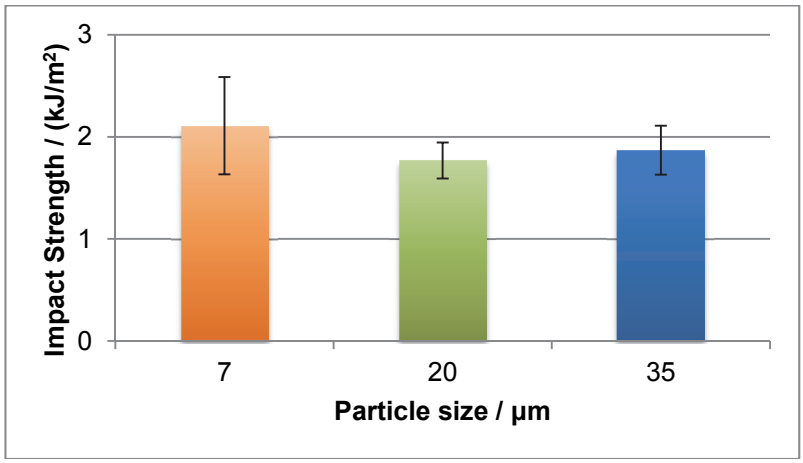

Figure 3.9 Particle size influence to impact strength

The crack surface reveals that the crack mechanism changes while the crack progresses (Figure 3.10). Higher stresses at the prelude of the crack lead to particle-matrix interface debonding and possibly particle halving so the filler is exposed. As the stress descends the crack is unable to overcome the interface forces and makes its way through the matrix. This is evident with all specimens. This confirms the necessity of a coupling agent.

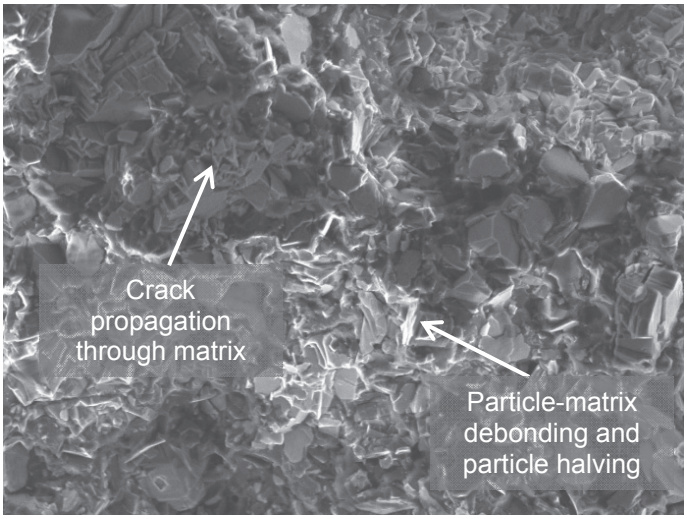

Figure 3.10 SEM image of crack surface of composite with 35 µm reinforcement

The crack pinning mechanism should obstruct crack propagation by making it deflect or cause bifurcation. The latter is visible with 7 µm composite. There are two or more branches at the beginning of the crack and chipping can be seen. All this contributes to the slowing down of the crack. Crack deflection is visible with all particle sizes. Finer powder has more particles and thus more crack pinning sites.

Although the 35 µm composite is in the suggested range of particle sizes where crack bridging should occur evidence of the mechanism is hard to witness on the crack surface due to the high filler fraction. The crack bridging mechanism might explain the better performance of 35 µm composite than the 20 µm composite.

A factor that catches attention is the deviation of the impact strength values of different particle sizes. With coarser particles the deviation decreases. The effect could be explained by the better particle packing. The specific density of aluminium hydroxide is 2400 kg/m^3. The bulk density of 7 µm aluminium hydroxide is 950 kg/m^3 but the same value for 35 µm is 1100 kg/m^3. This implies that the particle packing of 35 µm particles is better. Moreover, the density of the composite reinforced with 35 µm particles is 1660 kg/m^3 but in case of 7 µm particles the density is 1640 kg/m^3. All in all, this means that a coarser filler produces a denser composite with more uniform properties.

From the bulk density and specific density the porosity can be calculated:

$$\varphi = 1 - \frac{\rho_{bulk}}{\rho_{specific}}. \quad \textbf{(3.7)}$$

The porosity of aluminium hydroxide with 7 µm particles is 0.60 but with 35 µm particles it is 0.54.

The effect of particle packing was also pointed out by Katz [2]. Although, there is discrepancy in the effect to toughness the effect to deviation is clear. Nevertheless, the particle packing might explain the non-linear relation between particle size and impact strength. As 20 µm ATH does not benefit from a larger specific surface area effect or better particle packing effect it is the least beneficial particle size.

3.3.5 Results and discussion of filler content effect

In the current composite the filler mass fraction is 50 - 65%. The equations (3.2), (3.4) and (3.6) that relate composite strength to inter-particle distance are not applicable due to the high particle weight fraction.

The tests with different mass fraction of 7 µm particles did not show a clear trend either (Figure 3.11). Nevertheless, the deviation of the results decreased with increasing filler loading. With higher loading the composite becomes more homogenous and the properties more uniform. The crack pattern is clear proof of this (Figure 3.12). With 65 wt% of filler cracks are straight but with 50 wt% the crack deflects.

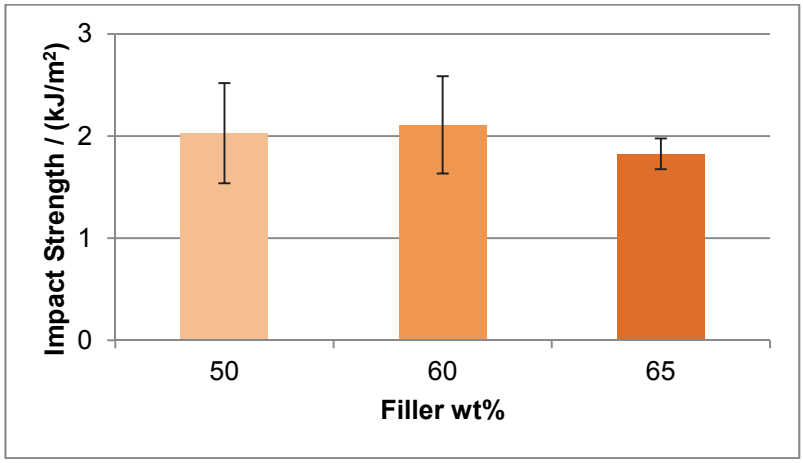

Figure 3.11 Filler mass fraction influence to impact strength (ATH d_{50} 7 µm)

None of the reinforced test specimens could compete with neat resin (NR). The latter showed 4 times higher impact strength as shown on Figure 3.13. It is clear that at this level of loading the properties of reinforcement dominate and that causes brittleness.

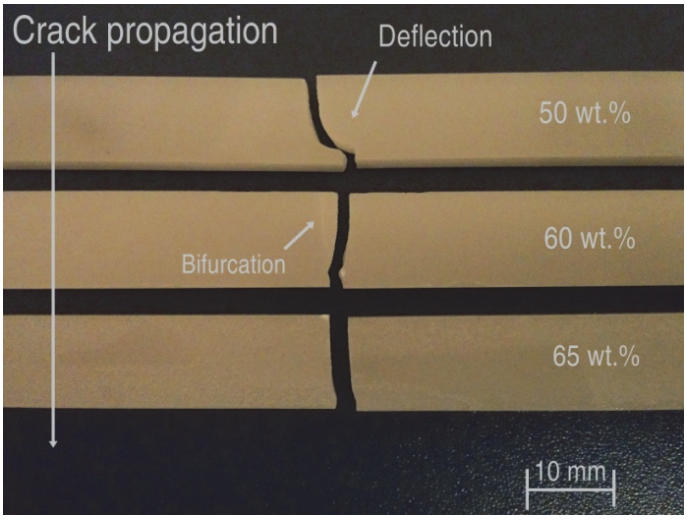

Figure 3.12 Crack pattern in specimens with varying filler mass fraction

3.3.6 Results and discussion of post-curing effect

Another source of brittleness is post-curing. It reduces the amount of unpolymerised material but in the same time also toughness. From a practical viewpoint there is not much choice – material with residual styrene cannot go into service.

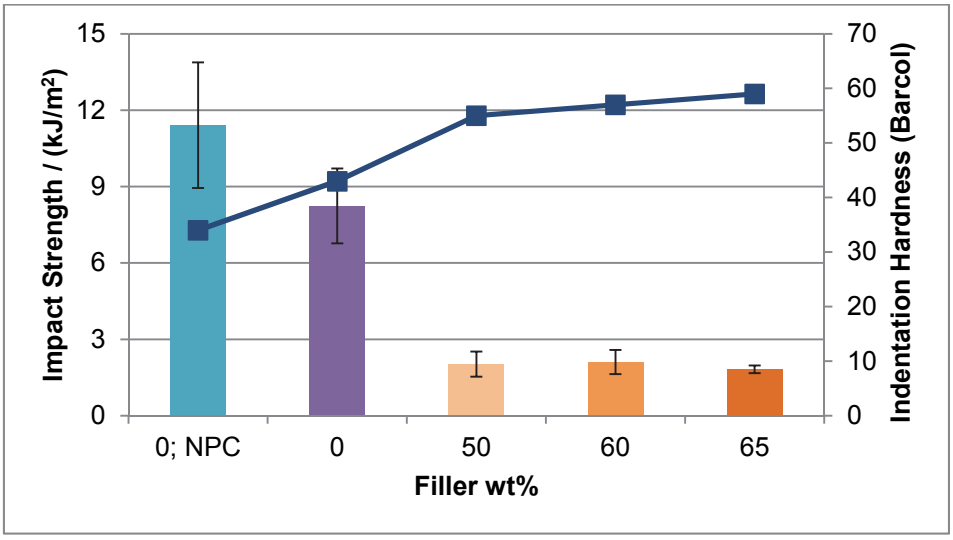

Figure 3.13 Impact strength (bars) compared to indentation hardness (line) (NPC – not post-cured)

3.3.7 Summary of impact resistance factors

The dominant toughening mechanism dictates the effect of particle size. Crack pinning favours finer particles and crack bridging coarser ones. With the current material better results are achieved with a finer filler.

If the results are put into larger perspective it is clear that filler at this concentration reduces the impact strength considerably. The general understanding that hardness is inversely related to toughness is clearly the case with particulate composites.

4. TECHNOLOGICAL PROPERTIES

4.1 Production process of the composite

The following graph describes, in a nutshell, the production process of the particulate polymer composite.

The quality control of raw materials includes moisture and fraction analysis of the reinforcement and curing kinetics of the matrix. The casting machine has a vacuum chamber that removes air from the dispersion. Based on the polymerisation process the dosing of catalyst and accelerator are adjusted. Customer feedback is the basis of product and material development.

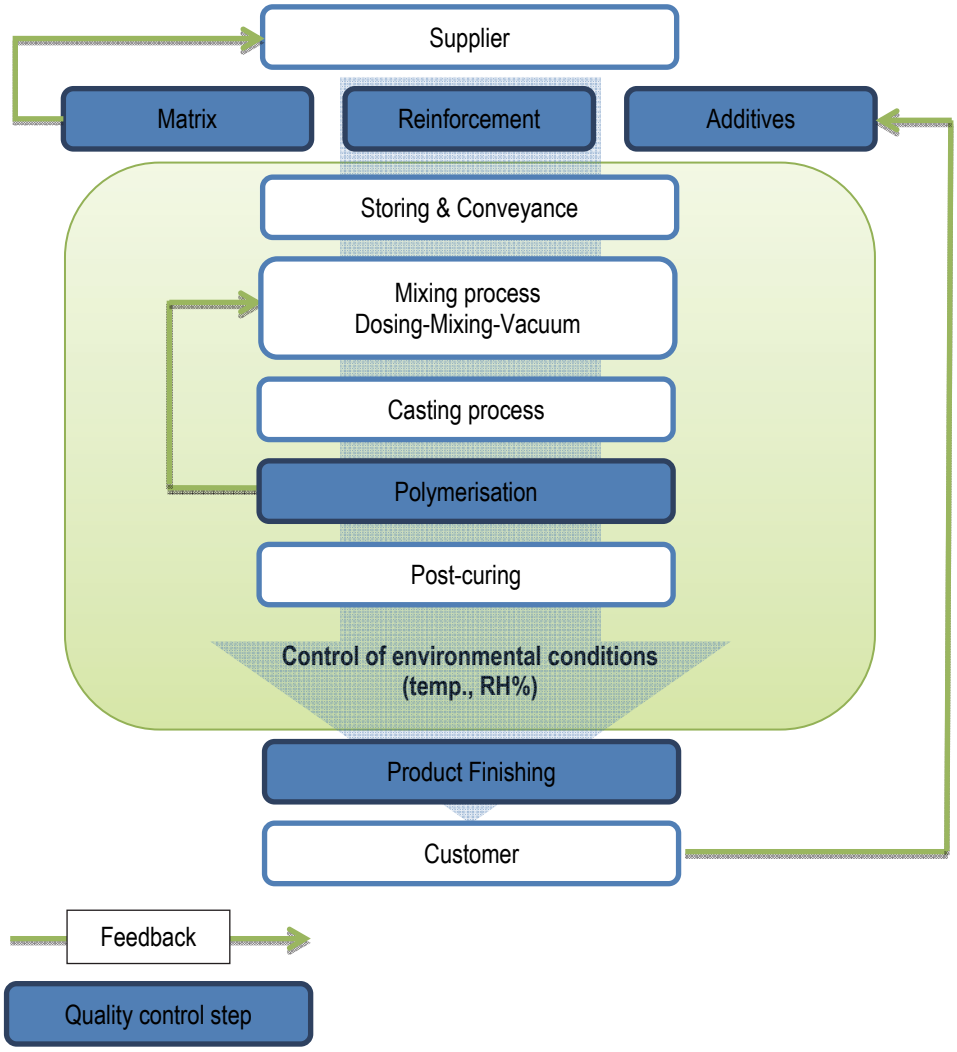

Figure 4.1 Production process of particulate polymer composite products

4.2 Post-curing of the composite

Knowledge about the need to post-cure thermoreactive polymers is widespread in the polymer composites industry. Nevertheless, there is limited information available on how to choose the parameters. Academic handbooks state the facts but do not provide any methodology. Commercial handbooks and technical data sheets (TDS) provide a parameter band but do not specify the influence of different choices to the mechanical, physical and chemical properties. The suggestions are often contradictory. This sets the need to determine the post-cure parameters that suit best to this specific polymer composite so optimal material properties and process is achieved.

Unsaturated polyester resins are obtained by dissolving unsaturated polyester polymer in a low-viscosity monomer. The latter is mostly styrene. The copolymerisation of the resin solution is much faster than the homopolymerisation of the polyester polymer. The resin also has much lower viscosity and is thus easier to handle than polyester polymer. The polyester and the styrene both have reactive carbon-carbon double bonds. A radical-initiated polymerisation process leads to the reaction of those carbon-carbon double bonds and to the formation of a 3D polymer network with chemical covalent cross-links (the polymerisation process is often referred to as *curing* or *cross-linking)*. The process is irreversible contrary to thermoplastics because the cross-links are thermally and mechanically stable.

Organic peroxides like methyl ethyl ketone peroxide are used as radical initiators (thus referred to as *initiator* or *catalyst*). Radicals form by the decomposition of the peroxide. This is achieved with heat or with a redox reaction. Cobalt naphthenate metal salt solution (*accelerator* or *promoter*) is used for the latter. Cobalt ions react with the peroxide and radicals form which react with the carbon-carbon double bonds to form reactive places on the molecule. This leads to the cross-linking of polymer chains with the styrene molecules. It is an exothermic reaction. The polymer first becomes a gel and then a solid as the cross-linking progresses. The generated heat accelerates the reaction process even further.

The curing process is influenced by the initiator-accelerator system, the surrounding temperature and by the mass of the polymer [9]. Greater product thickness produces higher exothermic temperature. Mineral fillers on the other hand reduce the exothermic temperature [5]. It depends upon the concentration of the filler. Exothermic temperature is on the one hand necessary for a better cure but on the other hand can cause excessive shrinkage and distortion of the product or harm the moulds. Therefore the initial curing is usually done at room temperature (RT). At RT a complete cure is rarely achieved. After polymerisation there is usually 2 - 4% of unreacted styrene monomer present in the material [9]. This reduces the performance of the material, the evaporating styrene smells bad and the material is not suitable for food contact.

Based on the above, the process variables depend upon: 1) specific polymer, 2) initiator-accelerator system, 3) filler, 4) additives, and 5) product geometry.

Although there are some studies [94] that try to construct an algorithm the complexity of the formula determines the need for experimental tests.

The process variables were determined in **[Paper III]**. The cure state of the composite was evaluated based on mechanical properties, glass transition temperature, residual energy and solvent swelling test.

4.2.1 Literature overview on post-curing process

Thermoreactive polymers and composites with thermoreactive matrix are post-cured at elevated temperature after initial polymerisation to enhance the cross-linking of the styrene monomer and polyester polymer. This lowers the residual styrene content, improves the mechanical properties and chemical resistance of the material [5, 9, 95]. Higher temperature increases the reaction activity of molecules.

The most important post-curing process variable is temperature [96, 97, 98]. Other parameters that have to be considered are process duration, temperature profile gradient, and time between initial cure and post-cure [94, 99].

