RESEARCH REPORT

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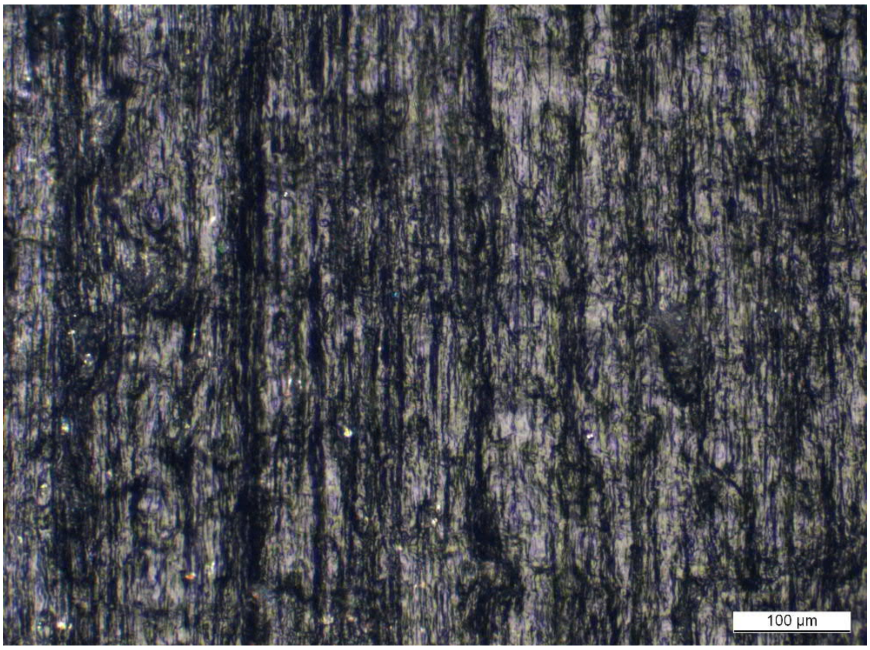

Durable and light weight polymer composites for extreme wear conditions

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Report's title

Durable and light weight polymer composites for extreme wear conditions -
Abrasive wear and scratch resistance of polymer composites

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Summary

The thermoplastic polymer compounds and polymer composites for enhanced abrasive wear resistance were developed based on commercially available polymers, compounded with micron-sized and nanosized fillers. PA1010, HDPE, UHMWPE were used as base polymers in the DURPOL compounds. Thermoplastic polyurethane (TPU) compounds with enhanced tear and scratch resistance, and glass fibre reinforced PA12 were also developed for enhanced scratch resistance.

The abrasive wear of polymers was determined as mass loss during the sand abrasion tests. The tests followed the standard ASTM 65-04 concerning the overall test setup, two loading levels was used to study the wear performance of polymers in different loading conditions. For the scratch resistance evaluation, the reciprocating scratch testing was performed on VTT REC tester. The influence of the scratches on the visual appearance of the polymer surface was measured with a gloss meter and 2D profilometry. For evaluation of tear resistance of TPU materials, the specific test samples were processed by injection moulding and by stamping the sample to specific form. The samples were tested according the ISO 34-1 standard (Method B). The polymers were characterised by optical microscopy and SEM after the wear tests. The indentation measurements were used to determine the plane strain modulus, indentation modulus and indentation hardness of materials. Atomic force microscopy, DSC and DMA analysis, tensile tests and Charpy tests were also carried out for selected materials.

In the cases where the polymer has no special requirements for strength or stiffness, the lowest wear can be gained with the soft elastomers. However, it was found out that when the TPUs were modified e.g. by preparing TPU-PA blends to increase the modulus, the abrasive wear of the developed material increased.

Concerning the neat polymers, PA1010 exhibits lower wear compared to PEEK, and high molecular weight tube extrusion grade HDPE polymer has similar abrasive wear compared to PEEK, but the modulus of these polymers is clearly lower compared to PEEK, around 2 GPa and 1.2 GPa, respectively. The PA compounds were developed in this project by using different fillers to increase the modulus of PA1010. The addition of 15 wt% silanized glass flakes, or 15 wt% halloysite nanotubes increased the indentation modulus from the 1.9 GPa range to 2.3 GPa level, while retaining the abrasive wear resistance of the PA1010 polymer. Indentation modulus and tensile modulus of PA1010 was increased also by electron beam crosslinking.

The semi-aromatic polyamide has high modulus combined with reasonable wear resistance, but the polymer is brittle. The polymer was toughened by blending it with UHMWPE and PA, which did not have a major influence in the wear performance. The lowest abrasive wear was achieved by PA soluble plasticizer additions to the semi-aromatic polyamide.

For the PE polymer the HDPE/UHMWPE blends were developed. UHMWPE polymers typically have high wear resistance, but they cannot be processed by injection moulding. In DURPOL project, we succeeded to develop injection mouldable UHMWPE and HDPE blends. In addition, different fillers were used in the blend to improve the performance. The UHMWPE/HDPE with fillers, such as γ-Al2O3, graphene oxide and fumed silica provided improved abrasive wear resistance with slightly reduced modulus. Addition of glass flakes increased the modulus of the blend while wear performance remained on the same level as for HDPE. Increase of modulus was also achieved with ultrafine precipitated calcium carbonate (PCC), interestingly reducing also the abrasive wear. In our preliminary studies the electron beam cross-linking raised the room temperature indentation modulus of UHMWPE/HDPE blend containing nanofillers, by roughly 15%. The observed abrasive wear resistance measured at ambient room temperature was similar, and typically slightly worse compared to the non-crosslinked reference blend.

For the development of soft polymers, in order to improve tear resistance and scratch resistance, the TPU composites with cellulose microfibre and hemp fibre reinforcements combined with the “soft touch” were developed. These new materials were processed without plasticizers using commercial mineral filler additives.

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Preface

This report provides information on technical work carried out in the Durable and light weight polymer composites for extreme wear conditions (DURPOL) project. The project was financed by Tekes (at present Business Finland), the participating companies and VTT.

The advisory group established for the project consisted of the representative of participating companies, Tekes and VTT.

The advisory group is highly appreciated for their advice, interest towards the project and the polymer development, and for the active participation in the project.

The polymer materials were manufactured at VTT in Tampere and evaluation of the material performance was carried out at VTT in Espoo during 2016 to 2018. The materials developed in the project, the tests carried out for the materials and the test results are described in this report.

The authors want to thank also the colleagues that participated in the research work, particularly we want of thank Simo Varjus, Asta Nurmela, Lauri Kilpi and Seija Kivi for their valuable contribution for the project.

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Contents

1. Introduction

The use of polymer materials had increased in engineering applications due to lightness and the versatility of polymer materials. The range of different polymers is wide and by using different type of fillers, their properties can be adjusted to meet wide range of functionalities. Despite the development of polymeric materials, there are still challenges to meet sufficient wear resistance in demanding applications.

The performance of polymer materials is not sufficient for applications were scratch and abrasive wear resistance is required or when the materials are under combined abrasive wear and high loading. This has prohibited the generation of new innovative, energy efficient solutions or forces companies to use substitute materials that require complicated manufacturing processes for production. To enhance the novel solutions, facilitate new and innovative designs providing new business opportunities, “Durable and light weight polymer composites for extreme wear conditions - DURPOL” -project was established to develop polymers with improved performance and manufacturing processes to participating companies and to the wider field of applications and companies outside the project consortium.

DURPOL-project combined the polymer development and processing development carried out at VTT. The participating companies formed an ecosystem that supported the polymer development and implementation into the industrial production of polymer based components and products.

2. Goal and development strategies

Main objective of DURPOL was to develop highly wear resistant polymer materials combined with functional properties, such as strength and toughness required for the applications, to fulfil the industrial needs of the polymer materials.

To reach the main objective the following approaches were adopted:

- To increase the abrasive wear and scratch resistance of polymers the nano- and micro-scale fillers were applied to provide enhanced performance of polymer matrix for highly loaded abrasive conditions.
- The compatibility of fillers, nanosize filler in particular, with polymers was improved by chemical surface treatments.
- Novel reactive melt state treatment was developed to increase the compatibility of fillers.
- The influence of the surface finish and texture of the polymer surface on the scratch resistance and scratch visibility was investigated, and the optimised surface texture for scratch resistance was searched by modifying the mould surface for injection moulding
- The tear strength of soft polymers in combination with the scratch resistance was also improved with different type of fillers.

The versatile characterisation techniques were utilised to gain a comprehensive understanding of the material properties. The filler - polymer -matrix interface and filler dispersion was also evaluated to optimise the polymer structures. The abrasive wear properties of developed materials was evaluated with different methods. An important task was to understand the connection of basic polymer properties and the wear resistance, and to find the most important basic properties dominating the wear performance.

The performance and functionality of developed materials was evaluated and the capability to provide high performance and sustainable polymer material solutions was verified in application-oriented tests. The relevance of the laboratory tests to the field tests was also verified. The developed polymer nanocomposites and polymer compounds with desired material structures and properties for specified applications were field tested by industrial partners to verify the capability of developed materials in operations conditions.

3. Impact

DURPOL-project aimed to combine material manufacturing route and novel filler technology to develop polymers with improved performance compared to the current state-of-the art of the commercial thermoplastics and composite materials. The project combined also several industrial partners throughout manufacturing value chain, from compounding to polymer processing and further to the manufacturers of consumer products and thus increased the understanding of polymer wear and knowledge of the new developments in a wide range of industrial companies.

During the project, the knowledge of material parameters influencing polymer performance in abrasive wear conditions was increased. Furthermore considering the attained results, it become obvious that understanding of the polymer structure-property relationships was the key for improving the properties of polymers. The novel nano- and microscale fillers with specific and sophisticated filler treatment techniques provided new route to improve the performance of polymer for demanding applications.

The goals set for the project were met in the following way:

1) Polymer compositions and polymer compounds were developed that had the elastic moduli comparable to engineering plastics (e.g. polyamides), combined with abrasive wear resistance comparable to the very best tribology polymers (e.g. UHMWPE). The wear performance of PEEK that was considered as the reference polymer for the new developments was greatly outperforming by the new polymer composites developed.
2) The tear resistance of soft TPU was increased by 95%, a result, which was previously unattained by the TPU manufacturers.
3) Effective additives were found for improving the scratch resistance of commercial glass fiber reinforced PAs and many TPU grades.

Most of the polymer blends and composite materials were manufactured in laboratory scale. The most promising material compositions were also up-scaled to small industrial (pilot) scale compounding line, and they turned out to perform as good as the materials compounded in laboratory scale.

Most of all, the amount of different recipes used during this project was over 200, generating a great database for selecting materials for a variety of different technical applications, and a good basis for further development of the recipes providing outstanding abrasive wear resistance.

Participating companies showed great interest on the progress of the project and on the results gained. In the future, the results of the developed polymers will be presented also to companies outside the project consortium and the results will be published in journals and seminars.

4. Description of methods and materials

4.1 Polymer processing and sample preparation

The thermoplastic polymer compounds and polymer composites for enhanced abrasive wear resistance were based on commercially available polymers, compounded with micron-sized and nanosized fillers, coming from commercial suppliers. Polyamide (PA1010), high molecular weight (HMW) high-density polyethylene (HDPE), and various commercial ultrahigh molecular weight PE (UHMWPE) grades were used as base polymers in the DURPOL compounds. Thermoplastic polyurethane (TPU) compounds with enhanced tear and scratch resistance, and glass fibre reinforced polyamide 12 (PA12) were also developed for enhanced scratch resistance.

Polyethylene materials (HMW-HDPE and UHMWPE) were available as fine powders, which could be effectively premixed mechanically with fillers and additives (antioxidants, stabilizers, liquid coupling agents, etc.) prior to twin screw compounding (TSC). TPUs, polyamide 1010 and glass fibre reinforced PA12 were received as pellets and the fillers and the other additives were fed into the molten polymer in the compounding process.

Three different types of TSC machines were utilized. For the smallest scale experiments, batches of 12–15 grams of the test materials were generated using MC15 HT (Xplore Instruments BV, The Netherlands), mixing volume 15 cm^3. The evolution of the melt viscosity was recorded during the mixing period. The residence time of the polymer melt in the batch mixer could be varied (typically between 3-6 min), which can be beneficial in achieving a reasonably good dispersion of the fillers. This is in contrast with the continuous TSC where the residence time in the mixer is typically very short (0.5–1.5 minutes).

