KEEMIA- JA MATERJALITEHNOLOOGIA TEADUSKOND
POLÜMEERMATERJALIDE INSTITUUT
TEADUS- JA ARENDUSTEGEVUSE AASTAARUANNE 2014

1. Instituudi struktuur

Polümeermaterjalide instituut, *Department of Polymer Materials*
Instituudi direktor Andres Krumme

- Polümeeride tehnoloogia õppetool, Chair of Polymer Technology, prof. Andres Krumme
- Puidutöötlemise õppetool, Chair of Woodworking, prof. Jaan Kers
- Tekstiilitehnoloogia õppetool, Chair of Textile Technology, prof. Andres Krumme
- Põlevkivi ja taastuvkütuste teaduslaboratoorium, Laboratory of Oil Shale and Renewables Research, Dr. Hans Luik
- Mööbli ja puitmaterjalide katselaboratoorium, Laboratory for Furniture and Wood Materials Testing, Dr. Triinu Poltimäe
- Tekstiili katselaboratoorium, Laboratory for Textile Testing, prof. Andres Krumme

2. Teadus- ja arendustegevuse iseloomustus

2.1 Polümeermaterjalide uurimisgrupp *Research team of polymeric materials, prof. Andres Krumme*

2.1.1 Uurimisgrupi teadustöö kirjeldus

- **(AR12135: Carbon Nanotube Reinforced Electrospun Nano-fibres and Yarns - *Elektroketruse teel valmistatud ja süsinik-nanotorudega armeeritud nanokiud ning lõngad*)** Main goal of the project is to develop and industrialize a technological process for production of ultra-strong and functionalised polymer nanofibres and yarns for various applications. The process combines electro-spinning of polymers with carbon nanotube (CNT) doping and additional functionalization tools. As a result pure nanofibres, nanofibre yarns and fabrics are produced. The main applications of the novel materials are: dynamically adjustable pore size filter for special filtering applications; substrates for cell growth; ultra-strong fabric for reinforcement of plastic film laminates; yarns for special textiles having exceptional strength and special properties as piezoactivity, conductivity and shielding capacity.
- **(ERMOS78: Flow-Induced Crystallization and Rheology of Polyester Amides and Their Composites –** *Polüesteramiidide ja nende komposiitide voolamisest tingitud kristallisatsioon ja reoloogia***)** Polymer processing technologies requires detailed information about formation of crystalline structure on micro- and macro-level under flow stresses. The main purpose of the project is to study the flow behaviour and flow-induced crystallization process of some novel thermoplastics, derivatives of cellulose and their composites with polyolefins. Studies will be done at different shear rates and elongation stresses which similar to that appearing in situation of real polymer processing. This gives important information about how mechanical properties and processability of the novel composite materials could be improved. To achieve promoted results an influence of molecular parameters of polymers (molecular mass, chemical structure of polymer, etc.) as well as type and magnitude of applied flow on rheological, nucleation and crystallization behaviour of the materials will be studied. As a consequence, melt flow/nucleation/crystallization/crystal structure interrelations will be obtained.

- **(AR10127: Basics of new utilization processes for oil shale combustion solid wastes -** *Põlevkivi põletamisega kaasnevate tahkjäätmete uute kasutusalade alused***)** The R&D project, advised by leading research scientist Rein Kuusik (Faculty of Chemical and Materials Technology, Laboratory of Inorganic Materials) deals among others with the problem, how to use fly ash of combustion of oil shale as additive to polyethylene (PE) for formation new, more cheap composite materials (leader of this subtask is prof. Anti Viikna). The possibility of blending of oil shale ashes with PE for producing blown films of these composites is investigated. Obtained materials are tested (density, melt flow index, thermal analysis, tensile strength etc.) and selected the best composites for producing blown film.