The suggested temperature together with duration varies a lot. Lipovsky [96] suggests that the temperature should be equal to the resin's glass transition temperature (T_g) or slightly above it (T_g of tested resin is 108 °C). Contradictory to this there is the statement that the temperature should not be over 107 °C because this causes discolouration and degradation of the material [95]. Other sources propose temperatures 60 - 120 °C and a corresponding decrease in duration 8 - 1 h [100]. What the sources agree on is that increased temperature allows shortening of the post-cure process.

It has been found that the post-cure cycle should be 80 °C 4 h in order to assure good stain resistance [101].

Thermoreactive polymers properties are to a large extent related to cross-link density. Highly cross-linked polymers are harder, stiffer, heat resistant and chemically less active [102].

Lipovsky [96] proved false the myth that a thermoreactive polymer will reach complete cure at RT over time. The maximum T_g of the studied resin was 76 °C. The resin had T_g 48 °C after 1 month as well as after 1 year when it was cast and kept at RT.

Below glass transition temperature (T_g) polymers are rigid and glassy but above it become rubbery [102]. The polymer softens and loses its mechanical properties before the T_g is reached. T_g actually represents the centre of a transition region. Therefore the service temperature of the material should be below T_g. T_g depends upon the specific polymer and its curing process. T_g can be increased by increasing post-cure temperature [103]. This also means that based on T_g the cure state of the material can be assessed [102].

4.2.2 Literature overview on post-curing technology

The post-curing technology is fairly simple. Depending upon the part dimensions an oven or special room is used. Sheet material is post-cured on the

same conveyer where it is produced. There are different ways to induce heat – infrared radiation, microwaves or conventional thermal heating.

Nightingale et al. [104] and Kwak et al. [105] have demonstrated that microwave energy can be successfully utilised for post-curing polymer composites and the method reduces processing time. Moreover, the ultimate strength of the material is improved (approximately 10%) compared to conventional methods. Conventional thermal process on the other hand gives higher tensile and flexural moduli [21].

Infrared curing reduces the process time up to 40% and power consumption by 33% compared to conventional thermal curing and gives same material properties [106]. Infrared radiation generates through thickness heating and thus uniform curing. With thermal heating the core layers are heated slower and because of non-uniform curing internal stresses develop [107].

Microwave curing system is far more complex than the alternatives. Infrared emitters are simple and the system is cost effective to build.

4.2.3 Experimental design of curing tests

Differential scanning calorimetry (DSC) is a common tool to study curing processes of polymers. DSC measures the difference of heat required to increase the temperature of the test sample and a reference. The chemical and physical changes of the material are expressed through exothermic and endothermic processes. Glass transition is an endothermic process. Curing gives an exothermic peak on the DSC graph. The cure state of the composite can be calculated based on the heat of cure ΔH/(J/g). Less residual energy means higher cross-link density [108]. By comparing the heat of cure of post-cured and room temperature cured samples one can calculate the cure state [109]:

$$C_{\%} = \frac{\Delta H_{uncured} - \Delta H_{cured}}{\Delta H_{uncured}} \times 100, \quad \textbf{(4.1)}$$

where
$C_{\%}$ – per cent of cure,
ΔH_{cured} – heat of cure of post-cured sample,
$\Delta H_{uncured}$ – heat of cure of room temperature cured sample.

The indentation hardness of the material was measured according to ASTM D2583 with Barcol impressor. Hardness is the material's ability to withstand external forces and consequent deformation by another body [110]. Because of the complex nature of the phenomena hardness is measured in different ways: indentation hardness, rebound and scratch hardness. Barcol hardness test characterises the hardness based on the depth of penetration of an indenter, thus indentation hardness [102]. It is used to assess the rate of cure of thermoreactive polymers [102].

Hardness measurement was also used in another test. Material specimens were placed into ethanol solution and the loss of hardness was measured. The polymer does not dissolve but ethanol is able to form secondary bonds with

linear polymer chains that are not cross-linked. The softening extent indicates the degree of cross-linking [111].

The flexural properties of the material were determined according to ISO 178 3-point bending test.

More detailed description of the experiments can be found in [**Paper III**].

Based on literature different post-cure cycles were constructed to determine the effect of temperature and cycle time to the material properties (Table 4.1).

Table 4.1 Post-cure modes (Paper III)

#	P-1	P-2	P-3	P-4	P-5
Temperature *T*/°C	40	60	60	80	90
Duration *t*/h	12	6	12	12	2

4.2.4 Results and discussion of experiments

As observed by Wu [103] and as can be seen from Figure 4.2 post-curing increases the T_g of the material. The process is more temperature than time dependent because the duration does not compensate for the higher energy that the system receives at higher temperatures. Nevertheless, there is a time factor because samples post-cured for 12 h at 60 °C give 14% higher T_g than those cured at the same temperature for 6 h.

As stated before T_g should be greater than the service temperature of the material. Based on analysis T_g should be 20 - 25 °C above service temperature. With bathware it means T_g of 85 - 90 °C. This is achieved if the material is post-curing above 40 °C.

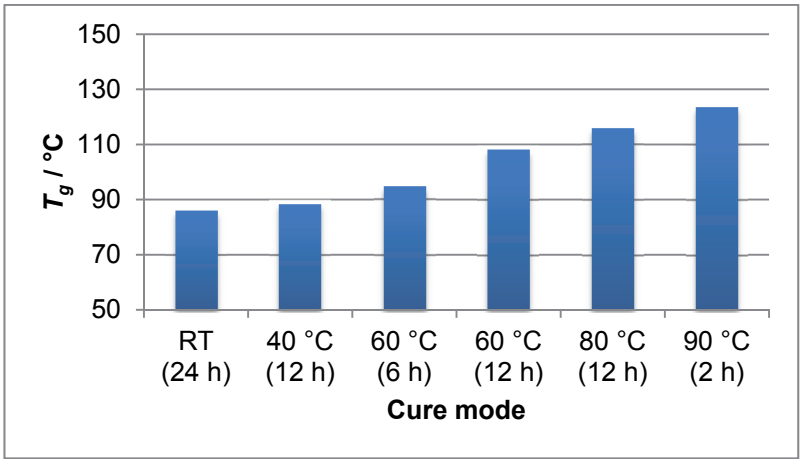

Figure 4.2 Post-cure effect to T_g (Paper III)

In addition to T_g the percentage of cure was determined from the DSC graphs. The results are depicted on Figure 4.3. With increased post-cure temperature less residual energy is left in the polymer and thus a higher cross-link density is achieved. Curing above 80 °C is necessary to achieve a 99% cure state.

In order to verify the cure rate and test the statement that highly cross-linked polymers are chemically less active the ethanol softening test was performed. As can be seen from Figure 4.3 the percentage of cure and softening correlate very well. Highly cured polymer constitutes fewer bonds with ethanol and maintains its mechanical properties because there are fewer linear polymer chains.

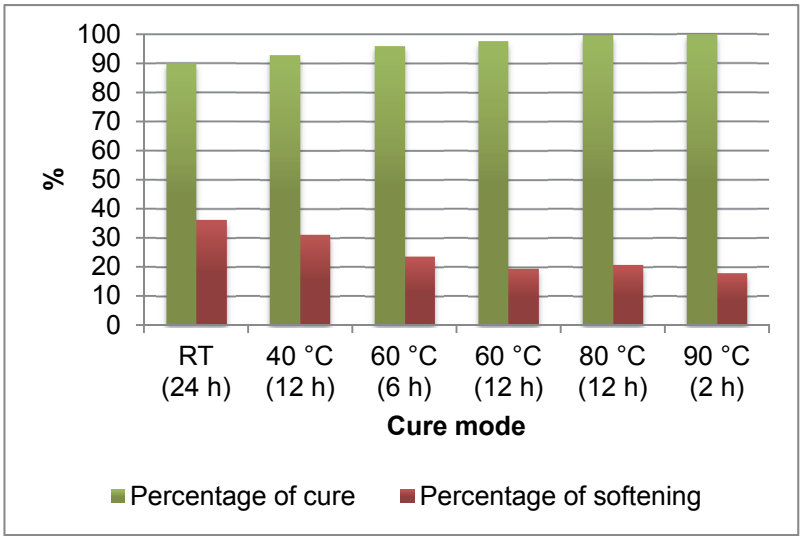

Figure 4.3 Percentage of cure achieved at different post-cure modes compared to materials loss of hardness in ethanol (Paper III)

The tests in [**Paper I**] showed that higher filler content increases the indentation hardness of the composite due to the greater hardness of the filler. But as Figure 4.4 proves the polymer also contributes to the hardness. Higher cross-link density makes the material more rigid and there is less plastic deformation. Nevertheless, the maximum is achieved already at 60 °C at 96% of cure. The remaining linear polymer chains do not influence the hardness in the way they do the glass transition temperature.

The increase in rigidity with increased post-cure temperature can be seen also from the flexural modulus values (Figure 4.5). The growth trend of rigidity slows down beyond 60 °C. Again it is visible that temperature has a greater effect than time in the post cure process.

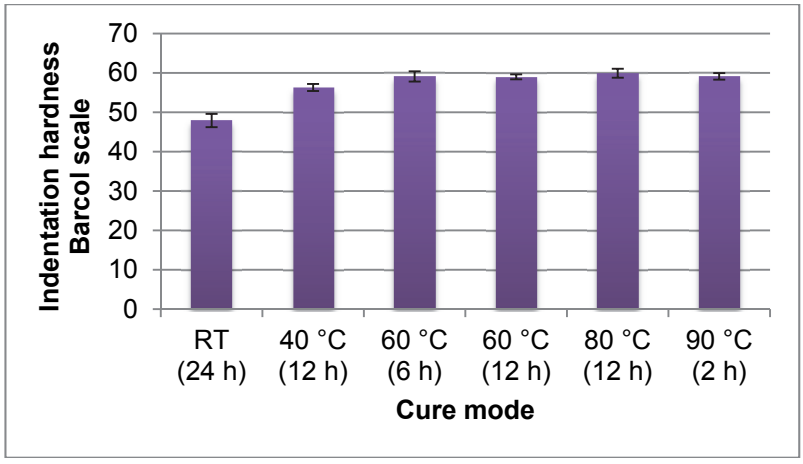

Figure 4.4 Effect of post-cure to the indentation hardness (Paper III)

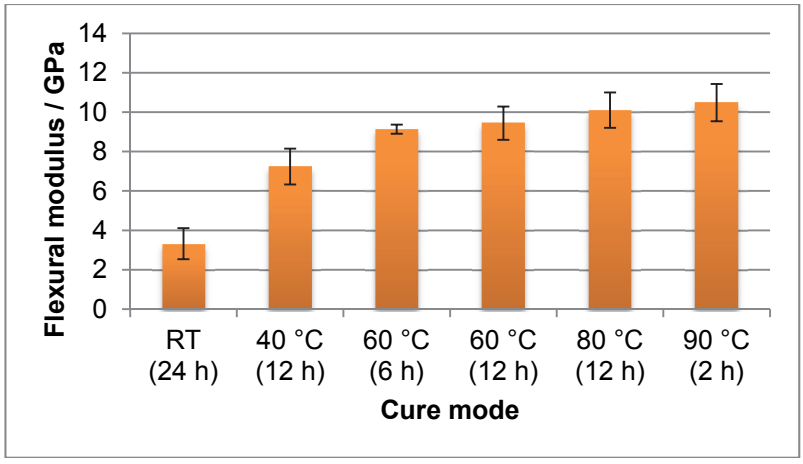

Figure 4.5 Effect of post-curing to the flexural modulus (Paper III)

4.2.5 Summary of post-curing

Complete cure of the polymer can be achieved by post-curing the polymer after initial cure at elevated temperature. The process temperature is a more important parameter than cycle duration. At higher temperatures the necessary energy to promote the polymerisation is transformed faster. Increased post-cure temperature increases the cross-link density and T_g of the material. In conjunction the mechanical properties and chemical resistance are improved. Well cured material that does not have residual styrene is compatible to food and skin contact. From a functional perspective the chemical inertness of a highly cross-linked polymer means improvement in stain resistance. This was also observed in [48]. Hardness increases the wear resistance of the material; this relation is studied more closely in [**Paper IV**] and [25]. The downside of the highly cross-linked and rigid polymer is its brittleness. This is demonstrated

in [**Paper V**]. Conclusive process parameters have to take into account all these aspects.

4.3 Aggregation of filler particles

4.3.1 Literature overview on particle aggregation

A common problem with particulate fillers is that they tend to aggregate. This leads to uneven distribution of the particles. The consequences are processing problems, decrease in mechanical properties and poor aesthetics [75]. The most important factors that drive aggregation are the size of the particles, their surface tension and the shear forces acting on them during processing [14].

The magnitude of aggregation is determined by the ratio of forces attracting and detaching the particles. The common attractive force is adhesion while shear forces lead to detaching. Finer particles tend to aggregate more due to their greater specific surface area [17]. Nevertheless, more important than the particle size is the particle size distribution because particles of the same size tend to attract each other [14].

4.3.2 Observations of particle aggregation

Experience shows that also environmental conditions play an important role in the formation of aggregates. Moisture is an effective attractive force. The heating in winter brings relative humidity down to 20 - 30% but during summer it reaches 70%. In $Al(OH)_3$ the moisture content fluctuates from 0.10 - 0.30%. Although this numerical value may seem insignificant the influence to the powder's flow properties is noteworthy. With high moisture content the powder flows poorly and particles tend to form aggregates. With narrow particle size distribution the effect amplifies. The consequence is aesthetic defects (Figure 4.6). Aggregation can be reduced with particle surface treatment, controlled environmental conditions and increased shear during processing.

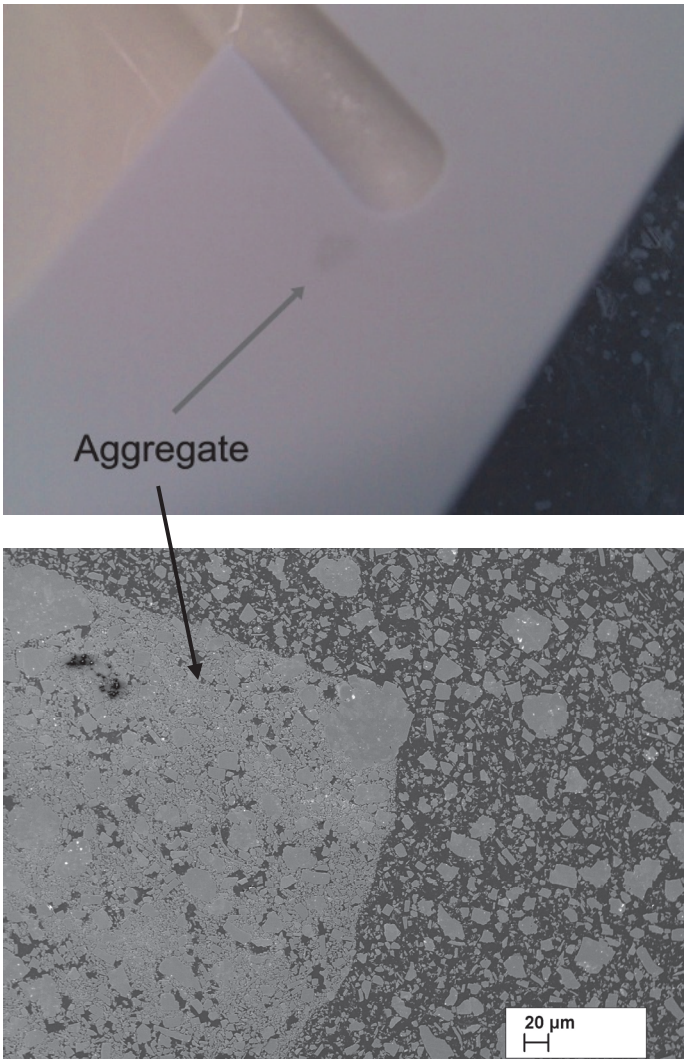

Figure 4.6 Upper image: aggregate as an aesthetic defect in a product; lower image: SEM image of the aggregate causing the aesthetic defect

4.4 Powder handling

The physical characteristics of the powder have a significant effect on the composite's mechanical properties. Moreover, the characteristics have to be included in the equation when designing the storing, conveyance and dosing systems for the powder. Because of the applied nature of this research these aspects were closely studied, although the findings have not been published.

4.4.1 Literature overview on particle packing efficiency

The particle size distribution has a great effect on the packing efficiency. Fuller and Thomson developed a theoretical model of ideal size distribution for maximizing packing efficiency in concrete [112]. Burmister found that the greater the size distribution of particles the greater the packing fraction [113]. Andreasen and Anderson [114] proposed a way to compose a system with minimum voids. The grading curve of percentage by weight finer than x follows the relationship:

$$W_s = 100 * (\frac{D}{D_{max}})^q, \quad \textbf{(4.2)}$$

where
W_s – weight per cent of each fraction,
D – max particle size in each particle size-fraction,
D_{max} – max desired particle size,
q – 1/3-1/2.

With maximised packing efficiency it is possible to increase the powder content in the composite. This is mostly motivated by the cost reduction that the filler offers. With electrical cable insulations the objective is to achieve compliance to stringent fire retardant requirements.

In practice powders (1 μm - 1 mm) are seldom mixed from different fractions. $Al(OH)_3$ powders are manufactured by grinding or precipitation. The particle size distribution depends upon the process (grinding gives wider distribution). Based on the particle size distribution chart and the theoretical models the powder packing efficiency can be calculated and suitable raw material chosen.