As the small lab scale processing is known to be less than optimal for the best possible dispersion and mechanical properties of the test samples, a powerful Brabender batch mixer W350 EHT (mixer volume >300 cc) and standard injection moulding of samples was utilized in some cases. Larger 2–10 kg batches of selected materials were also prepared with continuous TSC Berstorff ZE25 48D. In the last phase of the project, some larger 10 to 30 kg batches of four selected PE formulations were processed in industrial environment.

The small volume of material processed in the MC15 batch mixer was sufficient for direct injection moulding of wear test pins with cylindrical form (length 16mm, diameter 10mm), and for impact strength test samples by using a pneumatic ram injection moulding machine (ThermoHaake Minijet). Cylindrical test pins (Figure 1) were also injection moulded using Arburg Allrounder 260C 600–100 machine. Standard tensile test bars were injection moulded using Engel ES 200/50 HL (50 ton clamping force).

Electron beam (EB) cross-linking of PE and PA compounds was carried out via a commercial process provider. The optimum radiation dose for PE and PA polymer samples was studied. Also the concentration of the cross-linking additive for PA1010 samples was screened.

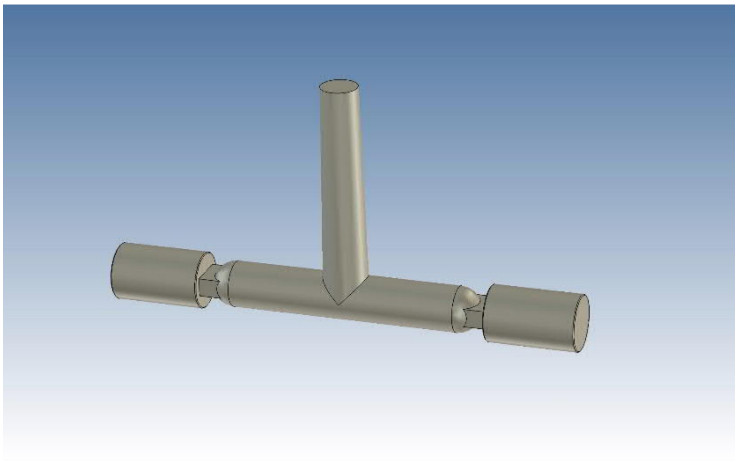


Figure 1. Schematics of the injection moulded part with two cylindrical test pins for the abrasive wear testing.

Related to scratch resistance studies of soft and hard polymers, samples with different topographies were processed. For this purpose a specific test specimen mould with four surface finishes was manufactured. The spark erosion VDI32 surface had the highest surface roughness. Spark erosion VDI24 and etched VDI24 are aiming for the same surface roughness by different manufacturing method. Polished surface, close to SPI A2 is the smoothest surface. Mould surfaces were characterized by 3D-profilometry and 2D-profilometry. Surface roughness Ra values measured by 2D-profilometry are listed in Table 1.

Figure *2* shows the finished mould and the injection moulded sample.

Table 1. The surface roughness (Ra) values of mould surfaces measured by 2D-profilometry. n=6.

	Polished	**Etched VDI24**	**Spark erosion VDI24**	**Spark erosion VDI33**	**Ra**
AVERAGE	0.03	1.17	1.96	4.49	µm
STDEV	*0.01*	*0.10*	*0.12*	*0.40*	*µm*

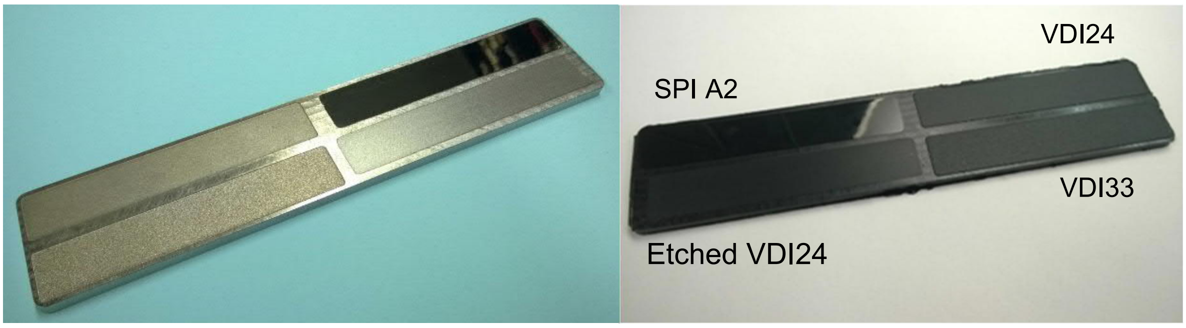


Figure 2. Mould insert used for scratch test specimens (on the left), length of 170 mm and width of 35 mm. The "black" surface is the polished surface and the closest to the camera on the left side is the spark erosion VDI33, which is the coarsest surface finish. The moulded polymer sample (on the right) showing the surfaces etched VDI24, polished SPI A2, spark eroded VDI33, and spark eroded VDI24.

4.2 Development of polymers in DURPOL project

The overall strategy in the development of the compounds was to first start from existing commercial polymers (PE, PA or TPU). The properties to be developed for these matrix polymers in DURPOL project were abrasion resistance evaluated by the sand abrasion test combined with Young's modulus and hardness for hard polymer materials, and the scratch resistance and tear strength for the TPUs. In addition, the price in relation to material performance was taken into account.

Up-grading the overall property profile of the existing composition was attempted using several commercial and developed additive systems, such as nanopowders with differently surface treatments, impact modifiers, and micron sized reinforcements (flakes, fibres, microbeads). Different polymer blending strategies were also applied. Moreover, it is well known that the thermomechanical performance of the PE and PA in elevated temperature can be enhanced by crosslinking. We studied EB crosslinking as a tool to extend the useful operating temperature range, that is, the retention of the mechanical stiffness and strength of the PE and PA to preferably close to +100°C or even higher, which for PE is in inaccessible range without the crosslinking.

The tear resistance of TPU generally correlates with the hardness of the TPU, soft TPUs having generally low tear resistance. In the many applications, some "soft properties" are required for the TPU, the hardness being in a suitable range (e.g. ShA 80). In fact, most high performance TPU materials are based on hard TPUs containing high quantities (>50 wt%) of liquid plasticizers. This approach is not generally ideal if fillers or reinforcements are used for the modification of the material properties due to poor adhesion between the fillers and the liquid extended polymer. In DURPOL project, new TPU composite with cellulose microfibre and hemp fibre reinforcements combined with the "soft touch" were generated. These new materials were processed without plasticizers. Concurrently with the tear strength, an increase in the scratch resistance of TPU was targeted. Commercial mineral filler additives were applied, as those have been suggested and already marketed for the purpose.

In each case of the different base polymer, it turned out that the chemical surface treatments of the fillers play a crucial role in the performance of the composite. Therefore, when possible, the coupling agent(s) was used for the polymer composites.

4.2.1 High modulus abrasive wear resistant polymers

Polyethylenes, particularly the UHMWPEs and linear high density polyethylenes (HDPE), are known for their abrasive wear resistance and attractive bulk price (<5 €/kg). The abrasive wear resistance is believed to stem from the toughness of the material and seems to correlate with the high molecular weight of the polymer chains.

However, the low E-moduli of PEs (<1.2 GPa for the HDPE and <0.9 GPa for the UHMWPE) set limitations for the applications. Moreover, UHMWPE cannot be practically processed by conventional plastics injection moulding technique, which is most suitable for the majority of technical applications. Therefore, blending of UHMWPE with melt processable HMW-HDPE and nano-sized fillers (e.g. graphene oxide GO, nanosilicas, nano aluminium oxide, halloysite nanotubes HNT) and micron-sized reinforcements (glass flakes) was used as tool to amend the shortcomings in the mechanical properties. EB-crosslinking was also applied, as the crosslinking of PE is known to improve the thermomechanical properties in elevated temperatures.

Polyamide 1010 has low abrasive wear, but the polymer also has relative low modulus for engineering applications. Therefore, various fillers, such as silanized glass microbeads, glass flakes, HNT and EB-crosslinking, were tested in order to boost the materials performance.

Semi-aromatic polyamide (PPA) has very high modulus and high tensile strength but very limited ductility and tensile elongation. Injection-moulded semi-aromatic polyamide is typically in amorphous state, and require further crystallization by heat treatment. Crystallization increases the modulus, but at the same time reduces the ductility. This can become a critical issue in technical use of the polymer. Moreover, polyamides in general have the propensity for water absorption, which renders the material properties, such as the ductility, rather dependent on the humidity in the service conditions. Soluble plasticizers are commonly utilized for aliphatic PAs and new suitable plasticizer and impact modifier systems were sought and investigated in the DURPOL to boost the performance of the polyamide PA1010 to increase the modulus, and semi-aromatic polyamide to increase ductility.

4.2.2 Scratch resistant thermoplastics and thermoplastic polyurethanes

In order to improve the scratch resistance polyester modified siloxane, a siloxane polyamide compound, antiscratch additive, glass beads, thermoplastic polyamide elastomer, graphene, submicron particles of amorphous silicon dioxide, nanosilica and hydrophobic fumed aluminium oxide were tested in glass reinforced PA12 compound. Electron beam crosslinking of PA1010 and PA1010-glass bead were also studied. PA12 was coloured by carbon black for the tests. The mixtures of commercial glass fibre (30 wt%) and glass bead compounds were produced with two glass bead loadings of 6 wt% and 15 wt%.

The additives to improve the scratch resistance of TPU were polyester modified siloxane, antiscratch additive, nanoclay, thermoplastic polyamide elastomer and graphene oxide.

The influence of surface roughness on the scratch formation and scratch visibility of polymers was evaluated by manufacturing test samples with different surface finish, as described previously.

According to literature and information from material suppliers it was expected that glass microbeads and certain platelet shaped clay mineral reinforcements were the most potential in increasing the scratch resistance of rigid polyamides (PA6, PA66, PA12). Moreover, it was hypothesized that EB-crosslinking could potentially improve the scratch resistance of PAs. In DURPOL project the glass beads and a multitude of other additives were studies in glass fibre (GF) reinforced PA12. Different fibre to bead ratios and varying additive loadings were investigated. Moreover, some polymer samples were cross-linked by electron beam treatment. For these samples, crosslinking additive was melt compounded during processing.

4.2.3 Tear resistance of TPUs

It was hypothesized that platelet shaped and long fibre shaped ductile and tough reinforcements could be the most suitable for increasing the tear resistance of TPU. Moreover, it was anticipated that the adhesion of the reinforcement and the TPU matrix could have a big role.

The effect of fillers and additives on the tear resistance were investigated in three polyether based thermoplastic polyurethane matrices. The commercial TPU grades were used. The studied fillers were Sillitin, hemp, cellulose microfibre, thermoplastic polyamide elastomer, graphene oxide, polyester chopped fibres and surface modified polyamide chopped fibres. The tear strength and Shore A hardness of TPU compounds modified with the antiscratch additives were also measured.

4.3 Polymer characterisation techniques

During the compounding in the MC15 HT twin screw mixer melt viscosity of the polymer blends and composites was monitored continuously.

Differential scanning calorimetry (DSC, TA Instruments 2920) was utilized in probing the crystallization behaviour of semi-aromatic polyamide. Furthermore, DSC was used in studying the evolution of the crystalline phases of the PA1010 upon electron beam crosslinking and the subsequent heating.