2.1.2 Uurimisgrupi aruandeaastal saadud tähtsamad teadustulemused

- **(AR12135)** Technological breakthrough was achieved in the field of production of nanofibrous yarns by electrospinning. Prototype of a device having new operation principle was also made. The key of the new technology is air vortex generated by reduced pressure in the spinning chamber. European patent application is submitted by the achievement. The new device can produce yarns approximately 100 times faster than the best methods known up to now and this is certainly not the upper limit of productivity. This is a significant leap towards solution to the biggest problem restricting industrial utilisation of electrospinning, namely, low productivity. Improved productivity opens route for commercialisation of several new fibrous materials for smart textiles, wearable electronics and medical textiles. The work will continue for improving post-treatment of the nanofibrous yarns and for developing spinning nozzles of higher productivity. Also, new composites of PAN, SAN and PANi with several carbon allotropes were produced by electrospinning. Dispersion of the allotropes and ion conductivity of the composites were improved by incorporation of ionic liquids. Mechanical properties and total conductivity of the nanofibrous composites were significantly improved. Two layer electrospinning was also successfully introduced by the research team. A new carbonous material was developed, in which good mechanical properties were achieved by having tough polymer in inner layer and good conductivity and high specific surface by having high carbon concentration composite on outer layer.
- **(ERMOS78)** Thermoplastic cellulose fatty acid esters were developed and studied. The fusion, crystallisation processes and flow properties of the melt were studied and described. Obtained data were used for evaluation of perspectives of application and processing of that type of materials. Rheological properties of the melts were studied in conditions similar to those polymer processed in industry. The properties of modified cellulose were compared to low density polyethylene what gives us some guidelines for targeted material development. The results of this work are accumulation of knowledge and experience in field of development and application of nature based polymers as thermoplastic materials. The melt behavior of studied cellulose derivatives and their crystallisation processes open perspectives to use them as strength enhancing compounds or as plasticizers and compatibilizers in composite materials made of polymer blends which contains commodity polymer and cellulose or wood products. What is important that conditions of processing and item production could be similar to those used in polymer industry without essential modification. It was proposed different ways of material improvement to achieve good thermoplastic properties which are important in polymer production. Also, the relatively easy modification procedure makes it possible to obtain additives with wide variable properties based on renewable and ecologically friendly materials.
- **(AR10127)** Composites of fly ash TPEF3 and LLDPE were investigated by SEM and mechanical testing methods. Composites of ash concentration of 0 to 30 wt-% were prepared by compounding and test specimens were prepared by injection moulding. Cross-sections of the specimens were cut for microscopy. It was observed, that no adhesion between ash particles and LLDPE exists if no adhesion modificators are used. This behaviour is not depending on ash concentration and decreases mechanical properties of the composite. Surface of the composite

turns rough at the ash concentration 30 wt-%. Adding silane improved adhesion between the ash and LLDPE which is expressed by improved mechanical properties. Also, the surface of specimens having higher ash concentration is smooth due do the additive.

2.1.3 uurimisgrupi kuni 5 olulisemat publikatsiooni aruandeaastal

- Viirsalu, M.; Kivirand, T.; Krumme, A. Device and method for preparing a continuous nanofibrous yarn. Priority number: GB1415820.8, Priority date: 08.09.2014.
- Krasnou, I.; Tarasova, E.; Märtson, T.; Krumme, A. (2014). Thermoplastic cellulose stearate and cellulose laurate: melt rheology, processing and application potential. International Polymer Processing, [ilmumas].
- Tarkanovskaja, Marta; Välbe, Raul; Põhako-Esko, Kaija; Mäeorg, Uno; Reedo, Valter; Hoop, Andres; Saal, Kristjan; Krumme, Andres; Kink, Ilmar; Heinmaa, Ivo; Lõhmus, Ants (2014). Novel homogeneous gel fibers and capillaries from blend of titanium tetrabutoxide and siloxane functionalized ionic liquid. Ceramics International, 40(6), 7729 - 7735.
- Gudkova, V.; Krumme, A.; Märtson, T.; Rikko, M.; Tarasova, E.; Viirsalu, M. (2014). The impact of 1-butyl-3-methylimidazolium chloride on electrospinning process of SAN polymer solutions and electrospun fiber morphology. Journal of Electrostatics, 72, 433 - 436.
- Aruniit, A.; Antonov, M.; Kers, J.; Krumme, A. (2014). Determination of Resistance to Wear of Particulate Composite. D. Loca (Toim.). Engineering Materials & Tribology XXII (188 - 191).Trans Tech Publications Ltd