4.4.2 Literature overview on particle size distribution

The measurement and analysis of particle size distribution is important because the properties of powder depend upon, besides the particle size, the particle size distribution (mass fraction of sequential particle grades in the powder). [115, 116, 117]

Particle size distribution influences the rheology, abrasiveness and abrasion resistance, particle packing, dispersibility, optics, chemical and mechanical properties [2].

4.4.3 Observations of particle size distribution

For the manufacturer of particulate composite it is important to understand the parameters that characterise a powder in order to specify its needs to the supplier of powder material and to guarantee a consistent quality.

Mineral fillers are usually fractionated – some of the particles from the original distribution are removed. The quality of the process is consistent if the producer does coarseness tests. Other methods like average particle size (d_{50}) analysis can be misleading. It is easy to imagine how different particle size

distributions can produce mathematically the same average. At the same time, different particle size distributions do not produce the same properties.

To exemplify this, below is a comparison of two ATH products with the same d_{50} of 10 μm but different particle size distribution. The results are a combination of sieving and laser granulometry analysis.

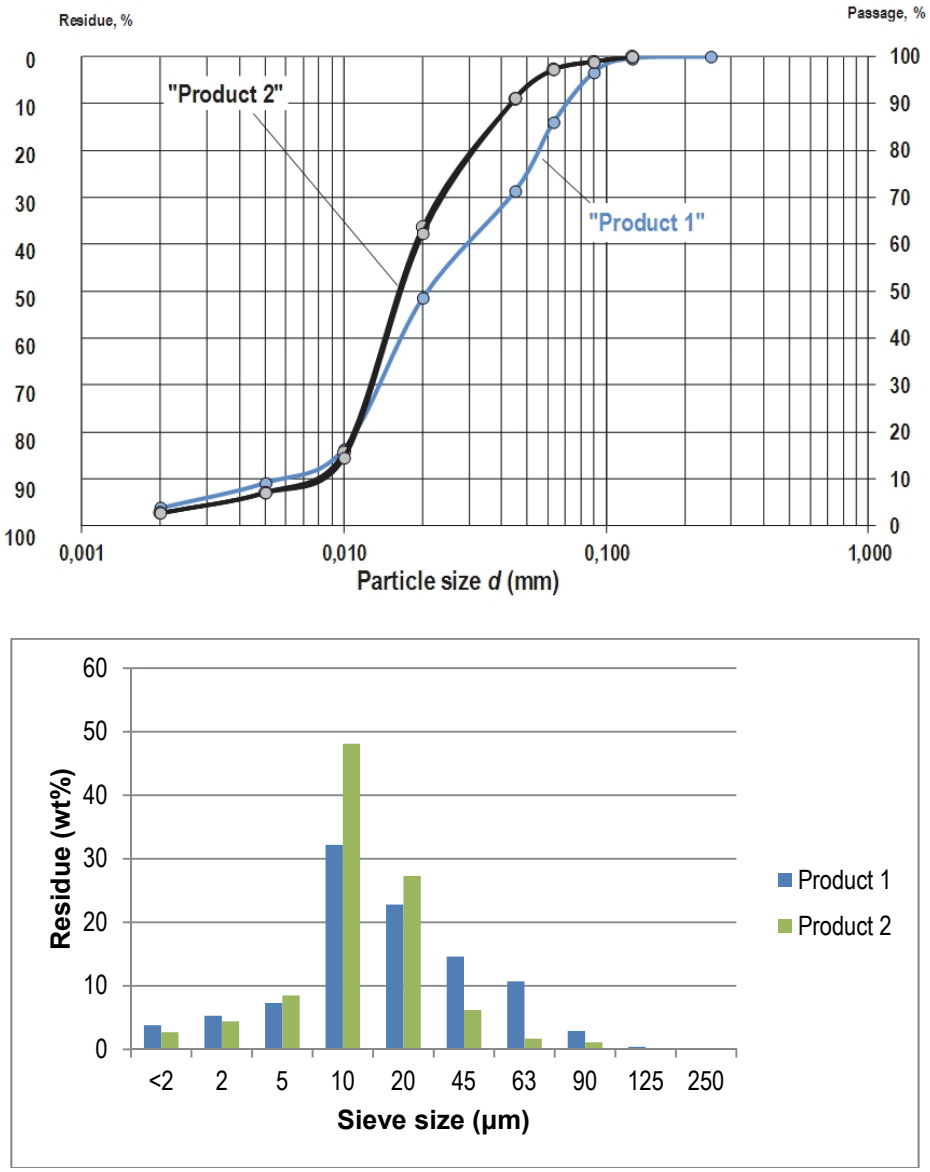

Figure 4.7 Comparison of two ATH products with the same d_{50} of 10 μm

"Product 1" has more coarse particles and due to this it has better particle packing. This changes the bulk density of the material. As the dosing is done by weighting, it influences the output of the powder. "Product 2" gave 21% higher

output than “Product 1.” This leads to filler fraction change in the material. Moreover, the better particle packing changes the rheological properties of the particle-matrix dispersion. As a consequence the mixing and casting parameters have to be adjusted.

“Product 2” on the other hand has a narrow size distribution and due to this is prone to aggregate. In addition, it flows poorly in hoppers and is troublesome to convey. The high amount of smaller fractions increases the viscosity of the particle-matrix dispersion and causes poor mould filling and air entrapment.

4.4.4 Observations of powder flow influence to hopper design

In a laboratory environment the handling of different powders is not a problem. One can easily switch between different materials or different grades of the same material without any trouble. In production this can cause major problems. Parameters like fraction size and particle size distribution have major contributions to the flow properties of powders and thus to the storing and conveying equipment design. Change in fraction size can mean a complete equipment redesign.

There are several parameters that influence the flow of a powder in a hopper: hopper wall angle, outlet diameter, hopper shape, and hopper wall material. If these parameters are chosen correctly the following phenomenon can be avoided: “ratholing”, funnel flow, arching, insufficient flow, flushing and time consolidation. The preferred flow mode is mass flow (Figure 4.8) where all the material is in motion. In other flow modes part of the material is stagnant. In the latter case the material needs external excitation. This leads to production pauses, labour and equipment cost.

The foundation for modern hopper design was laid by Andrew W. Jenike in 1964 [118]. Currently Dietmar Schulze is one of the prominent researchers in the field [119]. The core of the Jenike methodology is the testing of shear properties of the powder. This is done with Jenike Shear Cell or Schulze Ring Shear Tester; the procedures are respectively described in ASTM D6128 and ASTM D6773.

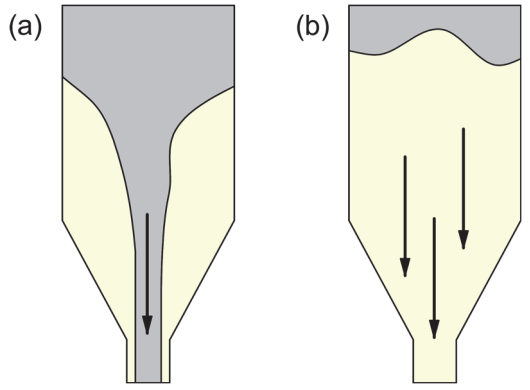

Figure 4.8 Powder flow patterns in hoppers: (a) funnel flow, (b) mass flow [119]

The Jenike methodology was used to design a mass flow hopper for ATH with d_{50} 7 µm. Two materials were compared as inner wall material: UHMWPE plastic and AISI304 stainless steel. Although the plastic showed better properties in the beginning the properties degraded over time due to abrasive wear and it was replaced by steel.

Figure 4.9 Hopper redesign: left old design and right improved design

4.4.5 Observations on powder moisture content

Powders are also moisture sensitive. The moisture content of $Al(OH)_3$ is 0.1 - 0.3%. Although it might seem insignificant in absolute numbers it has a considerable effect to powder flow properties. The routine fluctuation is between 0.12 - 0.19%. If the moisture content exceeds 0.2% it has noticeable effect on aggregation and reduced flow. Powders with narrow particle size distribution have higher moisture content. The analysis was done with special moisture analysing equipment that heats and weighs the lost mass. The method is extensively used in the timber, food, pharmaceutical, and plastics industries.

CONCLUSIONS

The thesis studies a highly filled polymer composite composed from unsaturated polyester resin and aluminium hydroxide. The research covers the mechanical and physical properties, chemical resistance, production process and economical aspects of the material. The literature on highly filled thermoreactive polymer composites is inconclusive. Therefore, the main objective was to design the material targeting economically viable and low density composition that assures good mechanical, functional, and technological properties.

Design

A material composition was proposed based on literature and experience that lowers the cost through extensive use of aluminium hydroxide and decreases the density through use of hollow glass microspheres. The design of the material evolves throughout the study with iterative process.

Mechanical properties

The first sub-objective was to study the effect of mineral filler content and hollow glass microspheres (HGM) to the physical-mechanical properties and economical aspects of the composite.

The physical-mechanical properties of the proposed compositions were tested experimentally. In addition, the effect of HGM was studied through numerical modeling.

The advantages of a higher filler concentration are greater stiffness, indentation hardness and reduced cost. The downside is a moderate decrease in strength and an increase in density. Based on these tests we can say that the **use of mineral filler in high concentration (65 wt%) in thermoreactive polymer is beneficial** in terms of cost reduction and mechanical properties improvement. However, the tests imply that high mineral filler contents causes brittleness. Therefore the combined effect of filler and post-curing was studied in [Paper III] and impact properties in [Paper V].

The inclusion of hollow glass microspheres (HGM) lowers the density of the material. It comes with the price of a considerable decrease in mechanical properties. Moreover, HGM do not deliver the expected reduction of cost. Therefore **the use of hollow glass microspheres is impractical** – the density reduction does not justify the decrease of mechanical properties and higher cost. An alternative that could be tested in future is cenospheres.

Functional properties

The second sub-objective was to evaluate if the good mechanical properties of the highly filled polymer composite also ensure good functional properties.

The stain, wear and impact resistance of the high filler content material were tested and the failure mechanisms studied.

The stain resistance is governed by the polymerisation rate of the composite. A more linear polymer is chemically more vulnerable than a cross-

linked polymer. Cure is improved with the increased content of cobalt compound. This implies that the filler reduces the exothermic temperature of the polymer so much that it inhibits the decomposition of the organic peroxide at conventional conditions thus reducing the cross-linking and the chemical resistance. The monitoring of **the exothermic temperature of room temperature cured highly filled thermoreactive polymers is a critical aspect** in production. However, the polymerization was studied with an indirect method. Therefore, the polymerization process should be studied more thoroughly and the implementation of ultrasound or temperature dependent polymerization detection solution should be tested in production.

Another factor affecting the stain resistance is surface roughness. **The stain resistance can be improved by lowering the surface roughness.** This implies that a low surface roughness has to be achieved in mould or by mechanical post-treatment of the surface in order to have a good stain resistance.

The wear resistance of the material was evaluated in 2-body and 3-body wear conditions. For 2-body wear the pin-on-flat setup was used. 3-body wear was examined with the dry sand/rubber wheel method.

In 2-body wear the filler has a reinforcing effect due to its greater hardness and the wear resistance improves compared to neat resin. Nevertheless, further **filler wt% increase is not accompanied with decrease in wear rate.** This is **due to the high brittleness of the filler**. The governing mechanisms were abrasive wear and particle cracking. The wear behaviour is improved with more complete cure of the composite.

The behaviour of the composite **in 3-body wear conditions** is contradictory with the general assumption – greater hardness does not improve the wear resistance. On the contrary, neat resin has the lowest wear rate. This is caused by the adhesive behaviour and low hardness of the matrix. Because of that, **the abrasive's particles form a wear resistant tribolayer on the composite's surface**. The results were independent upon particle size.

The shortcoming of ATH in wear resistance and indentation hardness can be overcome with additives with greater hardness and finer particle size. Aluminium oxyhydroxide proved to be a potential candidate.

The impact strength of the material was studied with Charpy methodology. In [Paper III] and article [48] the filler together with extensive polymerisation proved to be beneficial to the material's properties. However, both processes cause embrittlement of the material and decrease impact strength. The phenomenon was fought with finer particles. The improvement is achieved thanks to the greater total surface area of the **finer particles** that **improve the particle-matrix stress transfer**. In addition **mechanisms like crack pinning and bifurcation** were observed to **contribute to the toughening of the material**. A topic of follow up research could be the effect of elastic additives to the reduction of brittleness.

Technological properties

The third sub-objective was to develop an efficient production process and assure constant quality of the chosen material composition.

The equipment had to be redesigned in order to cope with the proposed higher weight fraction and finer particle size of the filler. The Jenike methodology was used for the latter. The particle size distribution and packing density were determined as the cause of rheological changes and aggregation. The filler was analysed with sieving and laser granulometry methods and moisture analyser. The **post-cure process** of the composite was optimised. The process **improved cross-linking of the material** and thus increased the glass transition temperature and mechanical properties of the composite.

Conclusion

The study fulfils the set objective – an economically viable material composition that assures good mechanical, functional and technological properties has been proposed and validated. The mechanisms of different processes have been studied.

The products made from the composite have taken a leap ahead. The company has know-how that differentiates it from competitors.

The obtained knowledge is applicable beyond the specific composite. The results and studied mechanism fill a gap in the field of high filler content thermoreactive polymers composites.

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Aare Aruniit

June 2014

KOKKUVÕTE

Suure pulbrilise täiteaine sisaldusega termoreaktiivne polümeerkomposiit

Käesolev doktoritöö uurib suure pulbrilise täiteaine sisaldusega polümeerkomposiitmaterjali. Täiteainena kasutatakse alumiinium hüdroksiidi ja sideainena termoreaktiivset polüestervaiku. Käsitletakse antud materjali mehaanilisi, füüsikalisi ja keemilisi omadusi, tootmistehnoloogiat ja majanduslikke aspekte.

Motivatsioon

Doktoritöö on valminud koostöös ettevõttega Wellspa OÜ, kus doktorant oli samaaegselt arendustöötaja. Sellest tulenevalt on tegemist rakendusliku kallakuga teadustööga, mis käsitleb laia teemade spektrit. Eesmärgiks oli esmalt saada head baasteadmised, töötamaks välja piisava rahvusvahelise konkurentsivõimega tooted. Selle alusel on võimalik edasi liikuda kitsama probleemistikuga ning saavutada juba konkurentsieelis.

Eesmärgid

Töö eesmärgiks on välja töötada majanduslikult ökonoomne, heade mehaaniliste, funktsionaalsete ja tehnoloogiliste omadustega materjal, mis sobib kujupindadega sanitaartehnika tootmiseks. Funktsionaalsete omaduste alla kuuluvad antud töö mõistes määrdumis- ja kulumiskindlus ning sitkus.

Metoodika

Töö on ekperimentaalse kallakuga, mida täiendavad optimeerimisülesannete ja tulemuste statistilise analüüsi juures kasutatud numbrilised meetodid. Põhimaterjale ei varieeritud, kuid vaadeldi täiteaine osakeste suuruse ja osiselise koostise mõju omadustele. Alumiinium hüdroksiidile lisati õõnsaid klaasmikrosfääre, kui madala tihedusega täiteainet ja alumiinium okühüdroksiidi, kui kõvadust tõstvat lisandit.

Töös kasutati nii mehaanika, keemia kui ka füüsika valdkonda kuuluvaid meetodeid. Materjali tõmbe, painde, kõvaduse, löögisitkuse ja määrdumiskindluse katsed viidi läbi vastavalt ISO ja ASTM standarditele. Polümeeri kõvenemiskineetika uurimiseks kasutati DSC aparatuuri ja etanoolis pehmenemise metoodikat. Materjali koostise, mikrostruktuuri ja purunemismehhanismide uurimiseks kasutati SEM ja FTIR aparatuuri. Täiteaine osakeste suuruse, osiselise koostise ning osakeste kuju määramiseks kasutati sõelanalüüsi ja lasergranulomeetria meetodeid. Täiteaine nihkeomadusi testiti Jenike-tüüpi nihkerakisega. Kulumiskindlust katsetati 2- ja 3-keha meetoditega.

Struktuur

Töö on jagatud neljaks osaks. Esimene osa käsitleb materjali põhikomponentide valikut. Teises osas tegeletakse mehaaniliste ja füüsikaliste omaduste optimeerimisega läbi numbriliste ja eksperimentaalsete meetodite. Kolmas osas keskendub materjali funktsionaalsete omaduste analüüsile

lähtuvalt tarbija nõudmistest ning viimane peatükk keskendub tehnoloogilistele väljakutsetele, mis on seotud õigete omaduste ja koostisega toodete efektiivse valmistamisega.

Tulemused

Töö tulemusel leiti, et täiteaine osakaalu suurendamine vähendab materjali omahinda, tõstab kõvadust ja jäikust, kuid vähendab sitkust. Madala tihedusega osakeste lisamine küll alandab tihedust, aga pole muid aspekte arvestades otstarbekas. Materjali järelkõvendamisega on võimalik tõsta temperatuuritaluvust, keemiakindlust, kõvadust ja jäikust tänu materjali täielikumale polümeriseerumisele. Samas kaotatakse jällegi materjali sitkuses.

Kulumiskatsete juures leiti, et antud polümeerkomposiit ei käitu vastavalt levinud arusaamale – suurem kõvadus ei andnud suuremat kulumiskindlust. Määrdumiskindlust mõjutab ennekõike sideaine polümeriseerumisaste. Täielikult "kõvenenud" materjal on inertne ja ei teki keemilisi sidemeid. Löögisitkust on võimalik parandada väiksemate täiteaine osakestega.