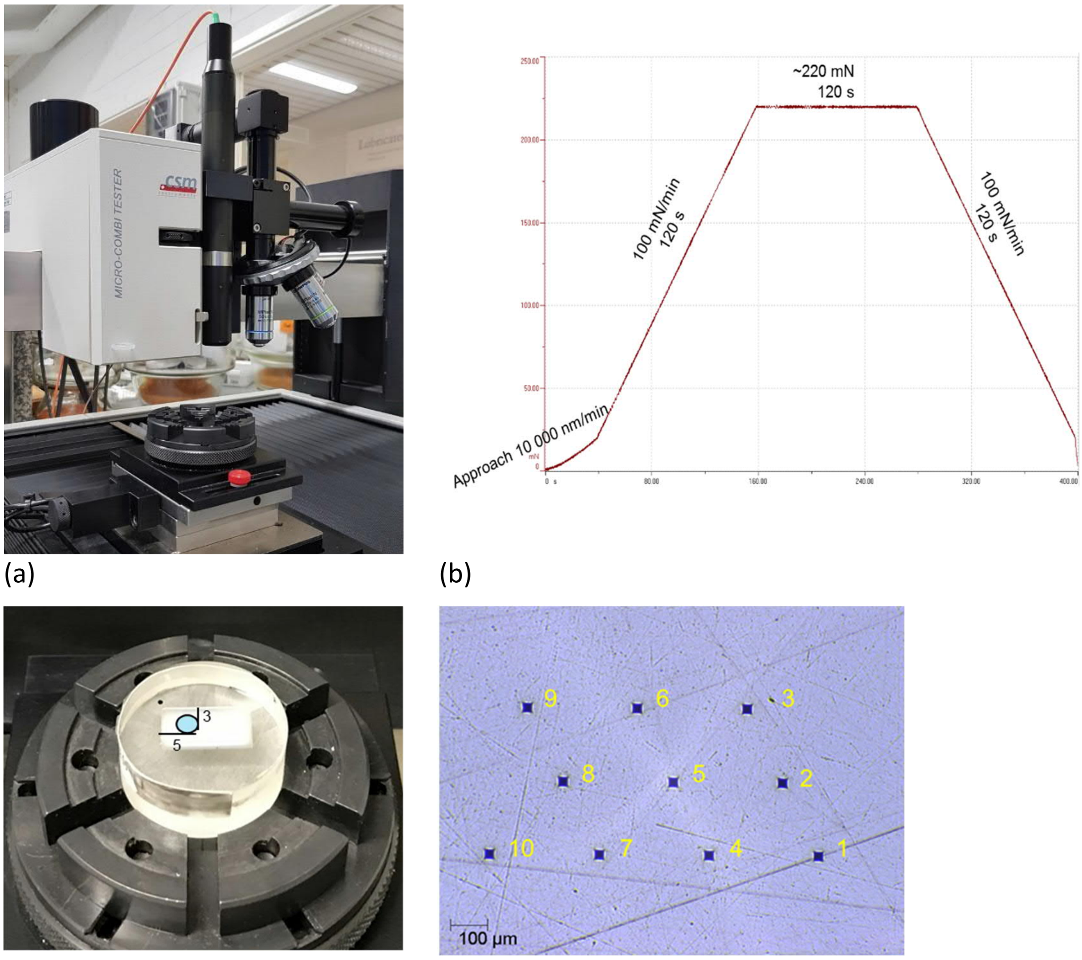
Dynamical mechanical properties of the PA1010 and glass ball filled PA1010 were measured using DMA SDTA 861E (Mettler Toledo).

Tensile testing (ISO 527-1) of the samples was conducted using Instron 4505H2190 system equipped with a video extensometer, drawing speed 1-10 mm/min. Notched Charpy impact strength (ISO 179-1) of selected test materials was measured from injection moulded samples using Ceast Resil 5.5 tester.

Tear strength was measured by Instron 4505 testing machine according to standard ISO 34-1 Rubber, vulcanized or thermoplastic-Determination of tear strength, Method B. procedure b, and Shore A hardness according to standard SFS-EN ISO 291 (2008). The temperature was 23.0 °C and the relative humidity was 50 %.

The Shore A hardness of soft thermoplastics was measured according to ASTM D2240-05 (Rubber Property-Durometer Hardness) standard, which is suitable for thermoplastic elastomer and rubber materials.

The indentation measurements were carried out to determine the indentation modulus and indentation hardness of polymers. The CSM Combi-tester with Vickers tip was used for indentation measurements with maximum load of 200 mN and loading rate of 100 mN/min. A dwell time of 120 seconds was used when maximum load was applied. The test device and the loading cycle used is described in Figure 3. The indentation measurements were carried out on the polished cross section on the polymer sample (Figure 3c) by making a matrix of ten indentations for one measurement and the values were calculated as average value of ten measurements if all the values were valid. In some measurement cases outliers appeared due to measurement related issues. In those cases, the average was calculated based on the remaining indentation values after outliers were omitted.



(a)

(b)

(c)

(d)

Figure 3. (a) The Micro-Combi tester used for indentation measurements, (b) loading sequence used for indentation measurements, (c) the cross section of the sample with the location of measurements and (d) the indentation matrix made for the determination of values.

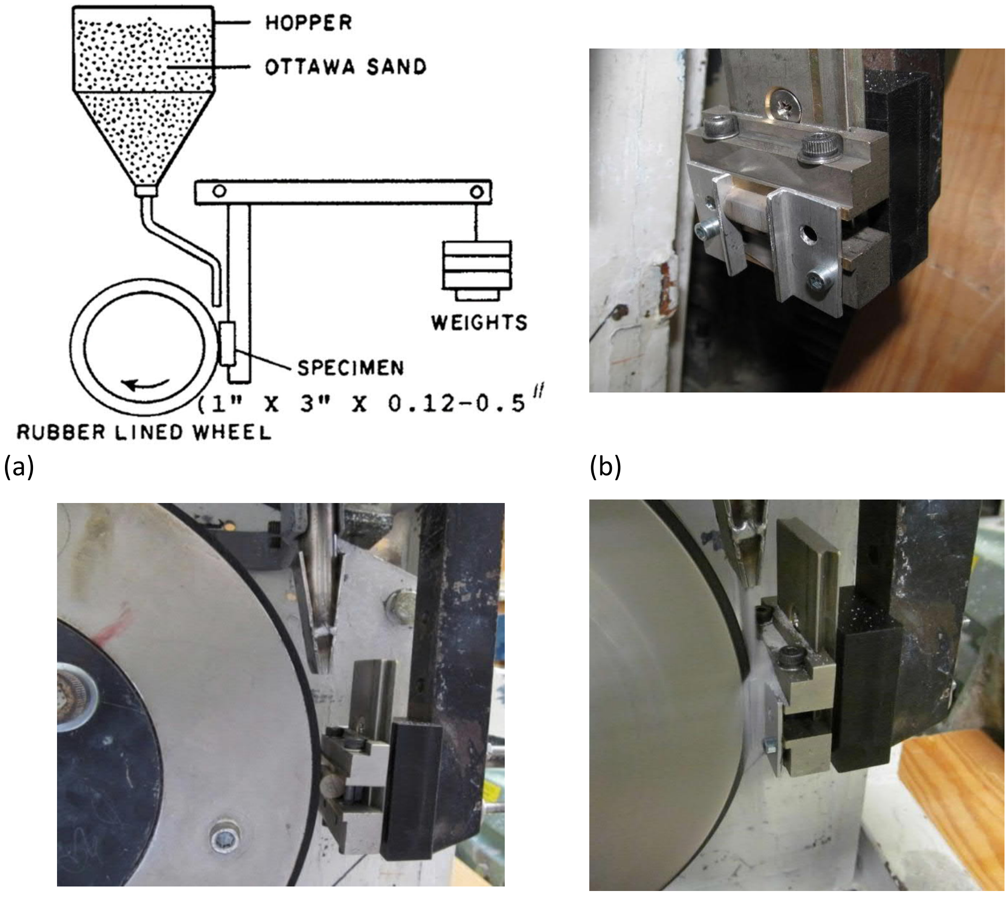
Optical microscopy was use to analyse and document the wear surfaces of all the tested materials. Zeiss ULTRAplus field emission scanning electron microscope (FESEM) equipped with Noran energy dispersive spectrometer (EDS) and a NSS software was used to study the wear surfaces of the selected materials and to observe the differences in wear behaviour between various materials and different loading levels.

Atomic force microscopy (AFM. Park Systems XE-100 system) Phase imaging technique was applied in the microscopy of the selected silica and alumina nanopowder (6 wt-%) composites in PA1010 and semi-aromatic polyamide blend. ACTA silicon probes (Applied NanoStructures. Inc. USA) was utilized, with nominal resonance frequency of about 300 kHz, spring constant 40 N/m and tip radius <10 nm were used in the imaging of polished nanocomposite samples in air.

4.4 Abrasive wear evaluation of polymers

The abrasive wear resistance of polymers was evaluated by sand abrasion tests. The tests followed the standard ASTM 65-04 concerning the overall test setup, except the loading conditions were varied. The samples were tested against the rubber-coated (Hardness ShoreA 61) steel wheel that had diameter of 235 mm. Quartz sand (average grain size 0.32 mm) at flow rate of 320 g/min was used to cause abrasive wear of the samples. The test device with the test sample is presented in Figure 4.

The tests were carried out with two loading levels to determine the material performance in different conditions. The parameters used in tests are presented in Table 2. To verify the repeatability of the sand abrasion tests during the project, a reference material (commercial PEEK Ketron 1000 rod) was used at certain intervals to ensure that the test results were comparable. The tests were carried out three times and the wear was determined as mass loss (g) during the tests. The mass loss was transferred to wear volume (mm^3) by dividing the mass loss with the density of material (g/cm^3). The wear surfaces of test samples were studied and documented by optical microscopy (OM) after the tests and selected cases were analysed by scanning electron microscopy (SEM).



(a) (b)

(c) (d)

Figure 4. (a) Schematic picture of the sand abrasion test device. (b) The cylindrical polymer sample attached to sample holder and (c) loaded against the rubber coated steel wheel. (d) The wear test ongoing at sand flow rate of 320 g/min.

Table 2. The loading levels used in sand abrasion tests for polymers.

	Load level 1	**Load level 2**
Normal load	19 N	45 N
Velocity	50 rpm ~ 0.62 m/s	100 rpm ~ 1.24 m/s
Test time	6 minutes	3 minutes

4.5 Scratch resistance evaluation of polymers

Scratch resistance of polymer samples was carried out with the VTT built REC tester. Test device was used to generate scratches on the sample surface and the scratch appearance was measured with a gloss meter and 2D profilometry. REC tester (Figure 5) was chosen for the tests because it was able to reveal differences in scratch resistance of polymers. The friction force was measured during scratch testing with the REC tester.

In REC testing a SiC abrasive strip (120 grit) was attached to a pin surface. The SiC strip was 10 mm wide covering the whole surface to be tested. The test duration was 20 passes (10 times back and forth) to ensure efficient scratching of the sample surface. The SiC strip was changed to a new one for each sample. The SiC strips were cut manually to fit the sample holder as precisely as possible. The abrasive used was commercial one and the grit size distribution and the alignment relative to the specimen during testing varied to some extent. Therefore, several experiments were run for each polymer surface to increase the reliability of results. The test parameters used in scratch testing are given in Table 3.

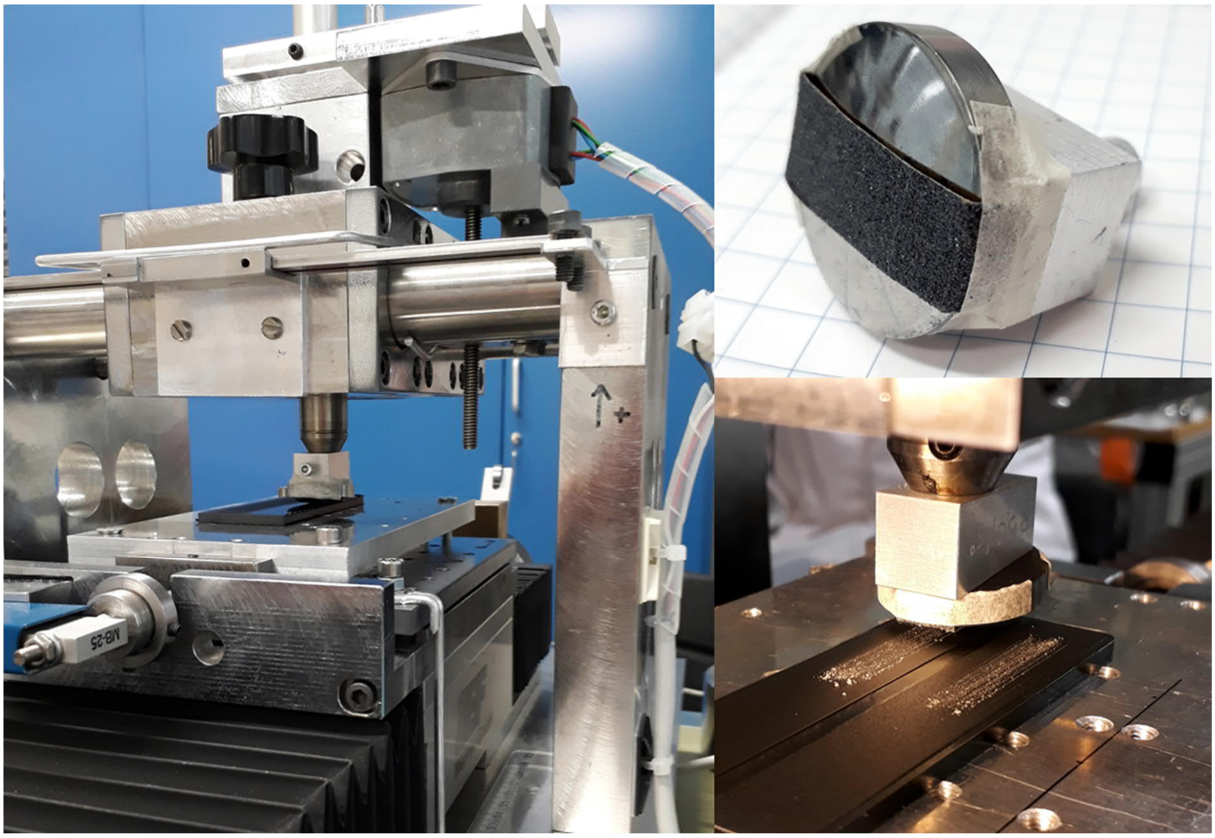


Figure 5. (left) The REC tester used for scratch resistance measurement, (right above) the tip with 120 grit SiC strip attached and (right below) scratch testing in progress.