2.2 Puitmaterjalide ja komposiitide uurimisgrupp *Research team of wooden materials and composites, prof. Jaan Kers*

2.2.1 Uurimisgrupi teadustöö kirjeldus

- **(Wood-Plastic Composites (WPC): Effect of artificial weathering on the mechanical and physical properties of WPC)** In this research, the main goal is to evaluate the effect of moisture absorption and UV radiation on the mechanical and physical properties of WPC materials. Objectives are also to investigate the importance of wood flour fraction size on the mechanical properties of WPC and their influence on the accelerated weathering results. Effect of different coupling agents was also under study. The composites were made with three different fraction sizes of birch (*Betula*) wood flour. Additionally Bleached-Chemi-Thermo-Mechanical aspen (*Populus tremula*) pulp (Aspen BCTMP) was also used. WPC specimens were prepared by injection molding (Battenfeld BA 230 E). Accelerated weathering tests (water absorption and thickness swelling, UV-radiation) were carried out to evaluate the influence of weathering on the mechanical and physical properties of composites. Three-point bending test and Charpy impact test were done to test mechanical properties.
- **(Improving fire resistance of bended laminated elements)** Plywood fire-retardant treatment methods include veneer impregnation, finished panel impregnation, fire-retardant adhesives, and surface coating or painting. With the collaboration of Tarmeko LPD, the goal is to find the most economical method to improve the fire resistance of bended plywood elements. Investigation of different impregnation processes and fire retardant agents is conducted. The idea is to get a bended element that has improved low flammability after bending process. The veneer or the glue has to have fire retardant properties. But the strength properties must remain the same.
- **(Cost Action FP 1303 "Performance of bio-based building materials")** A folding table with boards made from three different materials (i. e. Norway spruce, English oak and thermally modified Norway spruce) is used as test object. The boards are fixed with partly stainless and partly ordinary steel screws. Table is tested for optical, aesthetical, moisture and functional

performance and durability in ambient conditions. Performance data of table under climatically different exposure conditions around Europe is collected. Following measurements are evaluated regularly: decay, discoloration, development of mould and other staining fungi, corrosion, formation of cracks and moisture performance with automatic data logging device. Based on the results it is possible to estimate the exposure severity and performance to be expected of wood materials under climatically different exposure conditions.

2.2.2 Uurimisgrupi aruandeaastal saadud tähtsamad teadustulemused

- **(Wood-Plastic Composites (WPC): Effect of artificial weathering on the mechanical and physical properties of WPC)** Firstly, birch (Betula) wood chips were refined to three different fraction sizes of wood flour using disintegrator device DS-A, and Bleached-Chemi-Thermo-Mechanical aspen (Populus tremula) pulp (Aspen BCTMP) was ground to fine powder and used in composites. Thermoplastics (LLDPE-g-MAH and PP) were used to prepare composites. Wood flour and BCTMP surface were treated with two different coupling agents: 3-aminopropyltriethoxysilane (APTES) and polyvinyalcohol (PVA) and their effect on the mechanical and physical properties of WPC material was investigated. WPC specimens with concentration of 65 wt.% of polymer and 35 wt.% of wood flour and 80 wt.% polymer and 20 wt.% BCTMP were made by injection molding. Results showed that after the water absorption and swelling of WPC the flexural modulus (MOE) and strength decreased and impact strength increased by making the material weaker with increasing the deflection of WPC. It was observed, that UV radiation decreased composites flexural strength and MOE, while impact strength was increased. After the accelerated weathering cycles cracks and voids were found on the surface of WPC materials. After the UV radiation treatment, also the WPC color was lightened.
- **Laboratory for Furniture and Wood Materials Testing** has conducted the research of the mechanical strength of different joints used in furnituure manufacturing. The main objective of this study is to find the most suitable detachable joint for plywood furniture. Connecting fittings off different type were tested under failure loads. Both tensile and shear tests were used. Lamello AG products Clamex P10, Clamex P15, and Invis Mx and Minifix connectors with dowel as joint type have been used. The test results showed that the Invis Mx takes the highest average strength value in tensile test and Minifixwith beech dowel in shear test. Based on the test results, the best fitting for connecting plywood bended elemens and boards was determined. The aim of the mechanical testing dowel joints is to find out the strength of both the twisted birch dowel and the fluted birch dowel joints. Important parameters which are influencing the test results were determined during the experiments. The strength of tested joints was influenced by exact diameter of the dowel and accurate connection with dowel hole which should be drilled in the best possible fit. The methodology for analysing withdrawal and shear strength tests results was improved and the influence of external factors to the test results was minimized.