Pulbri osakeste suurus ja osiseline koostis mõjutavad suurel määral pulbri voolamist, pakketihedust ja sellest tulenevalt tema käsitsemist tootmises, segu reoloogiat ning lõpuks materjali omadusi.

Järeldused

Uuringute tulemusena töötati välja materjal, mille funktsionaalsed omadused vastavad tarbija ootustele. Tootmistehnoloogia projekteeriti ümber selliselt, et nõutud omadustega materjali oleks võimalik efektiivselt toota ning tagatud oleks järjepidev kvaliteet. Saadud teadmisi materjali omadusi mõjutavate mehhanismide ja tootmisparameetrite alal on võimalik rakendada teiste suure pulbrilise täiteaine sisaldusega komposiitmaterjalide arendustöös.

ABSTRACT

Thermoreactive polymer composite with high particulate filler content

The thesis studies the mechanical, physical and chemical properties, production technology and economic aspects of a highly filled thermoreactive polymer composite material. The filler is aluminium hydroxide and binder a thermoreactive polyester resin.

Motivation

The research was carried out in cooperation with Wellspa LLC where the author worked as R&D manager. Due to this the thesis has an applied nature and deals with a wide spectre of topics. The aim was to gain basic knowledge in the field and build a firm foundation for internationally competitive products. From there it is possible to develop a competitive advantage.

Aims

The aim of the research was to develop economically viable material that has good mechanical, functional, and technological properties and is suitable for casting shaped bathware products. The functional properties are the stain, wear and impact resistance of the material.

Methods

The thesis is built on experimental work that is complemented with numerical methods. The polymer and the filler were kept the same throughout the study only the particle size of the filler was varied. Hollow glass microspheres were tested as density reducing additive and aluminium oxyhydroxide as hardness improver.

Methods from various disciplines were used. The tensile, flexural, hardness, impact strength and stain resistance properties were tested according to ISO and ASTM standards. The polymerisation was studied with the DSC and the ethanol softening method. SEM and FTIR were used to analyse the material composition, microstructure and fracture mechanisms. The particle size, the particle size distribution and the particle morphology were studied with sieving analysis and lasergranulometry method. Fillers' shear properties were tested with Jenike shear-shell. Wear resistance was studied with 2- and 3-body wear test apparatus.

Structure

The thesis is divided into four paragraphs that each covers a specific topic. The first paragraph justifies the choice of the main components and proposes preliminary composition of the material. Second paragraph analyses the mechanical and physical properties of the composite through experimental and numerical methods. Third chapter deals with the functional properties of the material and studies their mechanisms in order to design a material that corresponds to the consumers requirements. Last paragraph looks into ways to achieve an efficient production process of the chosen material composition.

Results

It was found that high filler content reduces the cost, improves the hardness and the stiffness, but causes brittleness. Hollow glass microspheres reduce the density but are impractical from other aspects. The post-curing process improves temperature tolerance, chemical resistance, hardness and stiffness through better cross-linking of the polymer. A downside is that it causes brittleness.

The wear tests showed that the polymer composite acts differently from traditional understanding – greater hardness did not improve wear resistance. Tests showed that the fully cured polymer is chemically inert and has thus better stain resistance. Toughness was improved by using filler with finer particles.

The particle size and particle size distribution effect greatly the flow properties and the packing density of the filler. This in turn affects the conveying and storing of the filler, the rheology of the dispersion and finally the mechanical properties of the material.

Conclusions

A material composition was developed that corresponds to the expectations of the consumer of bathware products. The production technology was redesigned to be able to efficiently produce the desired material composition and to assure consistent quality. The acquired knowledge is applicable to other highly filled polymer composites.

APPENDIX I: PUBLICATIONS

PUBLICATION I

Aruniit, A.; Kers, J.; Tall, K. (2011). Influence of filler proportion on mechanical and physical properties of particulate composite. *Agronomy Research*, 5(1), 23-29.

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Influence of filler proportion on mechanical and physical properties of particulate composite

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Abstract. A particle reinforced composite material consisting of unsaturated polyester (UP) resin and fine dispersion of alumina trihydrate (ATH) has good mechanical properties. It performs well as laboratory or culinary bench top, in bathrooms as vanity top or sanitary ware, in maritime and agricultural applications. The goal of this study is to find out how the filler percentage in the composite influences the mechanical properties of the material and if it is possible to increase the concentration to lower the price. Test slabs with different proportion of filler were fabricated with vacuum assisted extruder. Test specimens were cut from post cured sheets and hardness, flexural strength, flexural modulus, deflection, and density were measured. It is shown that with higher percentage of ATH the flexural strength decreases and hardness and flexural modulus increases together with density.

Key words: Particulate composites, mechanical properties of particle reinforced material, filler proportion.

INTRODUCTION

There is a variety of particle filled composites consisting of thermosetting polymer matrix and particulate reinforcement. Resin is usually unsaturated polyester, acrylic, or polyester modified with acrylic type of resin. Most common fillers are sand, calcium carbonate, alumina trihydrate, and quartz (ICPA, 2003).

An important way to classify these composites is to make a difference between products having surface coat (gel coat) and others having consistent composition throughout the material. Products having surface coat are commonly referred to as artificial marble or artificial onyx. Products that are consistent throughout the material are known as solid surface or engineered stone (ICPA, 2003).

In addition, composite often comprises colour pigment, resin chips for imitating natural stone, accelerator or inhibitor to control the polymerisation process, additives to influence flow characteristics, internal release agents, etc. Nevertheless, the matrix and the reinforcement pose the main influence on all properties.

The choice of materials is based on the requirements. Unsaturated polyester resin modified with acrylic is the best compromise between the cost and mechanical properties. Alumina trihydrate (Fig. 1) is a non-toxic, non-corrosive, non-cancerogenic, odourless, flame retardant filler that provides good whiteness if white products are desirable. It is a mineral derived from bauxite. ATH has specific gravity of 2.42g cm^{-3} and Mohs' hardness index of 2.5–3.5 (Ash, 2007).

The composition of the composite depends on the product. Filler content

influences the morphological properties of the casting dispersion. If the product is a simple slab the filler content can be as much as 66–92 wt% (DuPont, 2008; 2009). When casting products like washbasins or bathtubs the filler content is usually around 55–62% (Cook Composites & Polymers, 2009). The filler content is lower because the casting dispersion has to have better flow characteristics to overcome narrow openings. The filler content influences the shrinkage of the product as well. More filler means less shrinkage and residual stress (Katz & Milewski, 1987).

Figure 1. Alumina trihydrate.

Besides the physical and mechanical properties the filler amount influences the cost of the product. By lowering the resin content in the composition of the particle filled composite one can lower the costs (Zurale & Bhide, 1998). Resin is relatively expensive compared to all kinds of fillers. This is the main motivation that drives the manufacturers to search for possibilities to lower the filler content.

Flexural strength and surface hardness are most important mechanical parameters for brittle materials like particle reinforced thermosets (Preis, 2004). Flexural strength describes the ability of materials to withstand deformation under load. Material hardness gives info about material resistance to plastic deformation by scratching, abrasion, or indentation. These are the most sought properties for products, such as bench tops, washbasins, shower trays, wall and floor claddings.

An important technological step in the fabrication of thermosetting composites is post cure of the material. Post cure is a process to increase the amount of cross linkage in the composite by raising the composite's temperature. The maximum cross-link density is when every carbon to carbon unsaturated group has been reacted and each end group of each chain is connected to another polyester chain. Short post cure times are made possible with ovens that elevate temperatures to the resin's Glass Transition Temperature (T_g) and higher (Lipovsky, 2006).

This study investigates how the amount of particulate reinforcement influences the mechanical and physical properties and cost of the particulate composite.

MATERIALS AND METHODS

For determining of mechanical and physical properties 3 material specimens were cast (Table 1). The filler percentage range was chosen based on the recommended filler concentration for casting of shapes (55–62% (Cook Composites & Polymers, 2009)).

For the fabrication of specimens an unsaturated polyester casting resin based on isophthalic acid and neopentyl glycol was used. The resin is developed to produce non-gel coated products and contains methyl methacrylate. It is a pre-accelerated, medium reactive, low viscosity resin. For curing a methyl ethyl ketone peroxide with resin to hardener ratio of 1/100 wt% was added. As filler, ATH with medium particle size was used. Preliminary cure was done at room temperature (23 ± 2°C). That was followed by post cure at 40°C for 12 h. 500 x 1,000 x 10mm slabs were cast. The slabs were cast with a closed mould with a special vacuum assisted casting machine ADM-KSA 10/15 VAC F. 0.85 bar vacuum was applied. A closed mould guarantees equal thickness and flatness of the slab. That is necessary to get the test specimens as specified in the testing standards. Vacuum chamber of the machine removes air from the casting dispersion and helps to achieve non-porous material. The proportion of filler and other components is controlled by the machine. From all materials 5 specimens were cut for all tests. The test specimens were cut from the slabs with water jet.

Table 1. Test specimens.

#	Proportion of filler wt.%	Post cure temperature °C	Post cure time h
1	55	40	12
2	60	40	12
3	65	40	12

The flexural properties of the material were determined by 3 point bending test (Fig. 2) as specified in ISO 178 Plastics – Determination of flexural properties. The test specimens were with dimensions 50 x 300 x 10mm. A test speed of 2mm min^{-1} was used.

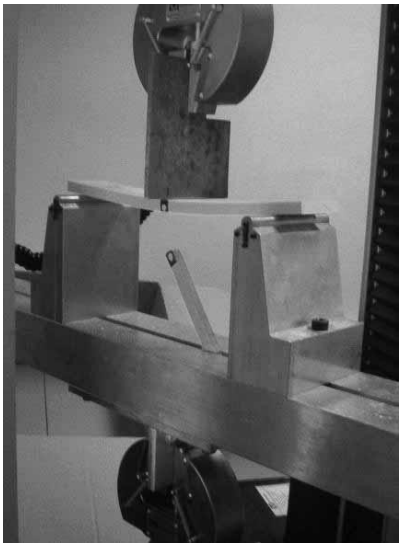

Figure 2. 3 point bending test.

The indentation hardness of the material was measured by Zwick-Indentec 8150 LK according to ISO 2039 Plastics – Determination of hardness. Rockwell M hardness scale was used (ball diameter 6.35mm and major load 980.7 N). Comparative hardness measurements were taken with GYZJ 934-1 Barcol impressor according to ASTM D 2583-99.

The density of the material was determined by weighting method. A kit of analytical scale and a weighting jig was used for weighting a specimen of the material in air and fluid. The density is determined by equation:

$$\rho = \frac{m_{S\tilde{o}} \cdot \rho_v}{m_{S\tilde{o}} - m_{Sv}} \tag{1}$$

where $m_{S\tilde{o}}$ is specimen weight in air, m_{Sv} is specimen weight in fluid, and ρ_v is density of the fluid.

RESULTS AND DISCUSSION

The test results are presented in Table 2. Besides the properties of the tested materials, the table contains also properties of similar material Corian® produced by DuPont™ that is fabricated from acrylic resin and ATH with 33:67 ratio (DuPont, 2009). The table contains properties of a 12mm thick Corian® sheet that is the closest thickness to the test specimens. Additionally, properties of pure resin are presented for comparison.

Table 2. Mechanical and physical properties of particulate composites and resin.

#	Proportion of filler wt.%	Flexural strength MPa	Flexural modulus MPa	Deflection mm	Barcol hardness	Density g cm^{-3}
1	55	61.4±3.21	10,960±1,168.10	8.85±0.45	50	1.64
2	60	60.2±6.51	13,094±2,047.09	7.23±0.40	51	1.69
3	65	57.5±7.32	16,955±2,147.60	5.10±0.50	53	1.77
Corian®	67	57.1–74.0	8,040–9,220	–	56	1.68–1.75
Resin	0	140	3640	–	40–45	1.10

The flexural strength is considered to be a demonstrative parameter for brittle materials, such as polymers and ceramics (Guhanathan, 2002; Preis, 2004). The stress-strain curves showed that the mechanism of fracture was brittle. Only slight plastic deformation occurred after elastic deformation before breakage. Due to unfavourable geometrical features particulate fillers could only moderately increase the modulus, while flexural strength remains the same or decreases (Julson et al., 2004; Xanthos, 2005). The same can be observed from the test results in Table 2. On increasing the weight percentage of the ATH from 55 to 60, the flexural strength decreases 1.2MPa.

On further increase of filler, the flexural strength decreases 2.7MPa. The decrease can be considered small or even nonexistent when considering the standard deviation of the flexural strength values. The material under observation shows similar values of flexural strength as in the commercially available Corian®. The flexural strength of neat resin is 2.3 times higher then that of the composite. This confirms that the elastic properties of the composite decline by lowering the wt% of matrix.

The increase of flexural modulus shows that the stiffness of the composite increases by adding more filler. That trend is confirmed by the deflection values that decrease as the filler content increases. As it was with flexural strength, the change in flexural modulus is small. But when comparing the composite with 65 wt% of filler to the Corian®, the flexural modulus is 7,735MPa higher. This is a great difference. Stiffness is a good property generally when considering the application of the material. On the other hand, the material gets more brittle as the flexural modulus increases. Brittleness is not the material property a manufacturer of bench tops or washbasins has sought for because it makes the products prone to cracks and breakage by falling objects. The flexural modulus of composites containing almost equal amount of matrix and resin is influenced by the ratio of the moduli of the 2 phases and the percentage of the filler (Xanthos, 2005). What is more, stiffness and impact strength are dependent on particle size (Hayes & Seferis, 2001). Smaller particle size provides higher stiffness. Impact strength can be increased by smaller particle size or by adding impact modifier. In this case it might be necessary to increase particle size to decrease stiffness, because the reduction of filler wt% is not desirable. At the same time the effect of bigger particles on other properties must be observed.

Hardness test is a simple one and gives good info on the microstructure relationships of polymer composites (d'Almeida, 2001). The composite was manufactured with a vacuum assisted casting machine that produces air void free casting dispersion. The filler is a medium fraction ATH and the filler wt% is more than half in the mixture. All this should assure homogeneous material. When the hardness test was conducted this assumption was verified by measuring the hardness on both sides of the test specimen. No discrepancy was found. The hardness values show that an increase in filler increases the hardness. Material with 65 wt% of filler has Barcol hardness of 53 compared to the 50 that was measured in material with 55 wt% of filler and 20% higher hardness than with neat resin. The comparison of hardness of plain filler and matrix is complicated because the hardness value of ATH is given in Mohs' index and there is no direct conversion to other hardness scales. An approximate conversion was done. The conversion of ATH's Mohs' index of 2.5 (2.5–3.5) to Brinell scale (10mm ball 500kg load) is 90. The hardness of resin on Barcol scale is 40 (40–45) and its conversion to Brinell scale gives a value of 25 (Jones et al., 1996). When comparing these values it seems understandable that the hardness of the composite increases by the increase in wt% of ATH. Nevertheless, the concentration of particles in the composite must be greater that 30% to obtain a useful increase in hardness. Besides the wt% of filler, hardness is also influenced by the fraction and size of the filler. The filler should contain both small and large particles to fill all the gaps (d'Almeida, 2001). Corian® has in datasheet besides the hardness in Barcol scale also Mohs' index of 2–3 that is lower than that of ATH (2.5–3.5) (DuPont, 2009). Table 2 shows that the hardness of the tested material is 5% lower than that of Corian.

A downside to the increase of the filler is increase in density that influences the

weight of the products. Heavier products are more difficult to handle in production and transport. Heaviness is an undesirable property in marine and other applications. The increase in density is 7% when increasing the filler 10 wt%.

As stated in the objective of the study, one of the goals is to evaluate the effect of filler wt% increase in cost. Fig. 3 presents the price trend when filler concentration rises. By adding 5% of filler the price decreases 3.5% and by adding 10% it decreases 7.5%. Cost reduction is the trend a manufacturer is looking for.

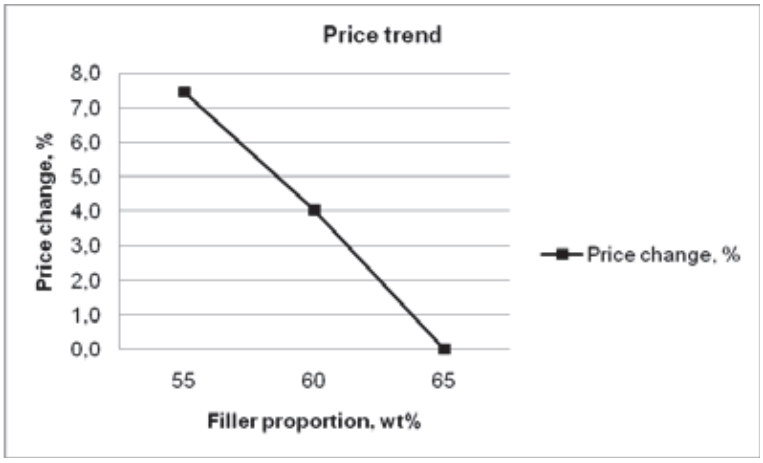

Figure 3. Price change compared to filler wt%.

CONCLUSIONS

This research was carried out to study the effect of filler wt% on the mechanical and physical properties and on the cost of particle reinforced composite. The experimental part included making material specimens and testing their flexural strength, flexural modulus, deflection, hardness, and density.

Flexural strength decreased 3.9MPa when 10% of filler was added. Contrary to that flexural modulus increased 35%. The same is confirmed by the deflection values. The hardness on Barcol scale increased 5.6% by the 10% increase of filler, but compared to neat resin the composite had a 20% higher hardness value. As more filler was added the density also increased 7% in all. Finally the cost reduction of the composite was calculated and that showed a 7.5% decrease in net price.