Table 3. Parameters used in scratch tests using REC tester.

Parameter	**Value**
Tip	120 grit SiC. 10 mm wide. on a curved surface
Constant force	5 N
Scratch length	30 mm
Scratching speed	70 mm / min
Number of scratches	3 to 4
Number of passes	20 / scratch
Friction force measurement	On
Controlled environment	22 +-1 °C with 50 +-5 % relative humidity

The influence of mould surface finish and surface texture on the optical appearance (visibility) of scratches was investigated by using injection moulded black test samples. Gloss measurements were carried out on the scratched samples with different surface textures.

Characterisation of the scratches was performed roughly 20 to 24 hours after scratching. The aim was to give the polymers equal time for recovery while having some room for chaining the characterisation steps for multiple specimens at a time. The characterisation involved 2D-profilometry, gloss measurements and visual inspection including repro photography.

2D-profilometer Formtracer SV-C3100 by Mitutoyo was used to measure the scratch profiles. Some measurements were verified using 3D-profilometer Plμ 2300 by Sensofar. The pictures of the tested materials were taken of all the samples tested enabling the estimation of visibility of the scratches.

Gloss was measured using ZGM 1120 gloss meter by Zehntner testing instruments. The aim was to measure the same locations before and after scratching, and to get a numerical value to represent the scratching resistance instead of simply trying to rank the polymers visually.

4.6 Tear resistance evaluation of TPUs

For evaluation of tear resistance of TPU materials, the specific test samples were first processed by injection moulding and then the test samples were stamped to specific form with a die. The test sample is presented in Figure 6. The injection moulded samples were tested according the ISO 34-1 (Rubber, vulcanized or thermoplastic-Determination of tear strength) standard by using Method B, procedure b (notched samples).

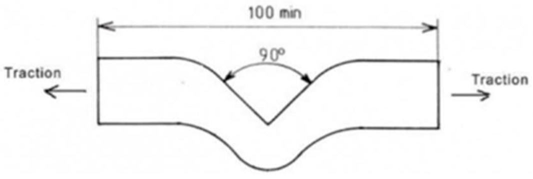


Figure 6. The test sample for tear resistance measurements.

5. Results of polymer characterisation

5.1 Dynamic mechanical and thermal properties

Dynamic mechanical and thermal properties were determined for semi-aromatic polyamides and PA1010 polymer and selected electron beam cross-linked PA1010 compounds.

The cold crystallization of semi-aromatic polyamide was evaluated by DSC measurements. The first DSC heating cycle of semi-aromatic polyamide at scanning rate of 10 K/min showed the distinct feature of the cold crystallization. This is particularly important observation, as mostly all injection moulded semi-aromatic polyamides parts have a 1-2 mm thick almost fully amorphous skin layer, which crystallizes in solid state by heat treatment of the moulded parts in oven.

DSC data showed the melting and crystallization for the electron beam cross-linked PA1010 and the neat PA1010 polymer. The cross-linked sample has a distinctly different melting behaviour, owing to a new metastable (meso)phase generated during the cross-linking. Formation of such new crystalline phase in radiation cross-linked materials is known to occur in PA6 but not previously reported for the PA1010 polymer.

DMA data showed the temperature dependence of the elastic modulus of radiation crosslinked PA1010 samples with crosslinking additive and crosslinking additive with 20 wt% glass beads. The E-moduli at room temperature were approximately 1.9 GPa and 2.35 GPa, which are higher than the E-modulus for the PA1010 at that temperature. The initial results are promising and suggest that the thermomechanical properties and chemical resistance of the PA1010 polymer and the PA1010 composite can be indeed improved by e-beam crosslinking.

5.2 Indentation modulus and hardness of polymers

The microindentation measurements were used to determine the Indentation hardness (H_{IT}), Plane strain modulus (E*) and the Indentation modulus (EIT). The Indentation modulus can be calculated from the Plain strain modulus when the Poisson ratio of the polymer is known. However, the Poisson ratio values for different polymers are difficult to find in the literature, and particularly for the newly developed materials they are not known. Therefore, the both values are presented in the figures. The Plane strain modulus and Indentation modulus will be discussed in more detail below.

Figure 7 shows the modulus values for the commercial polymers injection moulded at VTT. PEEK has rather high modulus values, about 4 GPa. The glass fibre (GF) reinforced polymers PPA, PPS and PEEK have high modulus, in the range 9 to 10 GPa, whereas POM reinforced with Kevlar had lower modulus (4 GPa).

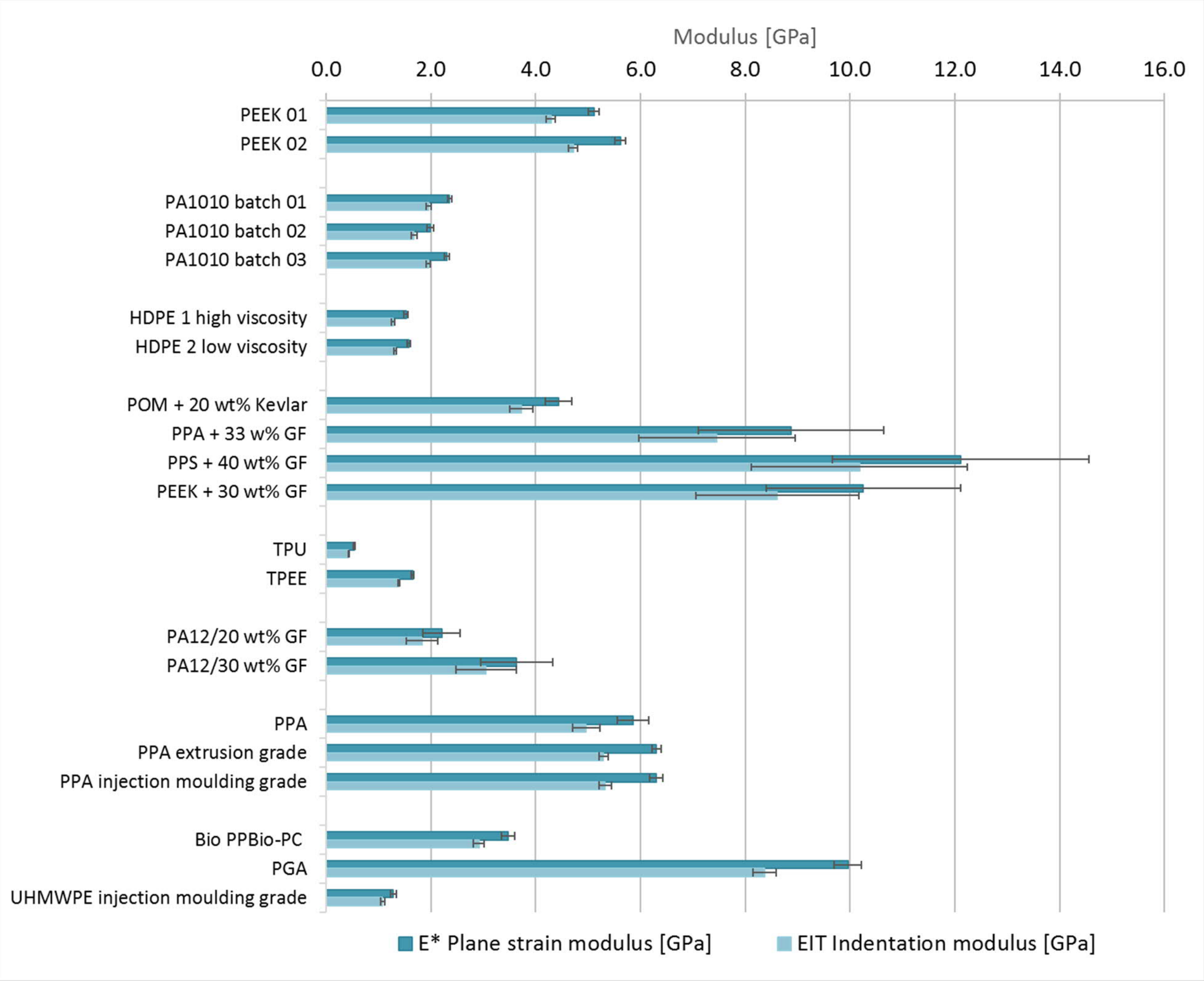


Figure 7. The Plain strain modulus E and the Indentation modulus EIT of commercial polymers.*

The modulus of PA1010 is about 2 GPa and the glass fibre reinforced PA12 polymer had values slightly higher with increasing fibre content. HDPE and TPU have low modulus values, about 1.5 and 0.5 GPa, respectively. Semi-aromatic polyamide had high values around 5 to 6 GPa and PGA in the range 8 to 10 GPa.

The soft thermoplastic polyurethane (TPU) had a very low modulus (0.5 GPa), which was slightly increased with glass bead additions (Figure 8). However, blending PA1010 into TPU was more effective increasing the modulus to 1 GPa and even close to 2 GPa. The commercial high strength TPU also had the modulus around 1.5 GPa.The soft thermoplastic polyurethane (TPU) had a very low modulus (0.5 GPa), which was slightly increased with glass bead additions. However, blending PA1010 into TPU was more effective increasing the modulus to 1 GPa and even close to 2 GPa. The commercial high strength TPU also had the modulus around 1.5 GPa.

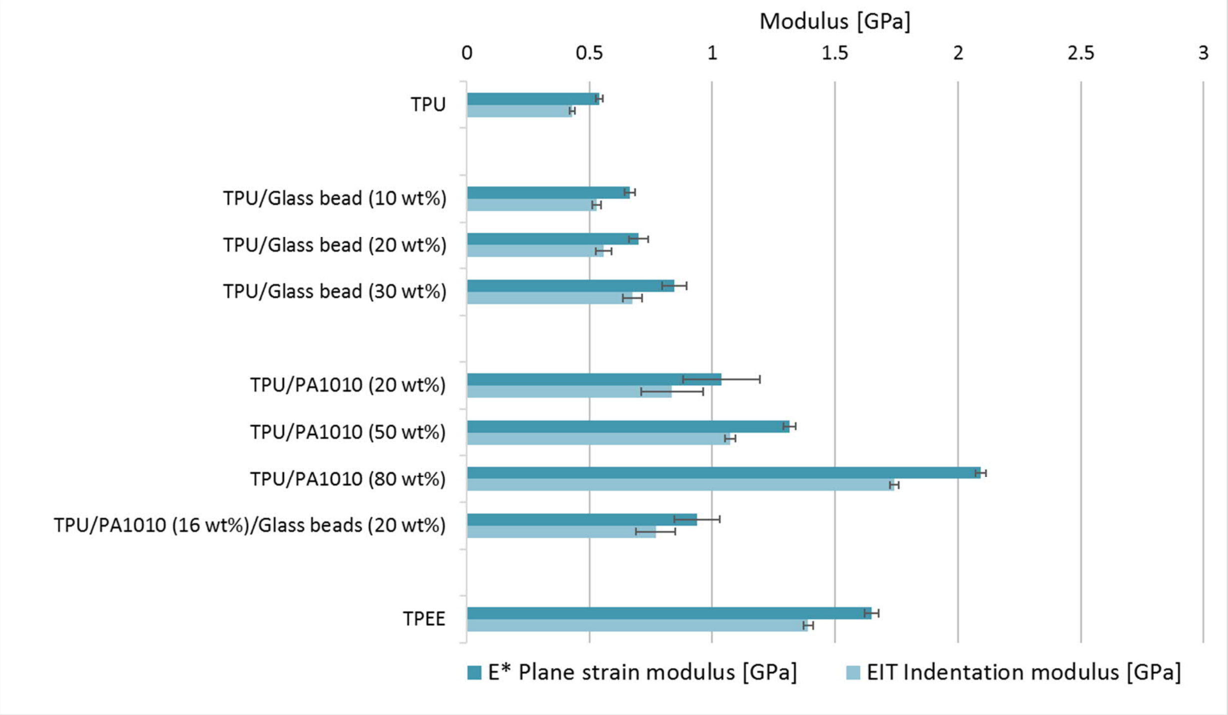


Figure 8. The Plain strain modulus E and the Indentation modulus EIT of TPUs.*

The modulus values of neat HDPE shown in Figure 9, were about 1.5 GPa. Blending HDPE with UHMWPE (blend ratio approximately 1:3.8) with additions of fillers (fumed silica, γ-Al_2O_3, GO, halloysite) decreased the modulus values. By adding glass flakes into UHMWPE/HDPE blend, the modulus could be increased close to 2 GPa.