2.2.3 Uurimisgrupi aruandeaastal saadud tähtsamad teadustulemused

- Aruniit, A.; Antonov, M.; Kers, J.; Krumme, A. (2014). Determination of Resistance to Wear of Particulate Composite. D. Loca (Toim.). Engineering Materials & Tribology XXII (188 - 191).Trans Tech Publications Ltd
- Kängsepp K., Poltimäe, T., Liimand K., Kallakas H., Süld, T.-M., Repeshova I., Goljandin D., Kers, J. (2014) The effect of wood flour fraction size on the properties of wood-plastic composites. Proceedings of the 9th International Conference of DAAAM Baltic, INDUSTRIAL ENGINEERING, p366-371
- Aruniit, A.; Kers, J.; Krumme, A.; Peetsalu, P. (2014). Particle size and proportion influence to impact properties of particulate polymer composite. In: Proceedings of the 9th International

Conference of DAAAM Baltic Industrial Engineering : 24-26st April 2014, Tallinn, Estonia: 9th international conference of DAAAM Baltic industrial engineering; April 24 -26, 2014; Tallinn, Estonia. TUT, 2014, p325-330

- Saar, K.; Kers, J.; Luga, Ü.; Reiska, A., (2014) Mechanical properties of connecting fittings for plywood furniture. In: Proceedings of the 9th International Conference of DAAAM Baltic Industrial Engineering : 24-26st April 2014, Tallinn, Estonia: 9th international conference of DAAAM Baltic industrial engineering; April 24 -26, 2014; Tallinn, Estonia. TUT, 2014 , p399-404
- Dobris, J.; Luts, A.; Meier, P. & Kers, J., Analysis of the twisted and fluted birch dowel joints; In: Proceedings of the 9th International Conference of DAAAM Baltic Industrial Engineering : 24-26st April 2014, Tallinn, Estonia: 9th international conference of DAAAM Baltic industrial engineering; April 24 -26, 2014; Tallinn, Estonia. TUT, 2014 pp. 331-336

2.3 Põlevkivi ja taastuvkütuste teaduslaboratoorium *Laboratory of Oil Shale and Renewables Research, Dr. Hans Luik*

2.3.1 Uurimisgrupi kuni 5 olulisemat publikatsiooni aruandeaastal

- **(SF0140028s09)** New technologies of thermochemical processing of oil shale and blended fuels (Põlevkivi ja kütuste segude termokeemilise töötlemise uued tehnoloogiad): Liquefaction and upgrading of Estonian fossil and renewable fuels and fuel blends with the aim of their more rational and appropriate utilisation will be investigated. Scientific and technological fundamentals to maximum conversion of oil shale, peat, varieties of biomass and plastic wastes into non-conventional petroleum by using novel thermal dissolution, hydrogenation and co-processing methods will be created. Bi- and multilateral interactions occurring between components at sub- and supercritical extraction and at upgrading of the viscous extracts by hydrogenation will be investigated. Probable positive synergistic effects in the yield and composition of the liquid product will be described. Mathematical models will be deduced for approximate description of the joint effect of the main factors on the yield and composition of the products in the complicated processes. The results obtained represent the science-based fundamentals for upgrading available natural fuel resources.
- **(ETF 9331)** Liquefaction of the organic matter of dictyonema oil shale with supercritical solvents and reagents (Diktüoneema põlevkivi orgaanilise aine vedeldamine superkriitiliste lahustite ja reagentidega): Regularities of thermochemical liquefaction and upgrading of the dictyonema oil shale with the aim of estimating its potential as a source for synthetic petroleum will be investigated. As a conversion method supercritical extraction in autoclave in the presence of various solvents and reagents is used. The effect of supercritical water, benzene, hexane, methanol, ethanol and acetone on products yield and composition will be investigated. In order to obtain the maximum yield of oil rich in hydrocarbons parametres of kerogen liquefaction process (temperature, liquefaction time, pressure in autoclave and weight ratio of initial substances) will be largely varied and some selected reagents (H-donors, NaOH, zinc) are added to evoke the hydrogenation, cracking and other reactions. Physical-chemical and technological fundamentals for the sustainable utilisation of the huge reserve of so far industrially unused oil shale type will be created.
- **(AR12004)** Fundamentals to oil shale maximum upgrading (Põlevkivi maksimaalse vääristamise alused): The project is a continuation of the competence in the field of oil shale liquefaction via complex investigations leading to the new technologies, and the direct goals of the project include working out novel technologigal fundamentals of shale oil production and complex upgrading scheme of liquid, gaseous and solid products formed in thermochemical destruction of different oil shales.