From the experimental data one can conclude that the manipulation of filler wt% influences many variables and there are aspects like particle size and fraction to be considered. When compared to the materials commercially available on the market today, the tested material showed comparable results with only flexural modulus being remarkably higher. Further study on the influence of particle physical properties on the mechanical properties of the composite should be carried out.

The test results obtained betoken a prospect for the tested material to be used commercially as a material for laboratory, culinary, marine or agricultural products.

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PUBLICATION II

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POLYMER SCIENCE

Influence of hollow glass microspheres on the mechanical and physical properties and cost of particle reinforced polymer composites

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Abstract. The goal of the study was to find a cost-effective composition of a particle reinforced composite that is light in weight but has sufficient mechanical properties. The matrix of the particulate composite is unsaturated polyester resin that is reinforced with alumina trihydrate particles. Part of the alumina trihydrate proportion was replaced with hollow glass microspheres to reduce weight and save costs. In order to find out the influence of the light filler on the physical and mechanical properties of composites, materials with different percentages of the light filler were prepared. Test specimens were cut from moulded sheets that were fabricated with vacuum assisted extruder. Tensile strength, indentation hardness measured with a Barcol impressor, and density were determined. Based on the experimental data a multi-criteria optimization problem was formulated and solved to find the optimal design of the material. Artificial neural networks and a hybrid genetic algorithm were used. The optimal solution is given as a Pareto curve to represent the distinction between the density and selected mechanical properties of the composite material. The composite material filled with 6% hollow glass microspheres showed 3% loss in the tensile strength and 26% loss in the surface hardness compared to the composition without the filler. The weight decreased by 13% compared with the initial composition. The addition of hollow glass microspheres did not lower the net value of the material, it increased 7%.

Key words: materials engineering, particle reinforced composites, particulate composites, multi-criteria optimization, hollow glass microspheres, polymer matrix composites, light-weight composites.

INTRODUCTION

Particulate composite material consisting of unsaturated polyester resin (UP) and alumina trihydrate (ATH) shows good mechanical and physical properties. The material is used for fabricating counter tops, sanitary ware, and furniture. The use of the material is limited in some applications because of its weight and cost. Lighter weight would decrease transportation costs, enable to produce larger products, and make handling and installation easier. Several solutions have been used to overcome these problems. A variety of lightweight fillers have been added to particulate composites in order to achieve weight savings. For example polymethylmetacrylate (PMMA) powder [1], hollow glass microspheres [2], and silicate based lightweight particulate fillers [3] have been used.

Microscopic hollow soda–lime–borosilicate spheres are low-density particles that are used in a wide range of industries. The hollow microspheres are used to reduce warpage and shrinkage, to adjust the rheological properties, to reduce part weight, and to lower cost. On the other hand, the increased concentration of lightweight particulate reinforcement such as micro balloons can aggravate the mechanical properties of the particle filled composite material [4]. If the filler is less resistant to penetration than the thermoset matrix, the filler will lower the indentation hardness of the composite [5].

The goal of the current study was to find a cost-effective material composition that has low density but sufficient mechanical properties.

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The procedure developed for solving the posed problem includes:

- design of the experiment;
- an experimental study for determining mechanical and physical properties of the material prepared with different filler ratios;
- response modelling;
- multi-criteria optimization;
- cost calculation.

The evaluation of the objective functions from experimental data is time consuming, too expensive, and thus not reasonable. A common technique for reducing the need for time resources and minimizing cost in optimal design problems is to use surrogate models for the approximation of the objective and constraint functions.

A number of surrogate model types are available, with applications in different areas ranging from sociology to space [6,7]. The most widely used types of surrogate models include Artificial Neural Networks, Radial Basis Function models, Rational Functions, Support Vector Machines, Kriging models, etc. In the current study, artificial neural networks were used for the modelling of response surfaces, corresponding to different mechanical properties of the composite material. Multi-criteria optimization problem was formulated on the basis of analysis of the relationships between mechanical properties of the material. Finally, the solution of the multi-criteria optimization problem was obtained by applying the concept of Pareto optimality and the methodology introduced by the authors in [8,9].

MATERIALS AND METHODS

A polymeric composite is characterized by a number of physical and mechanical properties. The most demonstrative properties to observe the effect of fillers are tensile strength, indentation hardness, flexural strength, and flexural modulus.

In the current study the percentage of the light filler and the matrix to reinforcement ratio were considered as design variables. The design of experiment was performed by varying the values of these parameters. In order to find out the influence of the design variables on the mechanical properties of the composite different material compositions were prepared and tested.

Test specimens were cut from moulded sheets, which were produced with vacuum assisted extruder-type mixing equipment. The vacuum chamber of the machine removes air from the casting dispersion and helps to achieve non-porous material.

Preliminary cure of the composite was done at room temperature ($23 \pm 2\,^{\circ}\mathrm{C}$) for 12 h. This was followed by post cure in a conventional thermal oven.

Tensile tests of the composite plastic materials were performed according to standard ISO 527-1:2000. The test specimens were cut from the casted slabs with a waterjet.

The indentation hardness of the material was measured with a GYZJ 934-1 Barcol impressor according to ASTM D 2583 "Standard Test Method for Indentation Hardness of Rigid Plastics by Means of a Barcol Impressor".

The density of the material was determined by weighing method. A kit of an analytical scale and a weighing jig was used for weighing a specimen of the material in air and fluid. The density was determined by the equation:

$$\rho = \frac{m_{\mathrm{Sa}} \times \rho_{\mathrm{w}}}{m_{\mathrm{Sa}} - m_{\mathrm{Sw}}}, \tag{1}$$

where m_{Sa} is specimen weight in air, m_{Sw} is specimen weight in fluid, and ρ_{w} is density of the fluid.

MODELLING OF THE PARTICLE FILLED POLYMER COMPOSITE

Let us proceed from a predetermined set of designs obtained from an experimental study. In the following, the output data obtained from the tests are treated as response values. Artificial neural networks are used for surface fitting. The surface constructed by the use of neural networks does not normally contain the given response values (similarity with the least-squares method in this respect).

Based on test data, the relationship between the mechanical properties of the material (output data) and design variables (light filler and matrix to reinforcement ratio) was established.

Analysis of the behaviour of the mechanical properties considered leads to the following conclusions:

- The mechanical properties describing general strength/stiffness characteristics of the material (tensile strength, flexural modulus) have similar behaviour with respect to design variables and can be combined into one group of properties. A reduced order model can be obtained by selecting one of these properties to represent this group (e.g. tensile strength);
- The surface hardness has similar behaviour with mechanical properties responsible for general stiffness/strength characteristics, but its physical meaning is quite different (it is responsible for local characteristics);
- Contradictory behaviour can be perceived between the tensile strength and material density, also between the surface hardness and material density.

To procede form analysis done so far, the multi-criteria optimization problem is formulated on the following bases:

- The three different objectives considered are tensile strength, surface hardness, and material density;
- Two objectives, tensile strength and surface hardness, are combined into one objective employing the weighted summation (or compromise programming) technique.

The relationship between the two combined criteria and material density can be determined by using the concept of Pareto optimality. Such an approach allows obtaining the 2D Pareto front.

According to the weighted summation technique, all the criteria combined are scaled, multiplied by weights, and summed into the general objective f_1 as

$$f_1 = \sum_{i=1}^{m} w_i f_{1i}, \tag{2}$$

where m is the number of the optimality criteria used, w_i is the weight of the i-th criterion and

$$\sum_{i=1}^{m} w_i = 1, \quad 0 < w_i \le 1. \tag{3}$$

In this case $m = 2$ and the scaling of the objectives can be performed as

$$f_{11}(x) = \frac{\max T_S(\bar{x}) - T_S(\bar{x})}{\max T_S(\bar{x}) - \min T_S(\bar{x})},$$

$$f_{12}(x) = \frac{\max S_H(\bar{x}) - S_H(\bar{x})}{\max S_H(\bar{x}) - \min S_H(\bar{x})}, \tag{4}$$

where T_S and S_H stand for tensile strength and surface hardness, respectively, and $\bar{x}$ is vector of design variables. Scaling the third optimality criterion, material density M_T, is a little different:

$$f_2(x) = \frac{M_T(\bar{x}) - \min M_T(\bar{x})}{\max M_T(\bar{x}) - \min M_T(\bar{x})}, \tag{5}$$

because it is subjected to minimization (the first two objectives, tensile strength and surface hardness, are subjected to maximization). As a result, there are two objective functions f_1 and f_2 subjected to minimization and given by formulas (2)–(5).

Thus, the multi-criteria optimization problem can be formulated as

$$f(\bar{x}) = \min(f_1(\bar{x}), f_2(\bar{x})), \tag{6}$$

subjected to linear constraints

$$x_i \le x_i^*, \quad -x_i \le x_{i*}, \quad i = 1, \ldots, n, \tag{7}$$

and non-linear constraints

$$\sigma(\bar{x}) \le \sigma^*. \tag{8}$$

In (7) x_i^* and x_{i*} stand for the upper and lower bounds of the design variables, respectively. The non-linear constraint (8) is imposed on stress σ and requires that it does not exceed the given limit value σ^*.

EXPERIMENTAL RESULTS

One of the most important characteristics of the composite material, its tensile strength, depends on the adhesion strength between the matrix and the reinforcement material [5,10]. The results of tensile tests are shown in Fig. 1. The increase of glass microspheres weight% in the material decreases its tensile strength.

Another important mechanical property, Barcol hardness, is largely influenced by the modulus of the matrix and the filler. The light filler is less resistant to penetration than the matrix and the Barcol hardness decreases as depicted in Fig. 2. The decline of hardness is much more drastic than of tensile strength. Loss of surface hardness means that the wear and scratch resistance of the material will decrease. These are important properties in service.

As expected, the low-density particles have a positive effect on the density of the material. The light filler reduces the density of the composite and thus lowers the mass of the product (Fig. 3).

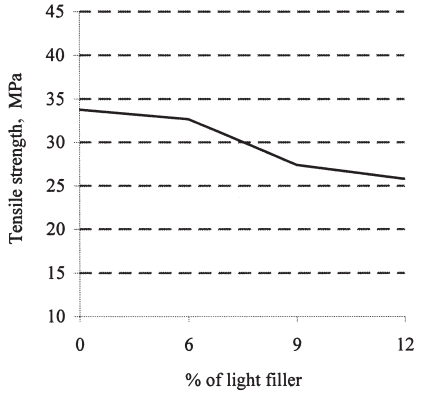

Fig. 1. Tensile strength vs. light filler content.

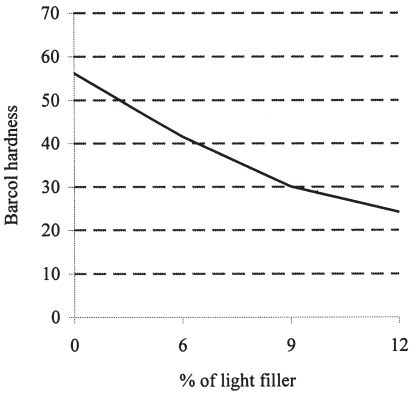

Fig. 2. Barcol hardness vs. light filler content.

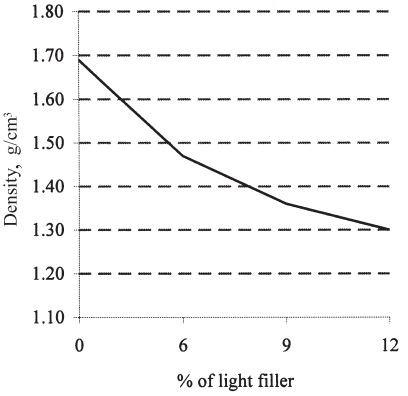

Fig. 3. Density vs. light filler content.

NUMERICAL RESULTS

Analysis and simplifications done in the section on modelling allow obtaining a reduced order model that contains two optimality criteria. The Pareto front of the combined objectives (2) and material density (5) are given in Fig. 4.

Note that an increase of the values of the combined objective $f_1(\bar{x})$ means that the distance of the tensile strength and surface hardness from their maximal values will increase, thus the values of the tensile strength and surface hardness will decrease.

It can be seen from Fig. 4 that the relationship between these two objectives is described by a Pareto curve consisting of two linear parts (may be approximated as linear). Reducing the material density

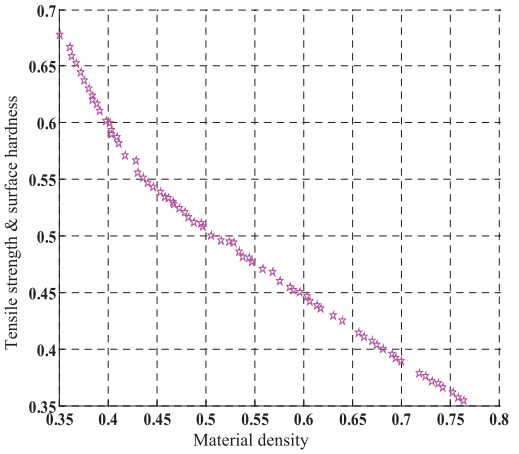

Fig. 4. The combined objective vs. material density.

function $f_2(\bar{x})$ from 0.76 to 0.43 leads to the proportional decrease of the combined function (from tensile strength and surface hardness), further reduction of the material density function leads to much faster reduction of the combined function. The optimal solution for the posed optimization problem can be selected as the intersection point of two linear parts of the Pareto curve, but not necessarily. In general, the selection of an optimal solution is still complicated and depends on a number of factors such as the specific problem considered, additional information available, etc. [11,12].

The Pareto front of the objective functions does contain more information than the physical programming approaches. The shape of the Pareto front provides valuable information.

It should be mentioned that the simplifications made in the modelling section are based on analysis and can be confirmed by simulations with more complex models.

In order to achieve higher accuracy a real-coded genetic algorithm is employed. In a standard formulation the genetic algorithm may converge close to an optimal solution to a not optimal solution. A refined algorithm, hybrid GA has been proposed for design improvement. A global–local approach for the optimization has been employed [13,14]. The hybrid approach used provides a global search with the GA and was subsequently further refined with a gradient-based search. The function approximation and optimization modules are realized in the MATLAB and C++ programming environment.

COST CALCULATION

The cost of the composite material can be calculated based on mass or volume. The composite consists of materials with different densities. Because of that, the mass price and cubic price have a difference when the composition is changed (Fig. 5). Correct net value calculations are based on the cubic price. Hollow glass microspheres cost more than ATH but have much lower density. Therefore it was expected that the mass price would increase but the volume would compensate for it and the net value of the product would lessen.

Unfortunately, the low density and large volume of the light filler did not compensate for the higher price. Nevertheless, the decrease of the mass was larger than the increase of the price. With 6% of light filler the mass reduction was 13.1% but price increase 7.2%. As it was pointed out earlier, the mass of the product influences also other costs, like transportation cost and custom duties. This means that the overall savings from the weight reduction might compensate for the price increase.

CONCLUSIONS

Test specimens of the material with varied composition were fabricated and their properties were determined. A new composite was modelled on the basis of testing results.

Analysis of the candidates for objective functions was performed and a reduced order model was developed. The mechanical properties responsible for global stiffness/strength of the material were grouped and replaced by one representative objective function.

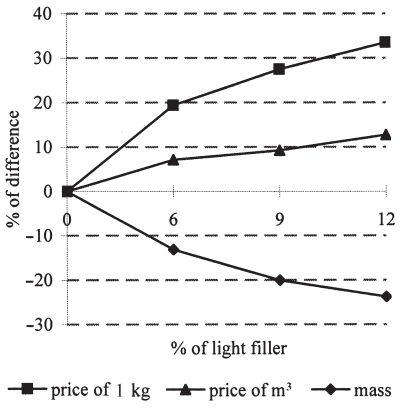

Fig. 5. Influence of the light filler content on the cost and mass.

A numerical procedure was developed for designing the new composite. Artificial neural networks and a real-coded genetic algorithm (GA) were used for modelling the response between objectives and design variables and solving the optimization problem, respectively.

The composite material filled with 6% of hollow glass microspheres showed 3% loss in the tensile strength and 26% loss in the Barcol hardness compared to the composition without the filler. The weight decrease was estimated at 13% of the initial composition. The addition of the light filler increased the net value of the material by 7%.

In conclusion, we can say that it is possible to find a compromise between lower density and loss in mechanical properties when using hollow glass microspheres as an additional filler in a particulate reinforced composite material. Nevertheless, thorough cost calculations should be made. It has to be considered whether the possible savings from the weight reduction compensate for the increase in the net cost of the material.