The neat PA1010 had the modulus of about 2 GPa, which could be increased with glass bead (GP) and glass flake (GFL) additions (Figure 10). The highest modulus values were gained by 30 wt% addition of glass beads or glass flakes in PA1010 matrix. Halloysite and graphene oxide fillers slightly increased the modulus of PA1010.

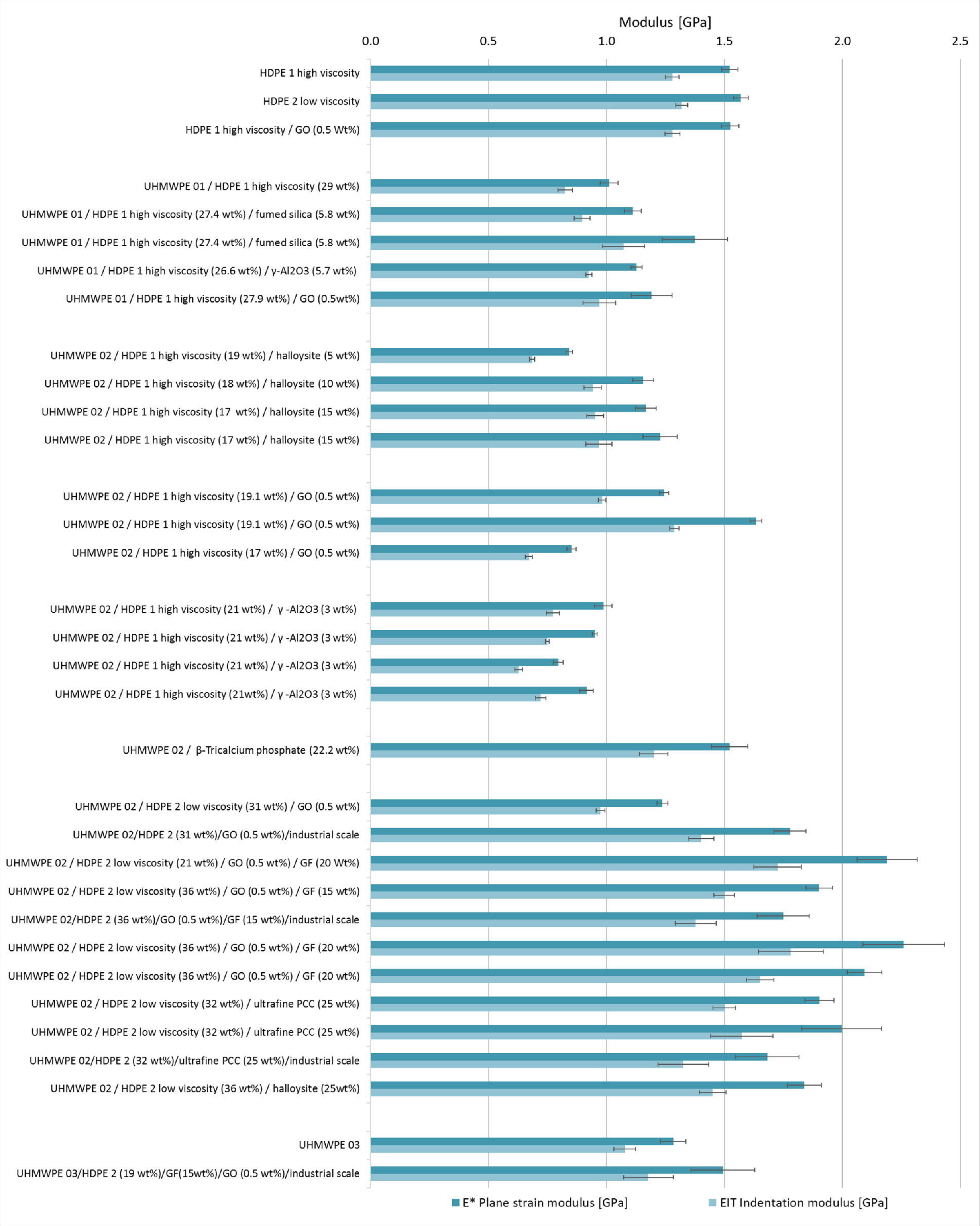


Figure 9. The Plain strain modulus E and the Indentation modulus EIT of neat HDPE and UHMWPE/HDPE blends. UHMWPE 01 and UHMWPE 02 refer to different polymer grades.*

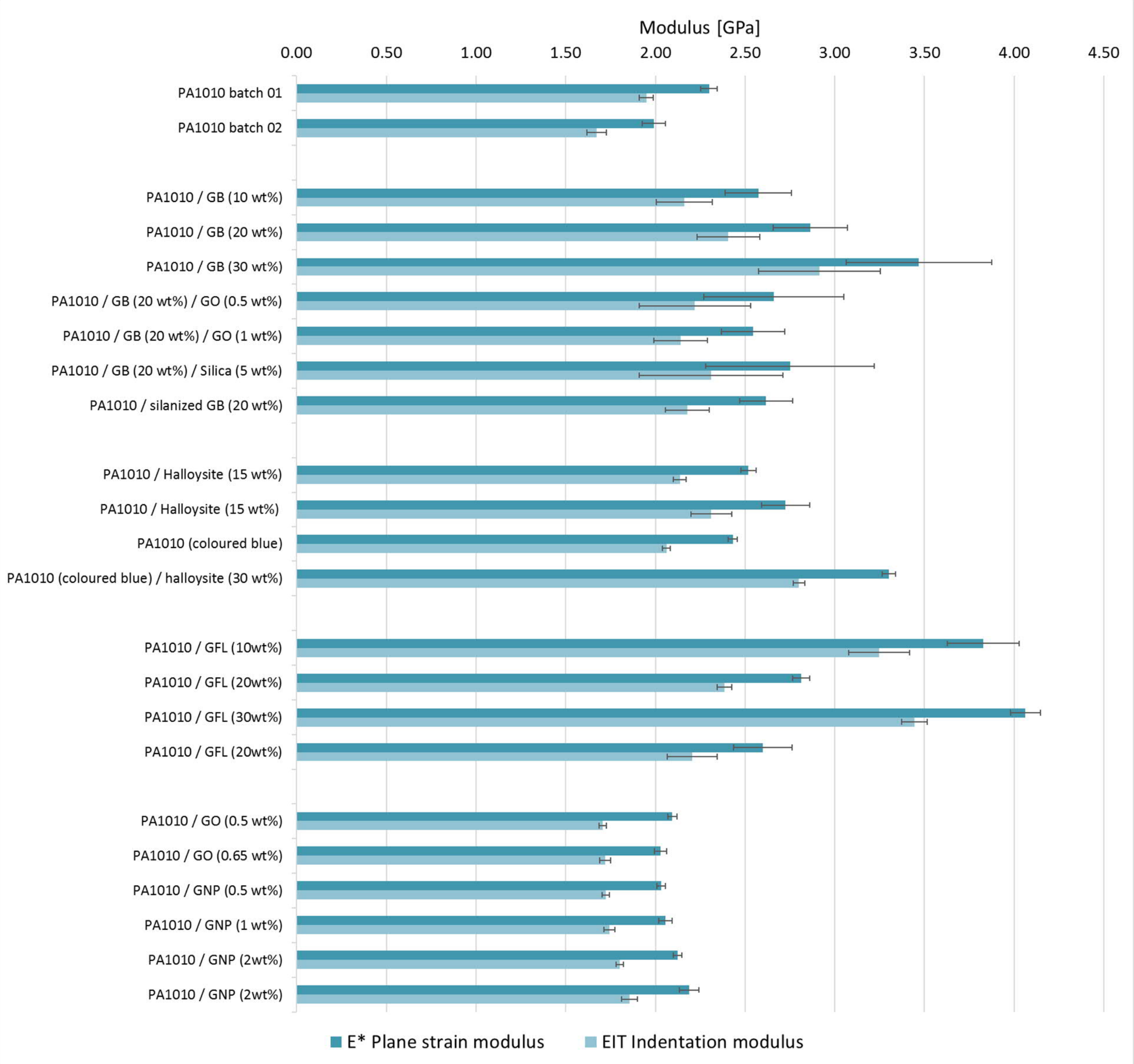


Figure 10. The Plain strain modulus E and the Indentation modulus E_{IT} of PA-based polymers.*

The PA12 based glass fibre (GF) reinforced polymer has modulus values in the range of 3 to 4 GPa (Figure 11). Addition of polysiloxane or glass beads (GB) had no influence in the modulus. The compound with lower glass fibre content (20 wt%) had lower modulus compared, but with glass bead addition to balance the filler content, the modulus values were comparable.

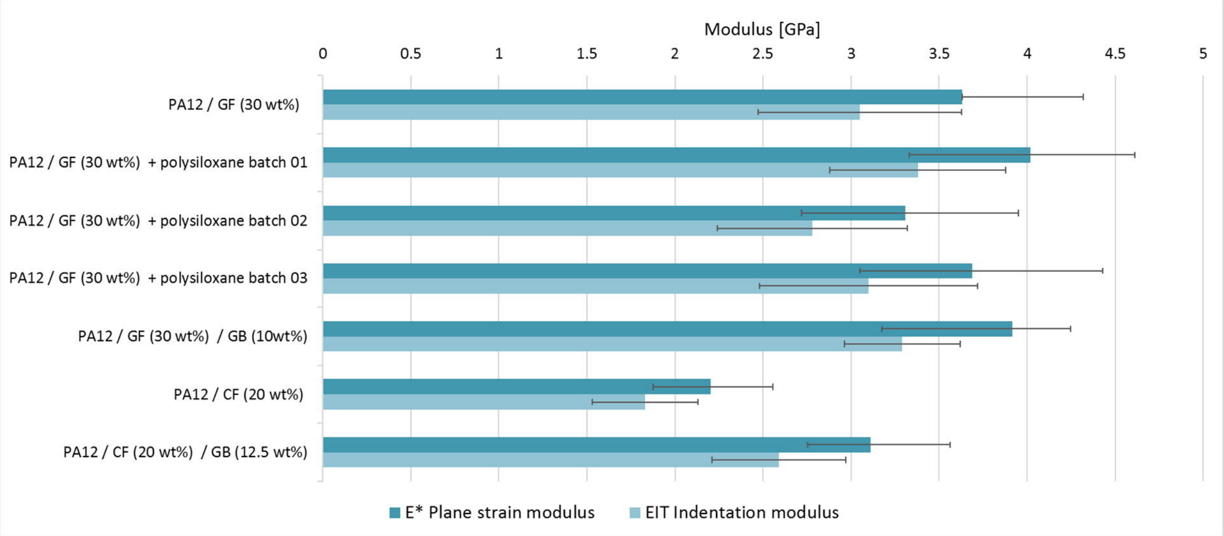


Figure 11. The Plain strain modulus E and the Indentation modulus EIT of glass fibre (20/30 wt%) reinforced PA12 polymers with polysiloxane PDMS and GB.*

The commercial semi-aromatic polyamide has rather high modulus around 5 GPa (Figure 12). The different grades and versions injection moulded with different mould temperatures provided similar values. Also, the heat treatment of samples for crystallisation did not change the modulus significantly. By blending semi-aromatic polyamide with UHMWPE and by adding polymeric impact modifier, the modulus values were consistently decreased. Similar trend was observed for the blends of HDPE and PA1010. By adding small amount of liquid toluene sulphonamide plasticizer, the modulus was slightly increased and by adding higher amount, the modulus was progressively lower when increasing the amount on the plasticizer.