2.3.2 Uurimisgrupi aruandeaastal saadud tähtsamad teadustulemused

- **(SF0140028s09)** Upgrading Estonian oil shale heavy bituminous residuum fractions (thermobitumen, 360 °C+ fraction, asphalthenes, heavy oil) via catalytic hydrocracking using KF-848, DN 3100TL, KGU-950 catalysts at varied temperature and time combinations was completed and 50–70% of heavy fractions turned to diesel fraction. Regularities of co-pyrolysis fuel blends of oil shale - renewables type were investigated, new synergistic effects were detected and mathematically described. Thermobitumenization process of different oil shales in solvent medium was elucidated and compared.
- **(AR12004)** Thermal dissolution of U.S., Jordan and Dictyonema oil shales in the medium of various solvents to generate maximum liquid yield followed with its maximum upgrading via catalytic hydrogenation process was investigated. It was demonstrated that the conditions found to be optimum for Kukersite maximum liquefaction and upgrading were not effective to other oil shales. Different oil shales varying in kerogen content at the same experimental conditions were demonstrated to give different yields of oil, gas and solid residue.
- **(ETF 9331)** Thermochemical decomposition of Dictyonema oil shale was investigated in modified Fischer assay pyrolysis and autoclavic thermal dissolution in the presence of alkali, acid, H-donor and molecular hydrogen and as a result liquefaction of the fossilized organic matter was favoured and the content of hydrocarbons in liquid increased.

2.3.3 Uurimisgrupi kuni 5 olulisemat publikatsiooni aruandeaastal

- Luik, H., Luik, L., Johannes, I., Tiikma, L., Vink, N., Palu, V., Bitjukov, B., Tamvelius, H., Krasulina, J., Kruusement, K., Nechaev, I. (2014). Upgrading of Estonian shale oil heavy residuum bituminous fraction by catalytic hydroconversion. Fuel Processing Technology, 2014, 124, 115–122.
- Johannes, I., Luik, H., Palu, V., Kruusement, K., Gregor, A. (2015). Synergy in co-liquefaction of oil shale and willow in supercritical water. Fuel, 2015, 144, 180–187.
- Kruusement, K., Luik, H., Waldner, M., Vogel, F., Luik, L. (2014). Gasification and liquefaction of solid fuels by hydrothermal conversion methods. Journal of Analytical and Applied Pyrolysis, 2014, 108, 265–273.
- Luik, H., Luik, L., Palu, V., Sharayeva, G., Gregor, A. (2014). Applicability of static supercritical carbon dioxide extraction in biogeochemical characterization of oil shales. American Journal of Analytical Chemistry, 2014, 5(3), 173–180.

3. Loetelu struktuuriüksuse töötajate rahvusvahelistest tunnustustest

Rahvusvahelised tunnustused 2014 aastal puuduvad.

4. Loetelu struktuuriüksuse töötajatest, kes on välisakadeemiate või muude oluliste T&A-ga seotud välisorganisatsioonide liikmed

Välisakadeemiate või muude oluliste T&A-ga seotud välisorganisatsioonide liikmed instituudis puuduvad.

5. Ülevaate teaduskorralduslikust tegevusest, teadlasmobiilsusest ning hinnang teadustulemustele

Korraldatud rahvusvaheline konverents:
Baltic Polymer Symposium 2014, September 24 – 26, Laulasmaa, Estonia.

Osaletud on järgmistel rahvusvahelistel teaduslikel konverentsidel:

- 20th International Symposium on Analytical & Applied Pyrolysis, 19–23 May 2014, Birmingham, UK (3 ettekannet).
- 5th International Conference on Engineering for Waste and Biomass Valorisation, August 24–28, 2014, Rio de Janeiro, Brazil (2 ettekannet).
- 34th Oil Shale Symposium, October 13–17, 2014, Colorado, USA (2 ettekannet).
- 2nd International Conference on Advances in Applied Science and Environmental Engineering - ASEE 2014, 20–21 December, 2014, Kuala Lumpur, Malaysia.
- 23rd Nordic Rheology Conference, August 13 – 14, 2014, Reykjavik, Iceland. (1 posterettekanne)
- 9th Annual European Rheology Conference, April 8 – 11, 2014, Karlsruhe, Germany. (1 posterettekanne)
- 3rd International Conference on Electrospinning, August 4 – 7, 2014, San Francisco, USA.
- 9th International DAAAM Baltic Conference INDUSTRIAL ENGINEERING - 24-26 April 2014, Tallinn, Estonia. (3 ettekannet)
- The Northern European Network for Wood Science and Engineering 13-14 Oktoober 2014, Edinburgh, Scotland. (1 posterettekanne)

Polümeermaterjalide instituudi teadustööd võib pidada väga heaks ja osalemist teadus-arendusprojektides suurepäraseks.