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Õõnsate klaassfääride mõju osake-armeeritud polümeerkomposiitmaterjali füüsikalis-mehaanilistele omadustele ja hinnale

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Uurimistöö eesmärgiks oli leida kuluefektiivne komposiitmaterjali kooslus, mis oleks väiksema massiga, kuid samas piisavate mehaaniliste omadustega. Polümeerkomposiitmaterjali maatriksmaterjalina kasutati polüestervaiku ja armeeringuks alumiiniumtrihüdraadi osakesi. Hinna alandamise ja massi vähendamise eesmärgil asendati osa alumiiniumtrihüdraadist õõnsate klaassfääridega. Uuriti klaassfääridest täiteaine mõju komposiitmaterjali füüsikalis-mehaanilistele omadustele. Ekstruuder-tüüpi seadmega valmistati vaakumvalumeetodil erineva klaassfääride sisaldusega katsekehad. Valmistatud katsekehadel testiti tõmbetugevust, Barcoli kõvadust ja tihedust. Leidmaks materjali optimaalset koostist, koostati ja lahendati katseandmete põhjal multikriteriaalne optimeerimisülesanne, milleks kasutati närvivõrke ning hübriidgeneetilist algoritmi. Koostatud arvutusmudelis pakuti komposiitmaterjali tiheduse ja mehaaniliste omaduste vastuolu likvideerimiseks välja optimaalne lahendus Pareto kõverana. Ilma kerge täiteaineta materjaliga võrreldes vähenes optimaalsete omadustega kuueprotsendilise klaassfääride sisaldusega komposiitmaterjali tõmbetugevus 3% ja Barcoli kõvadus 26%. Uurimistöö tulemusena väljatöötatud materjali puhul saavutati 13% massi vähenemine, kuid kergema täiteaine kasutamise tõttu suurenes omahind ligi 7%. Samas mõjutab massi vähenemine transpordikulu ja tollimaksu suurust, mille mõju lõpphinnale tuleb enne otsuste tegemist arvesse võtta.

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Preliminary Study of the Influence of Post Curing Parameters to the Particle Reinforced Composite's Mechanical and Physical Properties

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This study examines the effect of different post cure parameters to a polymer matrix particulate reinforced composite material. The goal is to evaluate the importance of different factors and to suggest a well-balanced post cure mode that supports the application of the material.

Polymer matrix composites are post cured at elevated temperature to increase the amount of cross linking to achieve better chemical and heat resistance and mechanical properties. Every material has an individual post cure process that depends from the raw materials. Post curing variables include temperature, duration of cure, the time between initial curing and post curing and temperature profile gradient.

There are several ways to determine the cure state of a polymer. It can be evaluated based on the mechanical and physical properties, residual styrene content, glass transition temperature, residual exotherm or solvent swelling test.

For the determination of the suitable post cure parameters test slabs were casted and post cured with varying time and temperature. Glass transition temperature, residual exotherm, softening in ethanol, surface hardness, flexural strength and flexural modulus were determined. It is shown that the material should be cured at 60 °C – 80 °C. With higher temperature and extended time of cure the glass transition temperature raises but the material becomes too brittle.

Keywords: particulate composites, particle reinforced polymer post curing, cross linking, thermal treatment, unsaturated polyesters, glass transition temperature.

1. INTRODUCTION

Thermosetting resins can be reinforced with continuous or short fibres or particles to form a composite material. Particulate reinforcement has many favourable properties. The addition of particles to the matrix material increases the stiffness, reduces the shrinkage and thermal expansion, lowers the cost and modifies the rheological properties [1].

Current study investigates particulate composites that are used in building and construction industry. More precisely the material is used for fabricating laboratory and culinary bench tops, vanity tops and sanitary ware like washbasins, shower trays and bathtubs.

There are a variety of resins and fillers available for such application. The most common filler materials for producing non-gel coated particulate composite products are alumina trihydrate (ATH), quartz, resin chips and recycled thermoplastics [2, 3]. To obtain pure white products ATH is the choice of filler material. Alumina trihydrate is a non-toxic, non-corrosive, non-cancerogenic, odourless, flame retardant filler material. It is a mineral derived from bauxite. ATH has specific gravity of 2.42 g/cm^3 and Mohs' hardness index of 2.5 – 3.5 [4].

Common resin systems used for producing particulate composites with this kind of application are acrylic, unsaturated polyester and unsaturated polyester modified with acrylic. Unsaturated polyester resin modified with acrylic is the best compromise between cost and properties.

Unsaturated polyester resin is widely used in a variety of applications. It has natural resistance to household chemicals and stains. Because of low viscosities that allow high filler content and easy casting it is the most common resin in manufacturing of engineered stone products [5]. Casting applications contribute around 20 % to the overall unsaturated polyester resin usage [6].

Polyester is formed by the reaction of difunctional acid and difunctional alcohol (glycol). Properties of polyesters can be varied by using different diacids and/or glycols depending from the application. For polyester resins meant for casting sanitary ware neopentyl glycol (NPG) and isophthalic acid (ISO) are a good choice. Neopentyl glycol provides good corrosion and weather resistance. Isophthalic acid based resins have high heat and chemical resistance [5, 6].

Styrene is used as comonomer for unsaturated polyester resins. The mixture will copolymerize many times faster compared to homopolymerization of polyester. Styrene also makes the polyester resin an easily handled liquid [6].

The curing of this kind of polyester resin is initiated by adding cobalt carboxylates that promote the polymerisation of monomers. During curing the resin goes through chemical reactions that finally cause the gelation and vitrification of the casting dispersion. Curing is an irreversible reaction where chemical covalent cross-links are formed that are thermally and mechanically stable. The curing process plays a major role in achieving the final mechanical properties and chemical resistance of the material. Complete cure is rarely achieved at room temperature. Not completed cure reduces the performance

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of the material. Moreover, residual styrene that remains in the material causes problems when the material is in contact with food and by evaporating and causing the material to smell. The solution to these problems is post curing of the material at elevated temperature. This is necessary to obtain extensive cross-linking of the system [6, 7].

There are several parameters that define the post-cure process. Two biggest variables are temperature and time, but also the time between initial curing and post curing and temperature profile gradient play a role. In literature it is stated that the post cure temperature is the most important factor that influences the extent of cross linking [5, 8, 9].

The goal of the study is to determine a post cure mode that brings out the desired properties of the material that suit best to this kind of products and to investigate the parameters that influence the post curing process.

2. EXPERIMENTAL

2.1. Sample preparation

The properties of composite plastics depend a lot on the manufacturing process. In order to get adequate results the material samples were prepared in the production facility.

For the fabrication of specimens an unsaturated polyester casting resin based on isophthalic acid and neopentyl glycol was used. The resin is developed to produce non-gel coated products and contains methyl methacrylate. It is pre-accelerated, medium reactive, low viscosity resin. The styrene content in the resin is 36 %.

For curing a peroxide mixture based on methyl ethyl ketone peroxide was added with ratio of 1/100 wt%. The peroxide is intended for room temperature cure of UP resins and it has low peak exotherm (suitable for thick parts) and good final cure (low residual styrene content). 60 wt% of ATH with medium particle size was used as filler material.

(500 × 1,000 × 10) mm slabs were casted. The slabs were casted with a closed mould with a special vacuum assisted casting machine. A closed mould guarantees equal thickness and flatness of the slab. That is necessary to get test specimens like specified in testing standards. Vacuum chamber of the machine removes air from the casting dispersion and helps to achieve non-porous material. The proportion of filler and other components is controlled by the machine.

Preliminary cure of the composite was done at room temperature (23 °C ±2 °C) for 12 h. That was followed by post cure. There are several different oven types that are used for post curing composite plastics – infrared oven, microwave oven and conventional thermal oven. A conventional thermal oven was used in current study to imitate accurately the production process. From all materials 5 specimens were cut for all tests. The test specimens were cut from the slabs with water jet.

2.2. Cure characteristics

As the cure characteristics are resin specific and depend on various variables these are usually obtained heuristically. Nevertheless, there are some numerical methods to simulate the curing process of composites, but these are not widely used [10]. From literature one can find the following suggestions to the post curing cycle of neopentyl glycol and isophthalic acid based polyester resin:

- 80 °C – 90 °C, 4 h – 6 h, not over 107 °C – the material begins to degrade and discolour [11];
- 24 h cure at room temperature (RT) followed by post cure at 60 °C for 8 h [12];
- 24 h cure at RT followed by post cure at 80 °C for 4 h [12];
- After demoulding 120 °C for 1 h [12];
- Post cure temperature should be at glass transition temperature (TG) or slightly above it (TG of current resin is 108 °C); [5];
- 80 °C for 4 h to achieve optimum stain resistance properties [13];
- 50 °C for 5 h – 15 h or 90 °C for 2 h (resin manufacturers suggestion).

It was decided that the tests would be made as shown in Table 1.

Table 1. Post cure modes

#	Post cure temperature, °C	Post cure time, h
1	40	12
2	60	6
3	60	12
4	80	12
5	90	2

2.3. Thermal analysis

Differential scanning calorimetry (DSC) is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature or time. The technique provides qualitative and quantitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity. It is a common tool in the research of post curing mode [9, 14 – 17]. The calorimetric measurements were conducted with a PerkinElmer Instruments DSC-7 differential scanning calorimeter. All samples were cured in a nitrogen atmosphere. The weight of the samples was 3 mg. Heating was performed from 20 °C to 200 °C with heating rate of 10 °C/min. The glass transition event is observed as an endothermic stepwise increase in the heat flow. Glass transition temperature represents the region in which the resin transforms from a hard glassy solid to a viscous liquid. With a further increase in the sample temperature, the resin eventually undergoes curing and this is observed as an exothermic peak. At the completion of cross linking the DSC heat flow returns to a quasilinear response [18].

The area under the exothermic peak can be integrated to give the heat of the cure ΔH_{cure} (J/g). The heat of cure maybe used to determine the percentage of cure. It is the heat of cure of a post cured sample (ΔH_c) compared to the uncured sample (ΔH_{uc}) (Eq. 1) [16 – 18].

$$\text{Percentage cure (\%)} = \frac{\Delta H_{uc} - H_c}{H_{uc}} \times 100 . \quad (1)$$

2.4. Indirect assessment of cure

Polymer softening in ethanol solution was used as an indirect evaluation of the degree of cross-linking. Firstly the specimens were stored in air at 37 °C for 24 h and the Barcol hardness was measured. After that the specimens were placed into 80 % ethanol-water solution at 37 °C for 24 h and the Barcol hardness was determined again. The measurements were done promptly after the treatment.

2.5. Indentation hardness

The indentation hardness of the material was measured with GYZJ 934-1 Barcol impressor according to ASTM D 2583-99. Barcol hardness can be used as a basic determination of how cured a material is, or as an indication of the wear resistance of a surface.

2.6. Flexural properties

The flexural properties of the material were determined by 3 point bending test (Fig. 1) as specified in ISO 178 "Plastics – Determination of flexural properties". The dimensions of the test specimens were (50×300×10) mm. A test speed of 4 mm/min was used. The support span was 250 mm. The tests were conducted with Instron 5866.

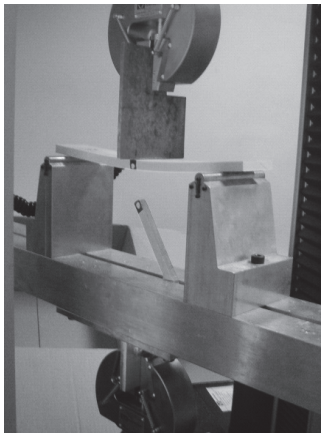

Fig. 1. 3-point bending test

3. RESULTS AND DISCUSSION

3.1. Thermal analysis

Glass transition temperature (TG) is a thermodynamic and thermo mechanical characteristic. TG is a characteristic, which indicates the softening point at elevated temperatures, effectiveness of curing agents and percentage of cure. The TG depends on different factors, including composition of the resin molecule, cross-link density, curing agent, cure time and temperature. The cure time and temperature have a considerable effect on the TG. Therefore, TG can be a measure of the cure of a material. The TG increases progressively in thermosetting resins during curing. A general rule is that the TG achieved during a post cure will increase with increasing post cure temperature but will not exceed the cure temperature itself. When TG reaches the cure temperature the curing reaction stops [14, 19, 20].

As can be seen from Fig. 2 the TG increases rapidly between temperatures 40 °C till 80 °C. The trend line suggests that the increase in TG slows down at 80 °C, although the TG achieved with post curing at 90 °C is higher. As the TG reflects the mobility of polymer chains it can provide an estimate of the crosslink density. So the decrease in TG increase suggests that the polymer reaches its maximum crosslink density. The post cure temperature of the material under observation should be above 80 °C to reach high TG and thus high cross linking.

The time of post cure seems to play a role in the TG value at lower temperatures. The TG achieved with post curing the material for 12 hours at 60 °C is 13 °C higher than post curing it for 6 hours at the same temperature. Nevertheless, independent of the time the TG of the sample post cured at 60 °C for 12 h does not reach the TG that is achieved at higher temperatures. At higher temperature the system receives more energy and the TG is higher. This verifies the assumption that temperature plays more important role in post curing than time. The same has been observed by Lipovsky and Groenendaal [5, 21].

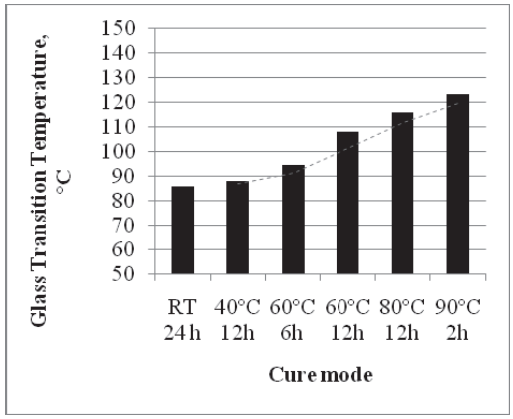

Fig. 2. Test materials TG dependence on post cure temperature

The physical significance of TG is that at temperatures above TG the values of physical and mechanical properties like tensile strength reduces and the coefficient of thermal expansion increases [19 – 22]. From practical view point it means that the TG has to be considerably higher than the materials service temperature because reduction in materials physical and mechanical properties start below the glass transition temperature. Heat deflection temperature is a method that is used for assessing the practical temperature where a polymer deforms under a specified load. The HDT is determined by the test procedure outlined in ASTM D648 and ISO 75. It has been proved by several authors that there exists a good correlation between the TG and HDT [5, 9, 23]. The HDT for sanitary ware would have to be around 70 °C because the maximum temperature of tap hot water is in the range of 60 °C – 65 °C. In kitchen environment the temperatures are up to 100 °C or even more, especially around heat emitting sources like cooker and kettle. Based on resin manufacturers tests the HDT of the UP resin is 20 °C – 25 °C lower than the TG. This means that the composite has to be cured at least at 60 °C to achieve the necessary

HDT for bathroom environment and at 90 °C for kitchen environment. It has been observed that also the stain resistance of the material is related to the TG. Materials with low TG will pick up dirt more easily compared to ones with higher TG (too tacky). It is related to the lower cross linking and thus lower chemical resistance.

The DSC graphs have a further value besides determining the TG. Since the DSC is measuring the heat flow then any heat flow from unreacted material of the sample is recorded on the graph. It is expressed as Jouls of energy left in a gram of material (J/g). Less residual energy means that the material is closer to fully cured state [24]. The DSC results are depicted in Figure 3 and are expressed as percentage of cure.

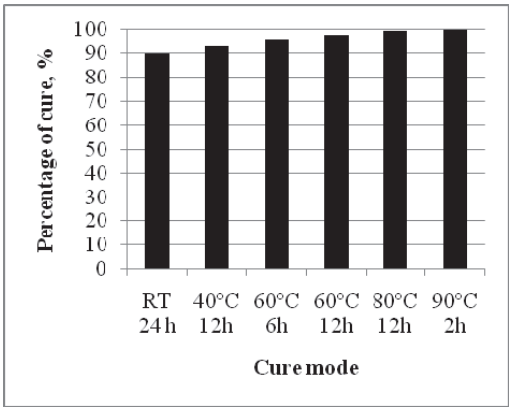

Fig. 3. Percentage of cure achieved with different post cure modes based on DSC graphs

The samples that were cured at room temperature or at 40 °C reach around 90 % of cure. The percentage of cure improves as the temperature rises. For a more than 99 % cure the system needs post curing temperatures above 80 °C. This correlates with the obtained TG results.

3.2. Indirect assessment of cure

Polymers properties are largely related to its crosslink density. Highly cross-linked material tends to be harder, stiffer, more heat and fracture resistant.

To assess the state of cure of the composite (crosslink density) the glass transition temperature and residual exotherm were determined with DSC. In addition to that a swelling test was conducted. Ethanol has softening effect on polymers. It is assumed that a more linear polymer softens more than a cross-linked polymer. It is explained by the interaction between solvent and polymer. A suitable solvent that is able to constitute secondary bonds with polymers chains replaces interchain secondary bonds and dissolves linear and branched polymers. However, the secondary bond cannot overcome primary valence cross links, so cross-linked polymers do not dissolve. Nevertheless, the cross linked polymers may swell and become soft depending from the cross link density. The swelling and softening effect gets smaller as the cross-link density increases [11, 25].

Figure 4 presents how much percentage a sample lost in indentation hardness when samples that were stored in air in 37 °C for 24 h were compared to samples that were placed into 80 % ethanol-water solution at 37 °C for 24 h. The samples that were post cured in elevated temperatures lost less than 20 % in indentation hardness. Samples that were not post cured or were treated at lower temperatures lost up to 36 % of their hardness. Post curing at 90 °C gave the highest hardness number after swelling test. When the hardness numbers of samples that were stored in air at 37 °C for 24 h were compared to hardness values of regular samples than a similar loss in hardness was observed. The loss is much smaller but the pattern is the same.