The influence of EB-crosslinking on modulus values was also studied for untreated and EB-crosslinked HDPE, UHMWPE-HDPE -blends with and without γ-Al2O3 fillers, PA1010, and PA1010 with glass beads. As a general trend, modulus values were higher when the EB-crosslinking radiation dose was increased. This was particularly clear for PA1010 samples. For the HDPE, slight increase was observed, but when the EB-irradiation dose increased above certain threshold, modulus values declined, which was likely due to excessive crosslinking disturbing the crystallization, chain scissioning and other types of irradiation damage

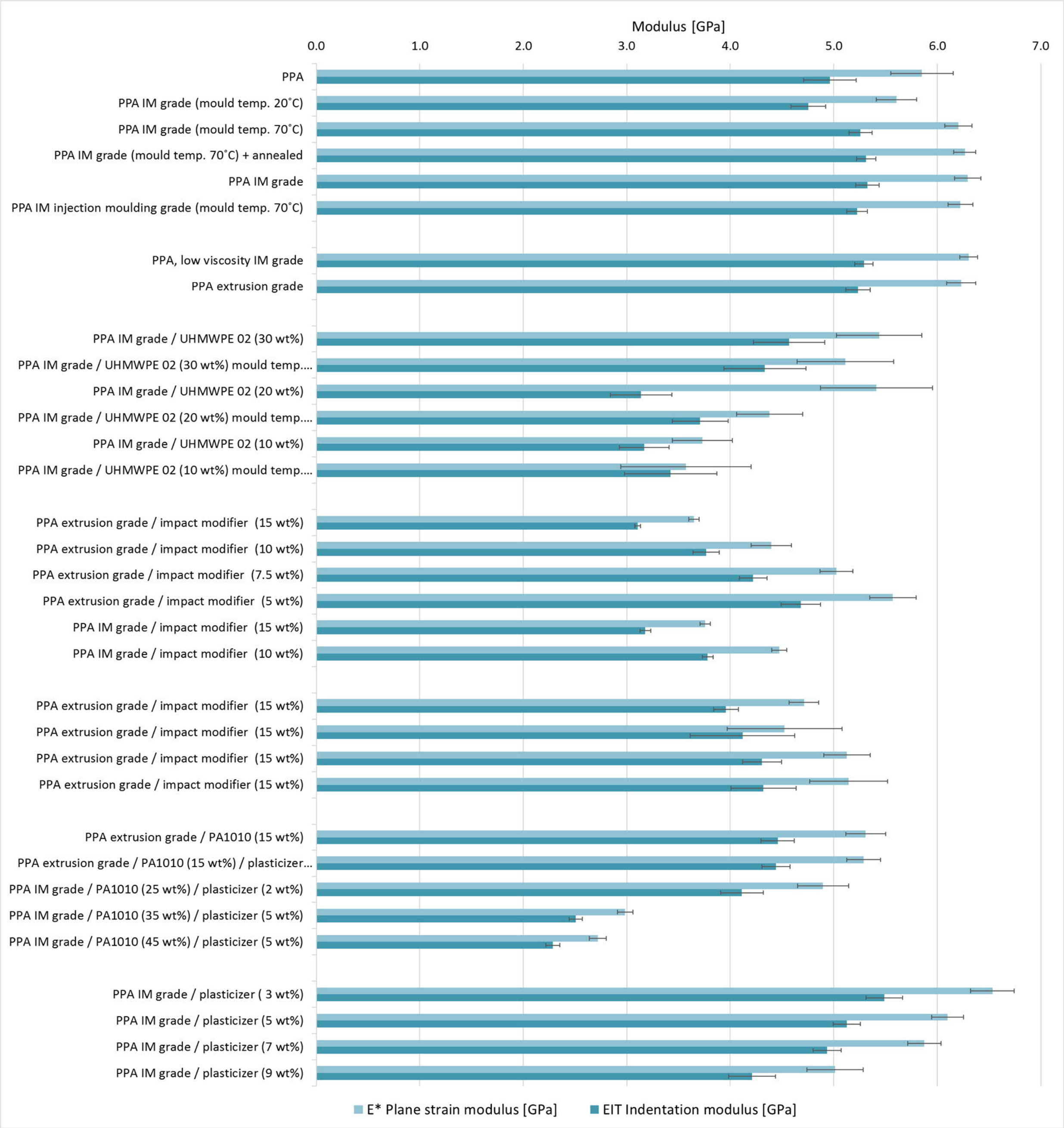


Figure 12. The Plain strain modulus E and the Indentation modulus EIT of semi-aromatic polyamides.*

5.3 Tensile and impact properties

Examples of the tensile test data for selected polymers are summarized in Table 4. It can be clearly seen from the tensile test data that the materials have quite different stiffness and ductility. Note that the semi-aromatic polyamide without any toughening additives is a very brittle material. Moreover, HDPE and the polyethylene compounds, with the exception of the one compound filled with 25 wt% ultrafine calcium carbonate (UFPCC) filler, were all ductile and have low Young's moduli ranging from 0.6 GPa to 1.1 GPa (strain rate 1 mm/min), for the unfilled/nano-filled or reinforced materials, respectively.

Notched Charpy impact strength values measured in room temperature for the selected samples are shown in Table 4. The corresponding room temperature tensile strength and E-moduli and the abrasive wear volumes at 19N and 45N test condition are reported on the other columns. Note that the selected samples do not present the highest attained wear resistances but rather demonstrate the correlations between the mechanical properties and wear resistance. Measurement done at VTT from injection moulded test samples are given with the standard deviations. In the tensile tests, the E-moduli was determined at strain rate 1 mm/min, tensile stress at 5 mm/min. Values in parentheses are from material datasheets, and likely present a slightly different test conditions, e.g. higher strain rates. Typically, very high Young´s modulus correlates with high abrasive wear resistance, particularly at the lower 19N load and in some cases at the higher 45N loading level. However, it is also associated with very low Notched Charpy Impact strength. This finding was the motivation for searching ways to toughen the stiff polymers.

Table 4. Notched Charpy impact strength, Young's moduli, tensile strength and their correlation with the abrasive wear volume (19N and 45 N load) of neat polymers and selected DURPOL compounds.

	Notched Charpy Impact Strength [kJ/m]	Young's modulus [GPa] *	Tensile strength [MPa]	Wear volume [mm^3]	
				19N	45N
Semi-aromatic PA 01	1.4 ± 0.2	- (4.7)	- (99)	13.8	52.0
Semi-aromatic PA 02	1.6 ± 0.2	4.4 ± 0.5 (4.7)	- (99)	13.6	45.3
PEEK	4.2 ± 0.2	3.6 ± 0.2 (4.0)	94.4 ± 0.3 (98)	19.9	37.2
PGA	2.0 ± 0.5 (2.2)	- (7.6. flex mod.)	- (117)	25.4	25.2
PA1010	4.6 ± 0.4	1.3 ± 0.02 (1.7)	45.7 ± 0.2 (54)	17.0	24.7
HDPE	113 ± 2 (P)	0.69 ± 0.08 (n.a.)	24.3 ± 0.7 (22)	19.7	34.1
Selected DURPOL compounds (1 mm/min strain rate for the E-modulus)					
PA1010 /GB (20 %)	2.8 ± 0.5	- 2.3 (DMA)	-	16.5	30.1
UHMWPE/HDPE/GO(0.5 %)	80 ± 20 (P)	0.62 ± 0.05	22.9 ± 1.6	16.2	26.8
UHMWPE/HDPE/SiO_2(5.8%)	-	0.72 ± 0.04	21.2 ± 0.5	16.6	24.8
UHMWPE/HDPE/GO	79 ± 22 (P)	0.38 ± 0.04	20.9 ± 1.7	17.1	23.3
UHMWPE/HDPE/GF(15%) /GO	40 ± 6 (H)	1.03 ± 0.02	25.2 ± 1.5	26.1	36.5
UHMWPE/HDP/UFPCC(25%)	54 ± 12 (H)	1.01 ± 0.01	21.6 ± 0.9	21.0	33.9
UHMWPE/HDPE/GF(15%)	48 ± 16 (H)	0.83 ± 0.07	24.5 ± 1.7	20.8	29.5
H = hinge, incomplete break. thin surface hinge which has no residual stiffness P = partial break, an incomplete break which is not hinge break NB = no break, specimen only bent through the support block. possibly stress whitening					

Different additives were used for modification of semi-aromatic polyamide and many polymeric additives were found to enhance the Charpy impact strength. Particularly effective additive was found which increased the impact strength by roughly 400% at 15 wt% loading. Unfortunately, the wear resistance of the toughened material was typically much reduced. N-Ethyl toluene sulfonamide was the only additive having little or no negative effect on the wear resistance of semi-aromatic polyamide.

However, it is noteworthy that the abrasive wear resistance of many of the developed DURPOL compounds was better than the commercial toughened materials. Also, the heat treatment (@130 ºC for 1 hour) showed the influence on impact strength of semi-aromatic polyamide.

6. Abrasive wear of polymers

6.1 Abrasive wear of selected commercial polymers

The test samples were injection moulded from selected commercial polymers. The sand abrasion tests for the commercial polymers were carried out with sand abrasion tests with two different loading levels. The results are presented in Figure 13.

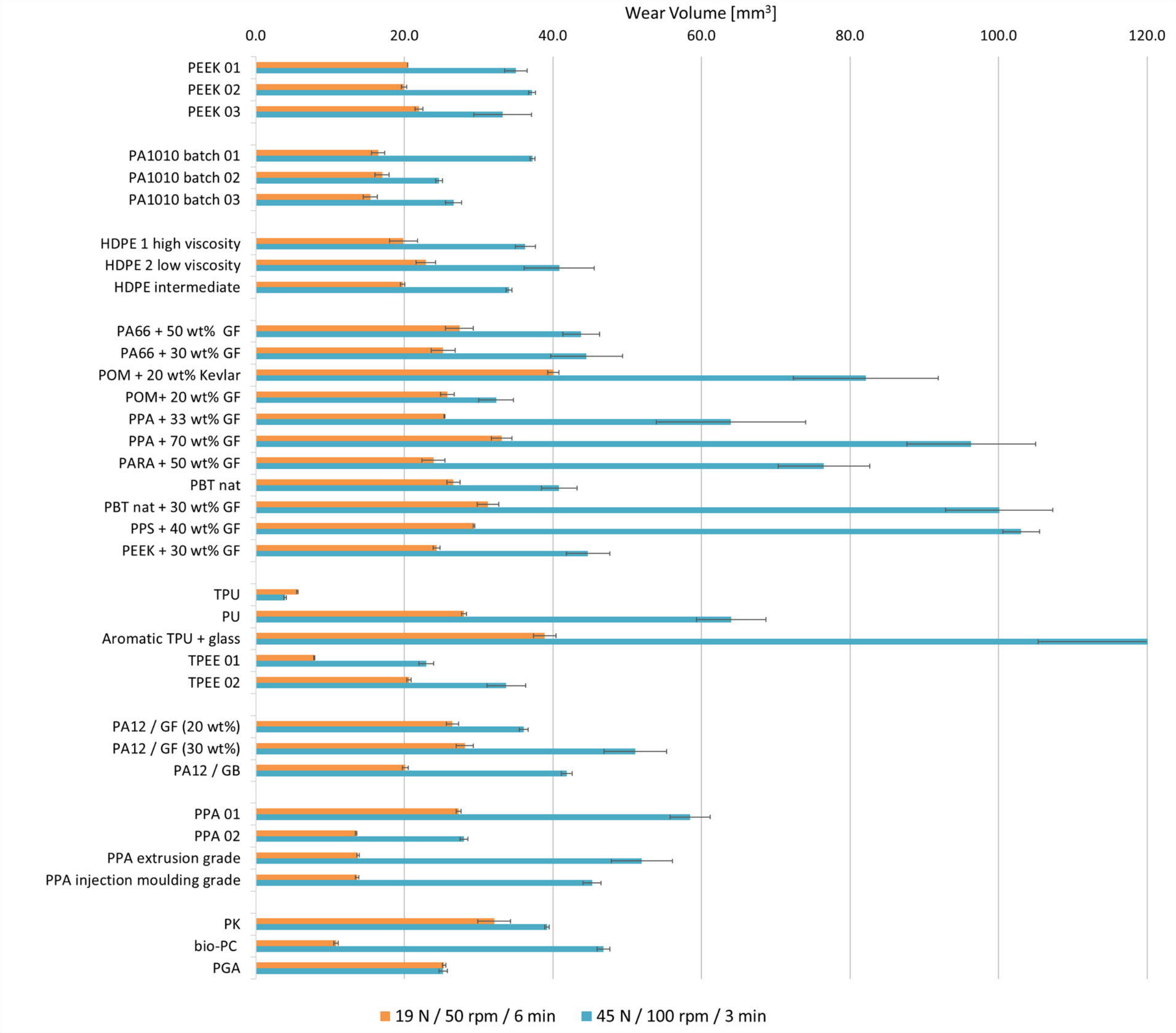


Figure 13. Abrasive wear volumes of commercial polymers tested using (i) 45 N load, 100 rpm speed, and 3 minutes duration (indicated by blue bars) or (ii) with 19 N load, 50 rpm speed, and 6 minutes duration (orange bars).