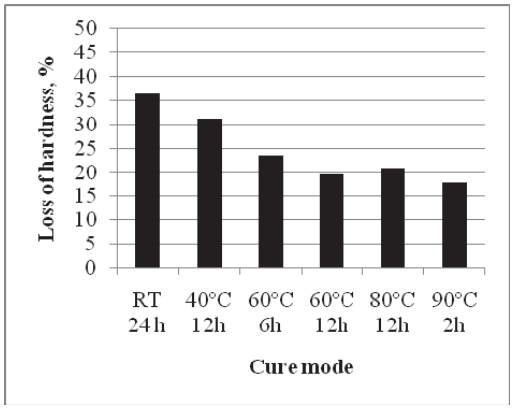

Fig. 4. The cross-link density increases with increased post cure temperature (smaller loss of hardness in swelling test)

If the cross link density is evaluated based on this test than it can be seen that post curing at higher temperature gives higher cross link density, although the difference gets smaller as the temperature rises. The time of post curing plays a role at lower temperatures. Similar trends can be observed from the DSC graphs that present the TG and residual exotherm.

3.3. Indentation hardness

The Barcol hardness values of differently post cured samples are presented in Fig. 5. The composite was manufactured with a vacuum assisted casting machine that produces air void free casting dispersion. That should assure a homogeneous material. When the hardness test was conducted this assumption was verified by measuring the hardness on both sides of the test specimen. No discrepancy was found. The hardness values show that the increase of post curing temperature increases the hardness of the surface. A bigger step can be observed when the hardness of at room temperature and at 40 °C post cured samples are compared to the ones treated at 60 °C. The next step is much smaller. The hardness value increases only 1.5 % when the temperature is raised from 60 °C to 80 °C. At 90 °C for 2 h post cured material shows even a minor loss in hardness when compared to the sample post cured at 80 °C for 12 h.

The application of the material demands great scratch and wear resistance so the indentation hardness of the material is of great importance to the manufacturer. The recommended Barcol reading by the ICPA is between 45 and 65. A lower number might indicate an under cured material and higher number too brittle material [2]. The

surface hardness also depends on the resin and filler materials, from the concentration of filler material and other factors. The Barcol values obtained are in the upper range of the suggested numbers. This indicates that there is not a necessity to post cure the material above 60 °C because of the surface hardness.

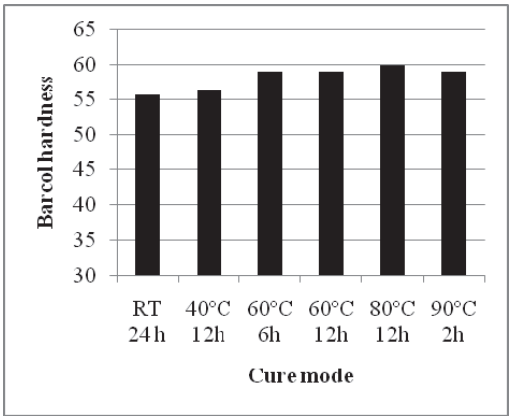

Fig. 5. Necessary Barcol hardness can be achieved with post curing at 60 °C

3.4. Flexural properties

The flexural strength is considered to be a demonstrative parameter for brittle materials like ceramics and particulate composites. The tensile strength tests of brittle materials are difficult to conduct and the results have a large deviation. From Figure 6 one can see that the flexural strength of the material changes a bit differently than TG or cross link density.

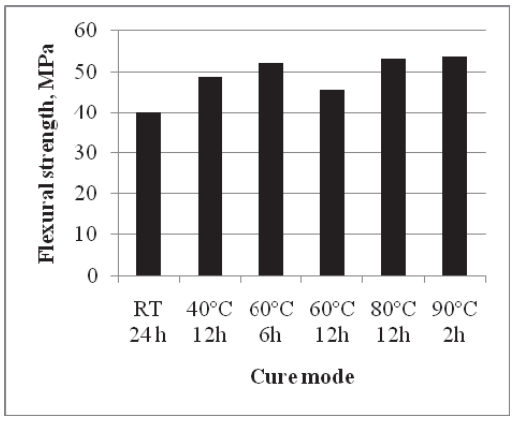

Fig. 6. Flexural strength rise comes to a halt at 60 °C

The flexural strength raises from 40 MPa to 52 MPa when the material is post cured at 60 °C for 6 h. Post curing at higher temperature than 60 °C does not give any remarkable rise in the flexural strength of the material. There is a drop in the flexural strength when the material is post cured for 12 h at 60 °C, but it does not seem to have any correlation with the temperature nor time and should be treated as aberrancy. From the manufacturer's point of view higher flexural strength is better because the product does not require elasticity on the contrary the products are expected to be rigid.

The other flexural property that was measured was flexural modulus. The modulus of the material increases remarkably after post curing it at 40 °C, from 3300 MPa to 7700 MPa. After that the rise is not as rapid and there is only 6.5 % rise in flexural strength when the post cure temperature is raised from 60 °C to 80 °C. The increase of flexural modulus shows that the stiffness of the composite increases. That trend was confirmed by the deflection values that were obtained during the testing. Stiffness is generally a good property when considering the application of the material. On the other hand the material gets more brittle as the flexural modulus increases. Brittleness is not the material property a manufacturer of bench tops or washbasins is looking for because it makes the products prone to cracks and breakage by falling objects.

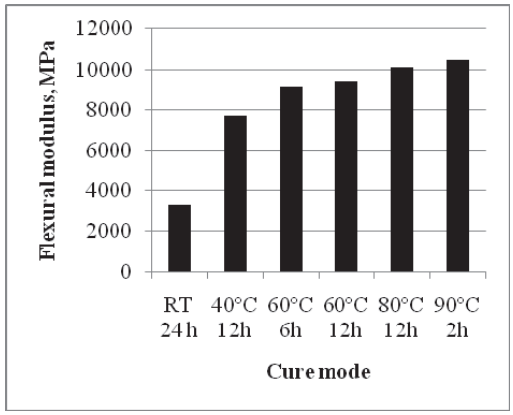

Fig. 7. Materials stiffness increases with higher post cure temperature

It is clear that post curing influences the stiffness and brittleness of the material but it is also largely related to the filler material. Particulate fillers increase the flexural modulus of the composite, while flexural strength remains the same or decreases [26]. The stiffness and impact strength are dependent on the particle size. Smaller particle size provides higher stiffness [27]. In this case it might be necessary to increase the particle size or decrease the filler wt% to decrease the stiffness.

A correlation exists between the content of unpolymerised material and the mechanical and physical properties of the material. Unpolymerised material is residual styrene and phlegmatizers. The unpolymerised material has negative effect on hardness, flexural strength, flexural modulus and chemical resistance. In the first days and up to a month the styrene will build very quickly. After that the polymerization reaction will slow down or come to a standstill that is caused by the increasing rigidity of the polyester network [5, 19]. The reaction continues when the network is flexibilised again. An optimal cure can only be achieved at elevated temperature. As test data shows high cross link density of ISO/NPG based UP resin is achievable at temperatures above 60 °C. The curing is less time dependent as the temperature rises. The rise of temperature increases the heat resistance and chemical resistance of the material but has unfavourable effect on

the flexural modulus and small positive effect on the hardness and flexural strength. Temperature of 60 °C and a cure time of 12 h seem to be optimum balance between cross link density and mechanical properties. Moreover, higher temperatures demands powerful post curing equipment. Nevertheless, the statement that the material needs post curing at 80 °C for 4 h to achieve optimum stain resistance has to be looked into.

4. CONCLUSIONS

The research was carried out to study the effect of different post curing modes to mechanical and physical properties of particle reinforced composite. Experimental part included fabrication of material specimens, heat treatment, DSC analysis, ethanol swelling test and testing of mechanical properties.

The test data acquired from DSC analysis and ethanol swelling test showed that increased post curing temperature increases the heat resistance and cross link density. The mechanical tests showed an ascending trend of the mechanical properties with increased post cure temperature. From the experimental data one can conclude that the manipulation of post cure temperature influences many variables. Aspects like brittleness and impact strength need to be considered.

The test results obtained betoken a prospect for the tested material to be used commercially as a material for laboratory, culinary, marine or agricultural products.

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PUBLICATION IV

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Determination of Resistance to Wear of Particulate Composite

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Keywords: Particulate filler, particle reinforced polymer composite, particle size, reinforcement mass fraction, wear resistance, abrasive wear, ASTM G65 dry sand rubber wheel abrasion test, indentation hardness

Abstract. Current paper concentrates on the wear resistance of a particle reinforced polymer matrix composite material. The composite material consists of unsaturated polyester resin that is filled with aluminium hydroxide. Aluminium hydroxide acts as the hard phase and polyester as the binding agent. The aim of the work was to understand how the particle size and the filler material's mass fraction influence the wear resistance of the composite. The wear properties were determined according to the ASTM G65 dry sand/rubber wheel abrasion test.

Introduction

Composite material consisting of unsaturated polyester resin filled with aluminium hydroxide is used in many interior design applications such as culinary bench tops, sanitary ware and wall cladding. The area of application dictates the properties. To perform well the material must have good wear resistance.

There is no straightforward formula to define what particle size and mass fraction (wt.%) of the reinforcement gives the best wear resistance to a composite material [1]. Moreover, the test parameters have a considerable effect on the wear rate and can produce unexpected results [2].

Several studies have reported that the addition of micro- or nanoscale fillers improve the wear resistance of polymers [3][4]. Most of the research concentrates on thermoplastic polymers [5][6]. Current paper investigates the change in wear properties when more than 50 wt.% of mineral filler is added to a thermosetting matrix.

A 3-body abrasive wear test was used to rank the materials in a similar relative order of merit as would occur in an abrasive environment. The severity of abrasive wear depends on several parameters - the abrasive particle size, shape, and hardness, the magnitude of the stress imposed by the particle, and the frequency of contact between the sample and the abrasive particle [7].

The wear tests were run as a completely randomized experiment with four levels of filler weight percentage (0 %, 50 %, 60 % and 67%) with three replicates and three treatments of particle size (7 μm, 20 μm and 35 μm) with three replicates. The specimens with different particle size had 60 wt.% of filler. The randomized test sequence is necessary to prevent the effect of unknown nuisance variables from contaminating the results [8].

Experimental

Materials. The matrix was an isophthalic acid and neopentyl glycol based unsaturated polyester resin. Reinforcing aluminium hydroxide had bulk density of 1000 kg m^{-3} and Mohs' hardness index of 2,5 – 3,5. SiO_2 sand from Ottawa that was used as abrasive had particle size fractions 0,2 – 0,3 mm, bulk density of 1450 - 1550 kg m^{-3} and Mohs' hardness index of 7 [9][10].

Fabrication. The test specimens were fabricated with a vacuum assisted extruder. The dispersion was casted into an aluminium mould. After room temperature cure the specimens were post cured at 40 °C for 12 h.

Indentation hardness. GYZJ 934-1 Barcol Impressor was used to measure the indentation hardness of the material. The indentation hardness test was conducted according to ASTM D2583. The Barcol Impressor is developed for testing fabricated parts and test specimens. It is well suited for reinforced plastics. It enables quick and simple ranking of materials by surface hardness [11]. Surface hardness is a signal of percentage of cure of a polymer composite but also depends from the concentration of filler material and the type of filler material [12].

Wear. Wear tests were conducted according to ASTM G65. The main value of this test method is the relative ranking of materials. This standard utilizes a test method where measurable mass loss occurs and is intended for material applications where low to extreme abrasion is observed [7].

An in-house designed and built rubber wheel/dry sand test equipment was used for conducting the wear tests. A speed of 2,4 m s^{-1} and a load of 130 N was used. The number of revolutions was decreased from 2000 as set in the standard to 500 and then to 300 based on the significant volume loss of the material.

The Archard wear relationship (specific wear rate) is a universal quantitative parameter of wear. It is the worn volume of material divided by the introduced mechanical energy. The contact energy is the outcome of the load and distance [13][14].

$$K = \frac{V}{F \cdot s} \tag{1}$$

K – specific wear rate coefficient
V – wear volume
F – normal load
s – sliding distance

Results and discussion

Particle size. The first part of the research was to examine the influence of particle size to the wear properties of the composite. Neither the indentation hardness test nor rubber wheel/dry sand wear test showed any big differences between the composites with different particle sizes as can be seen from Fig.1.

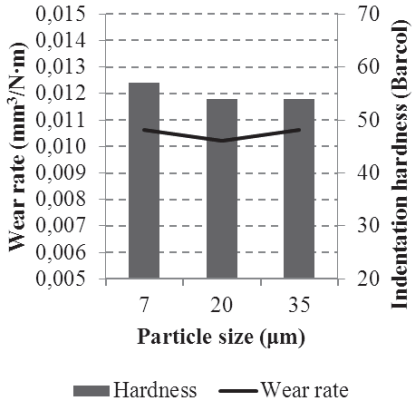

Fig. 1 Particle size influence

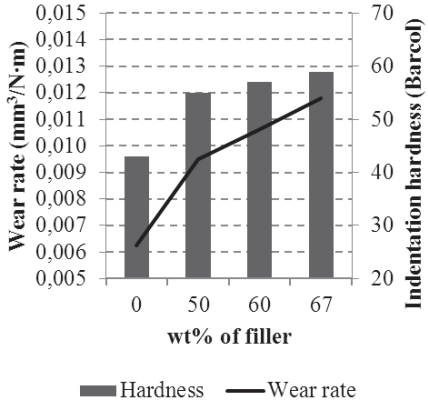

Fig. 2 Filler wt.% influence

Composite filled with aluminium hydroxide D_{50} 7 μm had 5,3 % higher indentation hardness than the rest. Aluminium hydroxide with D_{50} 20 μm gave 3,7 % lower wear rate to the composite compared to the others.

The analysis of variance was used to test null hypothesis H_0: means of the three treatments are equal $\mu_1 = \mu_2 = \mu_3$ against the alternative hypothesis H_1: some means are different.

Table 1 Analysis of variance for the wear rate data

	Sum of squares	Degrees of freedom	Mean square	F_0	$F_{0,05;2;8}$
Wear rate	3,04953E-07	2	1,52477E-07	6,42	4,46
Error	1,42571E-07	6	2,37619E-08		
Total	4,47525E-07	8			

As can be seen from Table 1 the between-treatment mean square (1,52477E-07) is larger than the within-treatment mean square (2,37619E-08). This indicates that it is unlikely that the treatment means are equal. Moreover, if the F_0 is compared to the selected $F_{0,05;2;8}$ then $F_0 > F_{0,05;2;8}$. The null hypothesis can be rejected and conclusion made that the treatment means differ.

Mass fraction. It is known that hardness is one of the important parameters affecting the wear resistance of a material - the harder the material, the lower its wear loss [2].

The results derived from the rubber wheel/dry sand tests of the composites do not support the general understanding. The increase of the filler's wt.% and thus the increase of the indentation hardness leads to a higher wear rate of the composite as depicted on Fig. 1.

To understand this phenomena SEM images were taken of pure resin test specimen and test specimen with 67 wt.% of filler. The upper halves of Fig. 3 and Fig. 4 show the unaffected area and the lower halves depict the wear surface of the composite.

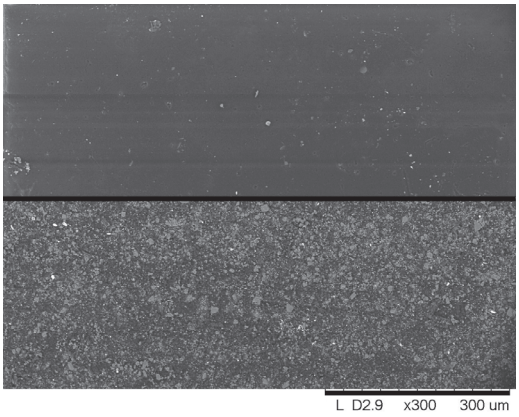

Fig. 3 Pure resin. Upper - unaffected. Lower - worn.

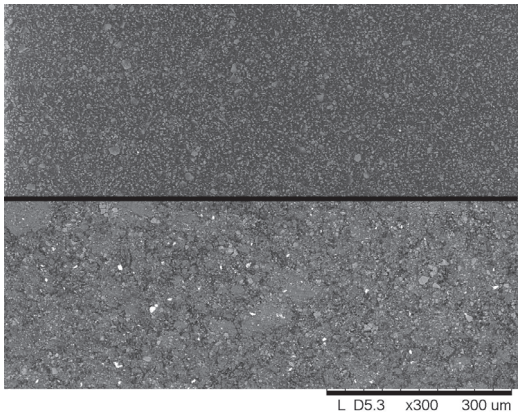

Fig. 4 67 wt.% filler. Upper - unaffected. Lower -worn.

The sand particles adhere to the composites surface and form a hard phase that reduces the wear rate. As the filler's wt.% increases the binder's surface area decreases and less sand particles adhere to the composite's surface. Due to the fact that SiO_2 has Mohs' hardness index of 7 and aluminium hydroxide has 3 the adhered sand has bigger effect on the wear rate than the increase of filler's wt.%. A second series of tests were conducted where the load was lowered from 130 N to 10 N. It was assumed that with the lowered force the sand particles would not penetrate the polymer's surface and would not form a wear resistant phase. With 130 N the pure resin sample had 47 % lower wear rate than sample with 67 wt.% of filler, with 10 N the difference was 51 %.

Summary

The particle size did not have any noticeable effect on the wear rate. Furthermore, the increase of the proportion of the reinforcement in the composite did not improve the wear resistance.

The results contradict the general assumption. This is related to the nature of the composite where the matrix and the reinforcement act differently under 3-body abrasive wear conditions.

Much of the results can be contributed to the binding behaviour of the matrix. Because of this the abrasive's particles form a wear resistant tribolayer on the composite's surface.

The remaining of the results can be attributed to the reinforcement and the abrasive. The difference in their hardness influences considerably the wear resistance of the composite.