The abrasive wear of different PEEK grades was on similar level, at about 20 mm^3 wear volume with the lower load level, and slightly below 40 mm^3 wear volume with the higher load level. These values of PEEK polymer were considered as reference values for the developed polymers. The abrasive wear of PA1010 was slightly less compared to PEEK and different grades of HDPE showed similar or slightly higher values to PEEK. In general, the lowest wear was measured for the soft TPUs. However, in contrast, some filled grades, e.g. with glass fibers, experienced significantly higher wear. Different grades of semi-aromatic polyamide had low wear rates in low load tests, but high loading level typically increased the wear above the reference level. The high modulus PGA polymer had particularly interesting behaviour in the wear test, showing similar wear with both load levels.

The microscopic studies revealed that PEEK experienced slightly deformed surface layer with some micro-scratching and sand particles embedded on the surface even after the low loading level tests. With the higher loading level the wear surface showed signs of ploughing and deformation of the wear surface increasing the wear. The PA1010 experienced micro-ploughing, some micro-scratching, and slight deformation of the surface during tests carried out with the lighter load conditions. There were also pits generated on the surface due to removal of detached material. The wear mechanism of PA1010 in the higher load tests was predominantly ploughing with heavier deformation of the surface compered to light load tests. HDPE 1 high viscosity grade experienced repeated micro-ploughing and scratching of the surface already in the light load tests, and with the higher load level tests, heavy ploughing with deformation of the surface was observed. The wear of these three polymers was on a similar level, PA1010 showing lowest wear, even though the wear mechanisms seem to differ, as well as the modulus and indentation hardness, PEEK having the highest modulus and hardness, followed by PA1010, and HDPE with the lowest values. A bio-based polycarbonate (bio-PC) resin differs in wear mechanisms showing scratched appearance with pits on the surface due to material removal. The wear surface in the high load level tests shows even more clear scratch formations with clear scratch grooves. The bio-PC has modulus and indentation hardness values lower than PEEK but higher than PA1010.

6.2 Abrasive wear of thermoplastic elastomers

The TPU-based test samples were injection moulded for the tests. The sand abrasion tests for the TPU-based polymers were carried out with sand abrasion tests using two different loading levels.

There is a clear correlation between the Shore Hardness and the wear rates. The soft TPU has very low wear in the sand abrasion test, probably owing the materials capacity for large elastic deformation under the abrading sand particles. To shed light to this correlation, two polyester elastomers with flexular modulus of 0.2 GPa and 0.8 GPa were studied, the latter being amongst the stiffest thermoplastic elastomers available. Their abrasive wear is lower than for the rigid plastics (e.g. PA1010), however, significantly more that the wear of the soft TPUs. An attempt was made to generate synergistic composition combining the low abrasive wear and higher elastic modulus by blending the soft TPU with 20-80% PA1010 or 10-30% glass microbeads (GP). The most satisfactory low wear rates were found for the blend composition of 20% PA1010 in TPU. The indentation modulus of the material was increased to 0.61 GPa (+69%), which is comparable to the addition of 30% glass beads into the same TPU. However, the addition of glass beads in TPU is not favoured, since the glass addition increased abrasive wear, particularly in high load level tests.

The wear surface of commercial high modulus TPU and TPU (80 wt%) + PA1010 (20 wt%) both have ridge formations (perpendicular to the direction of sliding) on the surface after low load tests, caused by the elastic performance of the material. However, this feature was not as clear as for the softer TPUs. With high magnification in SEM, features of reinforcement particles could be observed on the wear surface of commercial high modulus TPU. The TPU+PA-composite also has similar pit formations on the surface as PA1010. In the high load tests both materials showed coarse appearance with some scratches (along the direction of sliding), and sand particles embedded on the wear surface.

6.3 Abrasive wear of polyamide compounds

6.3.1 PA1010 compounds

Addition of small concentration 0.5 wt% to 0.65 wt% graphene oxide nanoplatelets (GO) and graphite nanoplatelets (GNP) with aminosilane seemed to enhance the abrasive wear resistance of PA1010 slightly, while more addition lead to increased wear as seen in followingFigure 14. At this low level of addition, these carbon nanomaterials had negligible effect of the surface indentation hardness or plane strain modulus of the PA1010. It is noteworthy that the dispersion of the carbon nanopowders in PA1010 was not optimal without the addition of wax dispersion aid during compounding. However, the dispersion additives are in fact detrimental to the abrasive wear resistance.

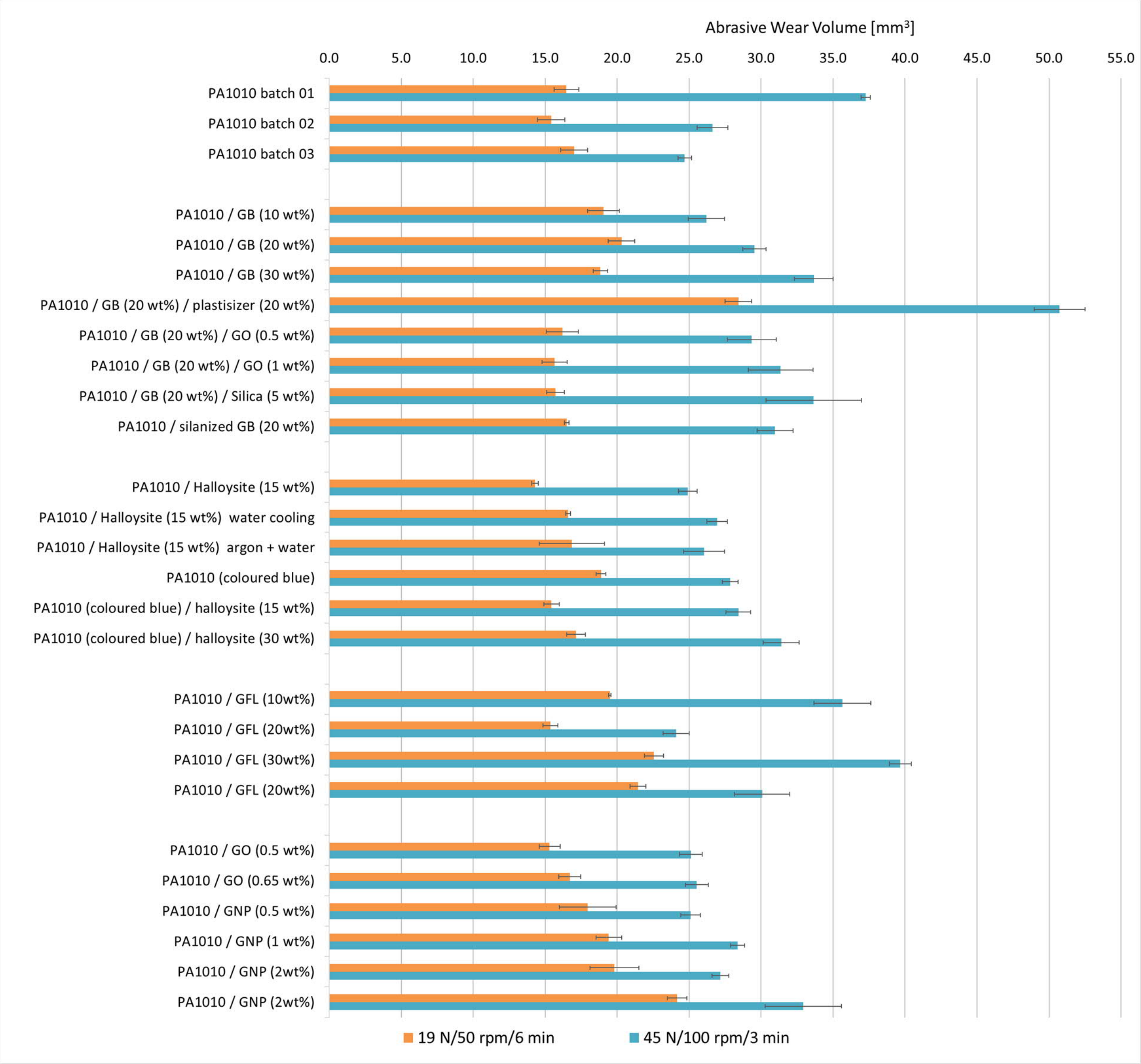


Figure 14. The abrasive wear volumes of PA1010 compounds in tests carried out with low load level (19 N load, 50 rpm speed, and 6 minutes duration), and in tests with high load level (45 N load, 100 rpm speed, and 3 minutes duration).

Moreover, dependent on the processing methods and the applied process parameter, the reference level (pure PA1010) showed great variance (more than 20%) in the wear resistance at the 45N load level. The abrasive wear resistance is likely in correlation with the surface indentation hardness of the polymer, and hence the degree of crystallinity and the surface crystallite (spherulite) size. This behaviour is typical to polyamides in general, showing variance in the crystalline morphologies upon different cooling rates from the melt. The evolution of the crystalline (meso) phases in injection-moulded specimen was verified by DSC analyses of PA1010. Based on microstructural characterization, it can deduced that nanopowders are potentially very effective in beneficially “homogenizing” the crystal morphology of the semi-crystalline polymer, which, in turn, makes the abrasive wear performance less dependent on the thermal history of the IM parts.

As described previously, PA1010 experienced micro-ploughing, some micro-scratching, and slight deformation of the surface during tests carried out with the light load conditions. PA1010+HNT composite also experienced micro-scratching and micro-ploughing mechanisms. On the surface, pits were formed due to detached worn material and some of the pits could have been caused by sand abrasives embedded in the matrix during the test, which were removed afterwards. Clearly, the wear mechanism at the higher loading is different, as the both materials experienced heavy ploughing and deformation of the wear surface, possibly due to surface melting. The PA+glassflake -composite showed similar wear mechanisms, with the exception of glass flakes protruding from the worn surface, particularly in low load tests. PA+GO composite showed higher degree of ploughing and surface deformation with both load levels compared to previous materials.

6.3.2 Glass fibre reinforced polyamide PA12 compounds

The glass fibre reinforced version of polyamide experiences heavy scratching and ploughing particularly in high load tests. Pullouts of glass fibres occurred increasing the wear of the polymer as described by the wear volume results. Polyamide with glass beads shows somewhat less ploughing and deformation of the surface. In addition, in this case the glass beads can be observed partially worn on the surface or detached from the surface leaving a round mark on the surface.

6.3.3 Toughened semi-aromatic polyamide compounds

In general, the most of the studied toughening additives tend to increase the wear of semi-aromatic polyamide, particularly at the higher loading conditions. One exception is the sulphonamide, that retained the wear resistance at loadings in the 3-5 wt% range, while still an significant 100% increase in impact strength of the semi-aromatic polyamide was measured. Regarding the abrasive wear and the impact resistance, a synergistic blend composition range of semi-aromatic polyamide with PA1010 and sulphonamide was found. The semi-aromatic polyamide and PA1010 formed an immiscible blend where the PA1010 formed a 2-4 µm dispersed phase in semi-aromatic polyamide matrix. The intermittent contact mode AFM images in Figure 15 shows clearly the blend morphology

Semi-aromatic polyamide commercial grades showed some signs of scratching wear, but mostly the material was removed by fracture caused by repeated loading, even in the tests with low load level. In the high loading tests, wide shallow grooves were observed on the wear surface. The wear mechanism was mostly cutting with some deep groove formations. Semi-aromatic polyamide with addition of toughening agent showed fractured surface with deep pits where material was removed, these features were visible particularly in high load tests. These are likely due to the removal of the soft and poorly adhering addition agent, which is in the form of small droplets in the matrix of semi-aromatic polyamide. The addition of PA1010 into semi-aromatic polyamide changed slightly the wear mechanisms of the compound, since besides fracture and cutting wear, the material also experienced local ploughing with polymer deformation. Semi-aromatic polyamide with plasticizer addition showed slightly grooved surface with signs of material removal by fatigue. In the high load tests the surface of the polymer was heavily embedded by sand particles, and also presenting crack generation on the wear surface.