Acknowledgement

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PUBLICATION V

Aruniit, A.; Kers, J.; Krumme, A.; Peetsalu, P. (2014). Particle size and proportion influence to impact properties of particulate polymer composite. – *Proceedings of the 9th International Conference of DAAAM Baltic Industrial Engineering: 24-26 April 2014, Tallinn, Estonia.* (forthcoming)

9th International DAAAM Baltic Conference
"INDUSTRIAL ENGINEERING -
24-26 April 2014, Tallinn, Estonia

PARTICLE SIZE AND PROPORTION INFLUENCE TO IMPACT PROPERTIES OF PARTICULATE POLYMER COMPOSITE

Aruniit, A.; Kers, J.; Krumme, A. & Peetsalu, P.

Abstract: *Current research concentrates on the impact properties of a particle reinforced polymer matrix composite material. The composite material consists of unsaturated polyester resin that is reinforced with aluminium hydroxide. Aluminium hydroxide acts as the hard phase and polyester as the binding agent. The aim of the work was to understand how the particle size and the filler material's mass fraction influence the impact resistance of the composite. Additionally was studied the effect of post-curing to the impact toughness of the matrix. The testing was done according to the ISO 179 Determination of Charpy impact properties. Smaller particle size increased the impact strength. Filler caused embrittlement of the matrix as did also post-curing.*
Key words: polyester composite, aluminium hydroxide filler, particle size, particulate reinforcement mass fraction, ISO 179 Charpy impact toughness

1. INTRODUCTION

Particulate polymer composite material consisting of unsaturated polyester resin and aluminium hydroxide powder is used in many interior design applications. It is known as engineered stone and produced in sheets or casted into shapes. The applications are culinary bench tops, sanitary ware and wall cladding.
The area of application dictates the properties. To perform well in service the material must have good impact toughness.

Fillers are used in polymers because of technical and economic reasons [1] [2] [3]. Aluminium hydroxide particles add many favourable properties to the polymer composite. It has flame retardant and smoke suppression quality. Moreover, it is non-toxic and chemically inert. Aluminium hydroxides low sorptive power makes it also economical as it has low liquid resin demand [1] [4].
Fillers reduce shrinkage of thermosetting polymers during the polymerisation process [1] [5]. This helps to avoid warpage or cracking that may occur with large moulded products. Moreover, the inclusion of mineral filler enhances the thermal conductivity of the composite and helps to bring down the exothermic temperature of the part and cool it faster [1]. This speeds up the cycle time and thus reduces cost.
Inorganic particulate fillers have much higher stiffness than polymers thus these improve the stiffness or Young's modulus of the composite [1] [6] [7].
There are also some unfavourable properties that particulate fillers add. The addition of a particulate filler reduces the elongation at brake of the polymer thus decreasing toughness or impact resistance [1]. Fracture toughness of a particle filled polymer composite depends mainly from the toughness of the matrix [8]. In composites with ductile matrix particulate filler causes brittleness [8]. Fracture toughness of ductile thermoplastics shows a significant decrease with particulate reinforcement [8] [9]. On the other hand, in composites with brittle matrix like thermosetting epoxy the brittleness is reduced with the addition of particulate

filler [2] [8] [10]. Generally, the thermosetting resins have a poor crack growth resistance compared to thermoplastics [7].

There are three properties of a particle that are considered to have the greatest effect on particulate composites properties: particle size, loading and adhesion with matrix.

There is strong evidence that particle size has direct impact on particulate composites toughness. Singh et al. [11] found that smaller particles give higher strength and higher fracture toughness at a given proportion in a thermosetting polyester. On the other hand, Radford [12] found that with a constant volume fraction of 0,295 the particle size increase improved the fracture energy of an epoxy-aluminium hydroxide particulate composite.

Particle loading is the second important factor that affects the mechanical properties of a particulate composite. The influence is varying to different properties and depends from the mass fraction of the filler. Surface hardness and flexural modulus of thermosetting polyester composite increases monotonically with increasing load of aluminium hydroxide [6]. On the other hand, fracture toughness increases till filler mass fraction of 10 – 20 % but decreases with higher loading in an epoxy composite [7]. In a thermoplastic the introduction of filler can dramatically decrease the fracture toughness compared to neat resin [7].

Third contributor to the mechanical properties of a particulate composite is the reinforcement-matrix interface adhesion [7]. Better adhesion improves the strength [7]. The adhesion is often enhanced with coupling agents. Aluminium hydroxide used in current research is treated with silane coupling agent. The effect of presence or absence of the coupling agent was not given heed to.

There is not any straightforward formula to define what particle size and mass fraction (wt.%) of the reinforcement gives optimal impact toughness to a composite material.

Besides the composition the mechanical properties of the composite depend from technological processes like elevated temperature post curing [13]. Moreover, one has to consider also other properties of the material when tuning the impact toughness to achieve a well-balanced entirety.

The composite has to have good wear and chemical resistance, surface hardness and it has to be economical to produce.

Since hardness and toughness are inversely related increased impact resistance is accompanied by reduced wear resistance [14].

A lot of research has been done on particulate composites with thermoplastic or epoxy matrix. Moreover, most of the research investigates low level filler loading of 1 – 10 %. Current research studies the particulate reinforcing of the most widely used and economic thermosetting matrix – polyester. Moreover, filler loading in the range of 50 – 65 % is studied as this would have considerable economical effect on the composites price.

The aim of the research was to find the particle size and proportion that gives good impact toughness to the composite without sacrificing other properties.

The tests were done as a completely randomized experiment with four levels of filler weight percentage (0 %, 50 %, 60 % and 65%) with ten replicates and three treatments of particle size (7 μm, 20 μm and 35 μm) with ten replicates. The specimens with different particle size had 60 wt.% of filler. The randomized test sequence is necessary to prevent the effect of unknown nuisance variables from contaminating the results [15].

2. EXPERIMENTAL

2.1 Materials

The matrix was an isophthalic acid and neopentyl glycol based unsaturated polyester resin with density of 1100 kg m^{-3}. Reinforcing aluminium hydroxide had density of 2400 kg m^{-3} and Mohs' hardness

index of 2,5 – 3,5 [4]. The aluminium hydroxide particles were pre-treated with silane.

2.2 Methods

The test specimens were fabricated with a vacuum assisted mixer. The dispersion was injected into a closed silicone mould having 12 cavities. The test specimen's dimensions were 80x10x4 mm (LxWxH). After room temperature cure the specimens were post cured 12 h at 40 °C.

The indentation hardness of the material was measured with a GYZJ 934-1 Barcol Impressor. The indentation hardness test was conducted according to ASTM D2583. The Barcol Impressor is developed for testing fabricated parts and test specimens. It is well suited for reinforced plastics. It enables quick and simple ranking of materials by surface hardness [16]. Surface hardness is a signal of percentage of cure of a polymer composite but also depends from the mass fraction and type of the filler material [13].

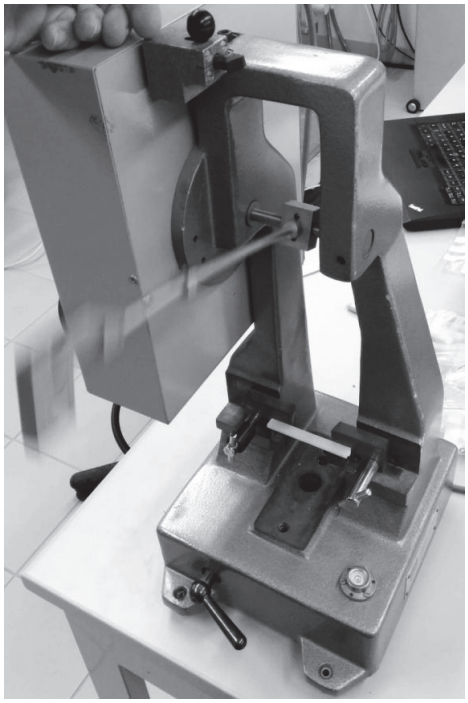

Fig. 1. Zwick/Roell 5102 Pendulum Impact Tester

Impact tests were conducted according to ISO 179-1 Plastics – Determination of Charpy impact properties [17]. The main value of this test method is the relative ranking of materials.

The tests were conducted with Zwick/Roell 5102 Pendulum Impact Tester (Fig. 1). The span between specimen supports was 40 mm. A velocity of impact of 2,92 m s^{-1} and pendulums of 0,5 J and 1 J were used.

3. RESULTS & DISCUSSION

3.1 Particle size

The first part of the research was to examine the influence of particle size to the impact properties of the composite. The results are presented on Fig. 2.

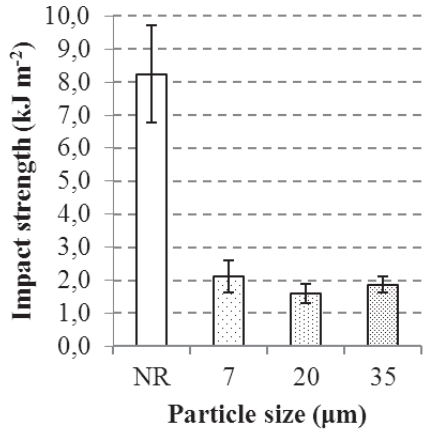

Fig. 2. Particle size influence to Charpy impact strength and comparison with neat resin (NR)

There is not a clear trend that with particle size reduction the impact strength increases. Nevertheless, composite with 7 µm particles differentiated from the rest and showed 24 % better impact strength than composite with 20 µm particles and 11 % better impact strength than composite with 35 µm particles. The 20 µm particles had 15 % lower strength than the 35 µm particles.

Smaller particles have a greater total surface area. This implies that the impact

strength increases with smaller particles through a better stress transfer between the matrix and the reinforcement. [7]
None of the reinforced test specimens could compete with neat resin (NR). The latter showed 4 times higher impact strength than the specimen reinforced with 60 wt. % of 7 μm particles. At this level of loading the properties of reinforcement dominate and cause brittleness.

3.2 Mass fraction

The second part of the study was done with 7 μm particles as these showed highest impact strength.
The impact strength peaked at 60 wt.% of filler. Further loading reduced the strength by 13 % and half-and-half mix showed 5 % lower values.
As in the first part of the research the results are incomparable to the neat resin (NR). The pure matrix is much tougher than the composite at different levels of loading as can be seen on Fig. 3.

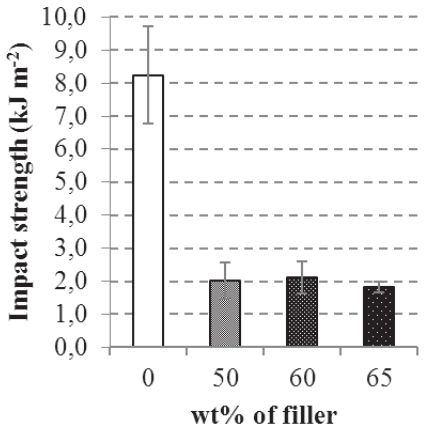

Fig. 3. Particle loading influence to Charpy impact strength

This confirms the fact that the crack growth resistance of a polymer – filler interface is considerably lower than that of pure polymer which deforms plastically and absorbs part of the impact energy. The impact strength is proportional to the rate at which the crack grows. The crack does not halve the hard particles but propagates through the relatively weak particle – matrix interface that is ruled by the adhesion forces between the two. [9] [18]

3.3 Post-curing

Thermosetting polymer composites are post cured at elevated temperature to increase the amount of cross linking to achieve better chemical and heat resistance and mechanical properties [13].
A correlation exists between the content of unpolymerised material and the mechanical and physical properties of the material. Unpolymerised material is residual styrene and phlegmatizers. The unpolymerised material has negative effect on hardness, flexural modulus and chemical resistance. [13] [19] [20]

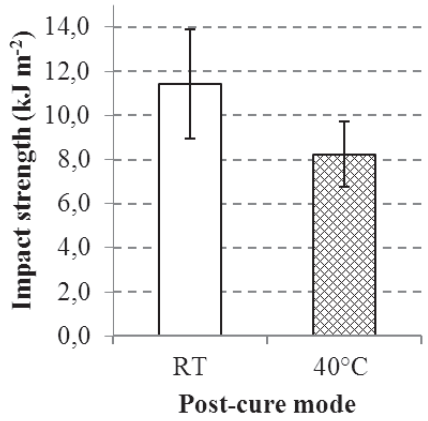

Fig. 4. Influence of post-curing (12 h @ 40 °C) to Charpy impact strength. RT – room temperature cured sample.

Fig. 4 depicts vividly how post-curing decreases toughness of the unsaturated polyester. The impact strength is 1/3 lower compared to the room temperature cured sample (RT).

3.4 Indentation hardness

Fig. 5 depicts the dilemma that is faced with highly filled particulate composites.

Some of the favourable properties increase with filler loading while others decrease. In this case higher filler loading improves indentation hardness but lowers toughness. The figure also demonstrates well the essence of a composite – filler improves a property that the matrix lacks.

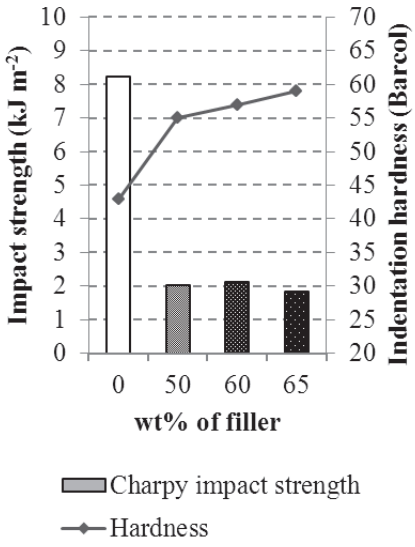

Fig. 5. Influence of filler loading to Barcol indentation hardness compared to Charpy impact strength

4. CONCLUSION

The composite with smallest particles had highest impact strength. Nevertheless, there was not a linear trend between particle size reduction and toughness increase.

The optimal matrix – reinforcement ratio from the point of strength was 40:60.

The tests demonstrated that the toughness of the particulate composite comes from the matrix and the filler makes the composite material brittle.

The brittleness is even further increased with post–curing. Post-curing is desirable when one wants to improve properties like indentation hardness, stain resistance or flexural modulus but it works concurrently with impact strength.

Since composite is a compromise between different properties the material has to be designed considering all the requirements.

Acknowledgment

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APPENDIX II: CURRICULUM VITAE

Name:	Aare Aruniit
Date of birth:	22.05.1983, Tallinn
E-mail:	aare.aruniit@ttu.ee
Citizenship:	Estonian

Education:

2010 -	Tallinn University of Technology PhD, Materials engineering
2005 – 2007	Tallinn University of Technology MSc, Product Development and Production Engineering
2006	Copenhagen Engineering College International Business Semester
2002 – 2005	Tallinn University of Technology BSc, Product Development and Production Engineering
1990 – 2001	Tallinn Secondary School nr. 21 Graduated with silver medal
1993 – 1998	Tallinn Art School

Employment:

02.2007 -	Wellspa LLC
Line of business:	Multi-functional spa equipment and engineered stone bathware
Position:	R&D Manager
02.2005 – 05.2006	Silbergroup Ltd
Line of business:	Mercedes-Benz vehicles rebuilding
Position:	Engineer
09.2004 – 11.2004	ABB Ltd Tallinn KHK
Line of business:	Electrical motors
Position:	Trainee

Language skills: Estonian: mother tongue
English: fluent
Russian: average
German: basic
Finnish: average

Research activities Thesis supervised:

Indrek Hioväin "Formula student racecar FEST14 monocock mould"

Katrin Kabun "Lamb wool based composite interior material"

Publications: 14

ELULOOKIRJELDUS

Nimi:	Aare Aruniit
Sünniaeg:	22.05.1983, Tallinn
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Kodakondsus:	Eesti

Haridus:

2010 -	Tallinna Tehnikaülikool Doktoriõpe, mehaanikateaduskond, mehhanotehnika õppekava, materjalitehnika eriala
2005 – 2007	Tallinna Tehnikaülikool Magistriõpe, mehaanikateaduskond, tootearenduse ja tootmistehnika eriala
2006 sügissemester	Copenhagen Engineering College International Business Semester
2002 – 2005	Tallinna Tehnikaülikool Bakalaureuseõpe, mehaanikateaduskond, tootearenduse ja tootmistehnika eriala
1990 – 2001	Tallinna 21. Keskkool Keele-reaalklass (lõpetatud hõbemedaliga)
1993 – 1998	Tallinna Kunstikool

Töökogemus:

02.2007 -	Wellspa OÜ
Firma tegevusala:	Multifunktsionaalsete massaažiseadmete, minibasseinide ja tehiskivist sanitaartehnika arendus- ja tootmistegevus
Amet:	Arendusjuht
02.2005 – 05.2006	Silbergroup AS
Firma tegevusala:	Mercedes-Benz mudelitel põhinevate erisõidukite konstrueerimine ja valmistamine
Amet:	Insener-konstruktor
09.2004 – 11.2004	ABB AS Tallinna KHK
Firma tegevusala:	Elektrimootorite tootmine ja hooldus
Amet:	Praktikant

Keelteoskus: Eesti keel: emakeel
Inglise keel: kõnes – väga hea, kirjas – väga hea

Vene keel: kõnes – keskmine, kirjas – keskmine
Saksa keel: kõnes – keskmine, kirjas – keskmine
Soome keel: kõnes – hea, kirjas - keskmine

Teadustegevus

Juhendamised:

Indrek Hioväin "Formula student võistlusklassi vormelauto FEST14 monokoki vormi projekteerimine"

Katrin Kabun "Lambavillal põhinevast komposiidist sisustusmaterjal"

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