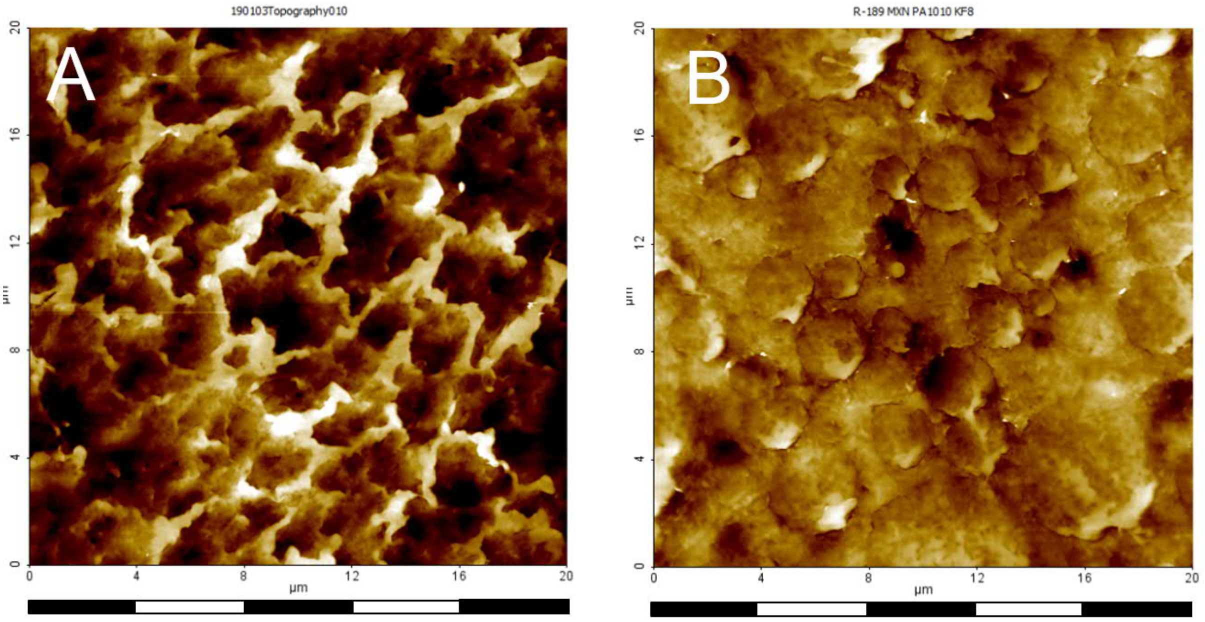


Figure 15. Intermittent contact mode AFM topography image of A) polished surface of semi-aromatic polyamide and B) semi-aromatic polyamide blended with 45% PA1010 and 5% sulphonamide. XY-scale bar 20 µm. Z-scale 100 nm.

6.4 Abrasive wear of polyethylene compounds

The abrasive wear volumes of PE based compounds are presented in Figure 16. According to the material data information, the UHMWPEs have even lower wear, but comparable data for these polymers could not be recorded in DURPOL project because it is generally not possible to process these polymers by injection moulding.

Blending UHMWPE and HDPE offer an attractive route to more processable materials, which have the lowest wear rates of all the studied samples during the DURPOL project. The wear volume of the best UHMWPE/HDPE blends and their nanocomposites generated in project is roughly 50% of the wear volume of the PEEK at 45N sand abrasion test.

The UHMWPE/HDPE blend system is inherently immiscible and these polymers do not normally mix in the melt state. Hence, a compatibilizer was added, which seemingly improve the compatibility between polyethylenes. However, the blend system has quite low E-modulus (<0.8 GPa) and indentation modulus of 0.9-1.2 GPa. The modulus can be marginally increased by the addition of nanofillers. Further increase in the E-modulus was possible by the addition of substantial amounts (10-30 wt%) of 1µm thick glass flakes. The addition of glass flakes reduced the achievable loading of the UHMWPE in the recipe. As anticipated, combined the addition of rigid micro-fillers and the lower amount of UHMWPE consistently increased the wear. However, this negative effect can be limited to roughly -30% (at 45N load level) by the special surface treatment of the glass flakes. At the optimum composition of the 15 wt% glass flake reinforced UHMWPE/HDPE blend the wear resistance of the material is still superior compared to the reference PEEK and the reference HDPE polymers, and in fact, comparable to the PA1010 composites.

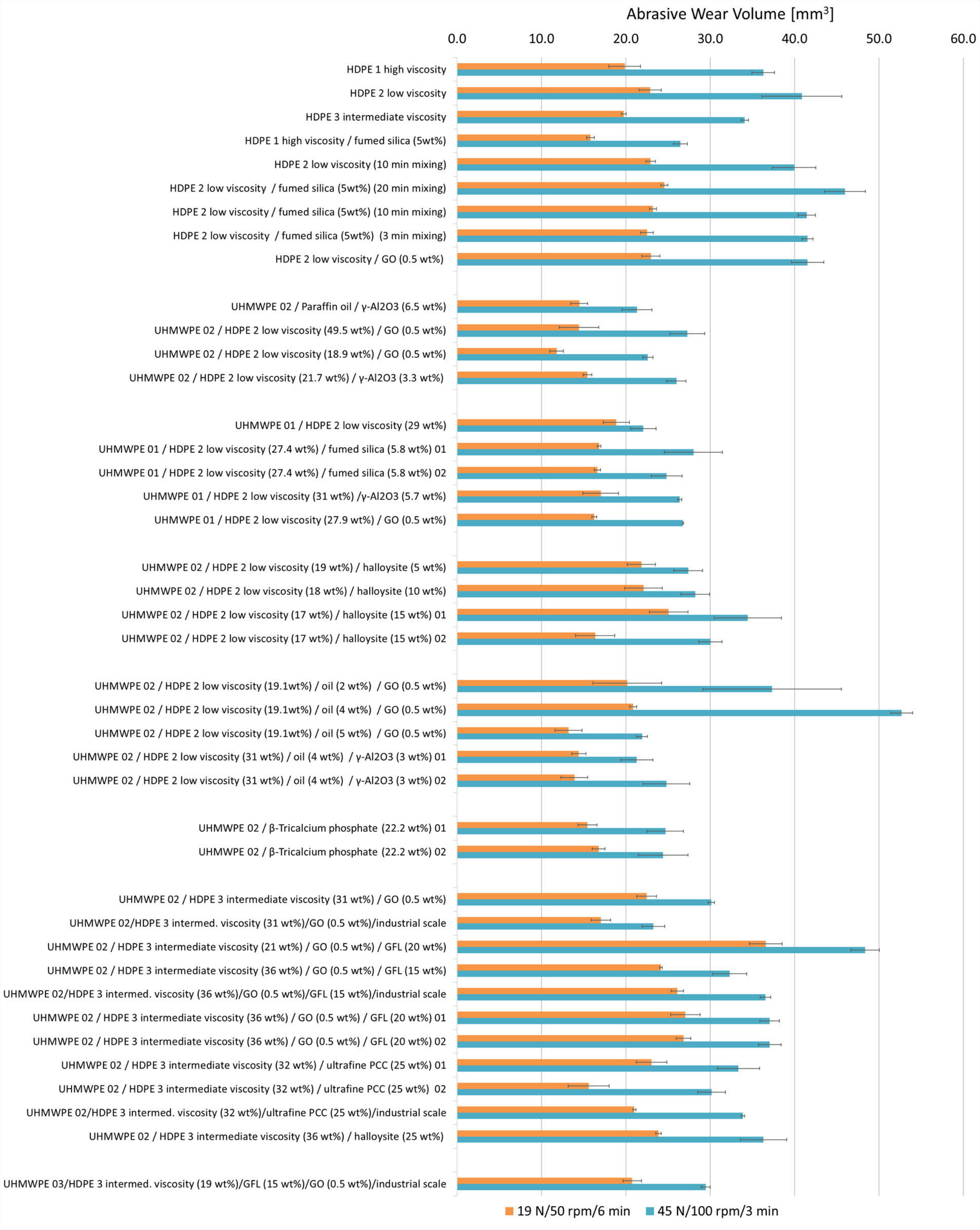


Figure 16. The abrasive wear volumes of PE-based compounds in tests carried out with low load level (19 N load, 50 rpm speed, and 6 minutes duration), and in tests with high load level (45 N load, 100 rpm speed, and 3 minutes duration).

The wear mechanisms of PE-composites were similar, micro-ploughing and deformation of polymer being the dominating mechanisms. Also, the PE-compounds compounded at industrial scale behaved in similar way, except the UHMWPE/HDPE/GO/GF compounds, since the wear surfaces showed that the UHMWPE and HMW/HDPE were not optimally mixed.

6.5 Abrasive wear of EB cross-linked polymers

The abrasive wear volumes of EB cross-linked polymers were compared against their references at three different power levels. The treatments were carried out for HDPE, UHMWPE/HDPE blend, and UHMWPE/HDPE/γ-alumina blend. The results showed that compared to untreated injection moulded samples, EB cross-linking typically increased slightly the abrasive wear of polymers. The only exception was UHMWPE/HDPE -compound that was lower wear in low load level tests with the lowest irradiation dose.

UHMWPE/HDPE/fumed silica, UHMWPE/HDPE/GNP, HDPE/GNP, PA1010- and PA1010 + silanised GB composites with similar irradiation dose were compared against their untreated versions for abrasion resistance. The results were similar also for these polymers, the EB cross-linking was slightly increasing the abrasive wear of materials compared to untreated references.

The wear surfaces of these EB cross-linked compounds clearly show that the wear mechanisms differ from the mechanisms seen in the same materials in untreated injection moulded state. In all cases, the wear mechanisms of EB treated materials seemed to be less ductile showing combination of deformation and fracture.

6.6 Up-scaling of polymer compounding

Up-scaling of compounding was carried out at industrial scale using a twin screw extruder using a low mixing screw configuration and short residence time in the extruder. To achieve good dispersion the sample reinforced with UF-PCC or glass flakes were compounded twice. The results in Figure 17 shows that the samples generated in the up-scaling trials were comparable to the samples generated in the laboratory scale. All of these test materials were sent to the application tests at the industrial partners.

The PE-compounds compounded at industrial scale behaved in similar way compared to materials compounded at VTT, showing micro-ploughing and deformation of polymer surface as the dominating mechanisms. One exception was that the wear surface of UHMWPE/HDPE/GO/GF blend showed that the UHMWPE and HDPE were not properly mixed.

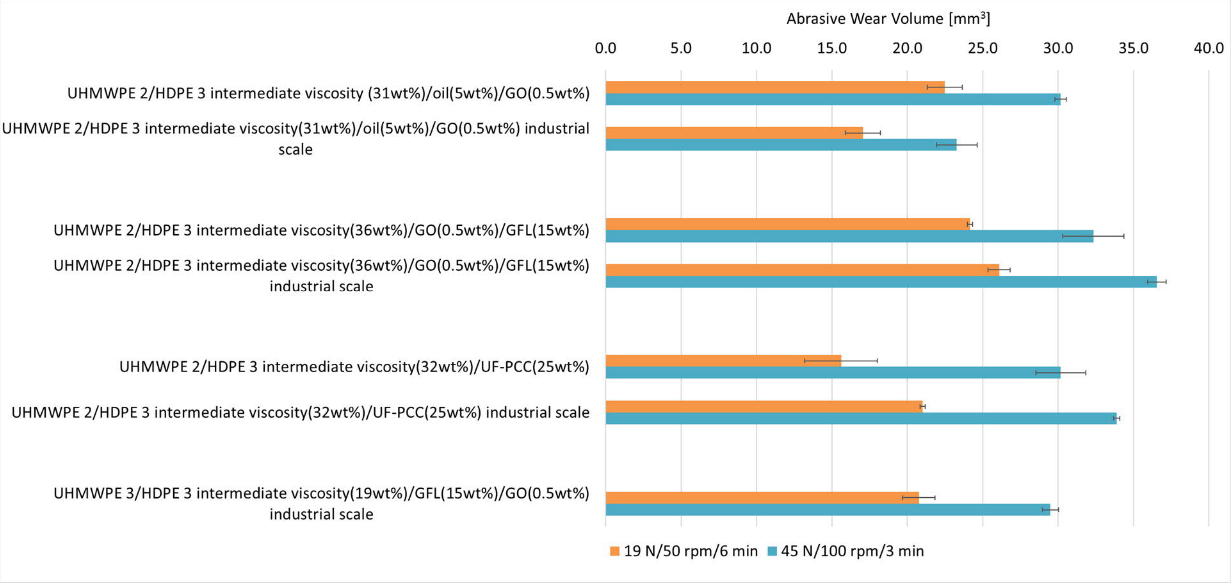


Figure 17. The abrasive wear volumes of up-scaled materials and their references in tests carried out with low load level (19 N load, 50 rpm speed, and 6 minutes duration), and in tests with high load level (45 N load, 100 rpm speed, and 3 minutes duration).

7. Scratch resistance and tear strength of polymers

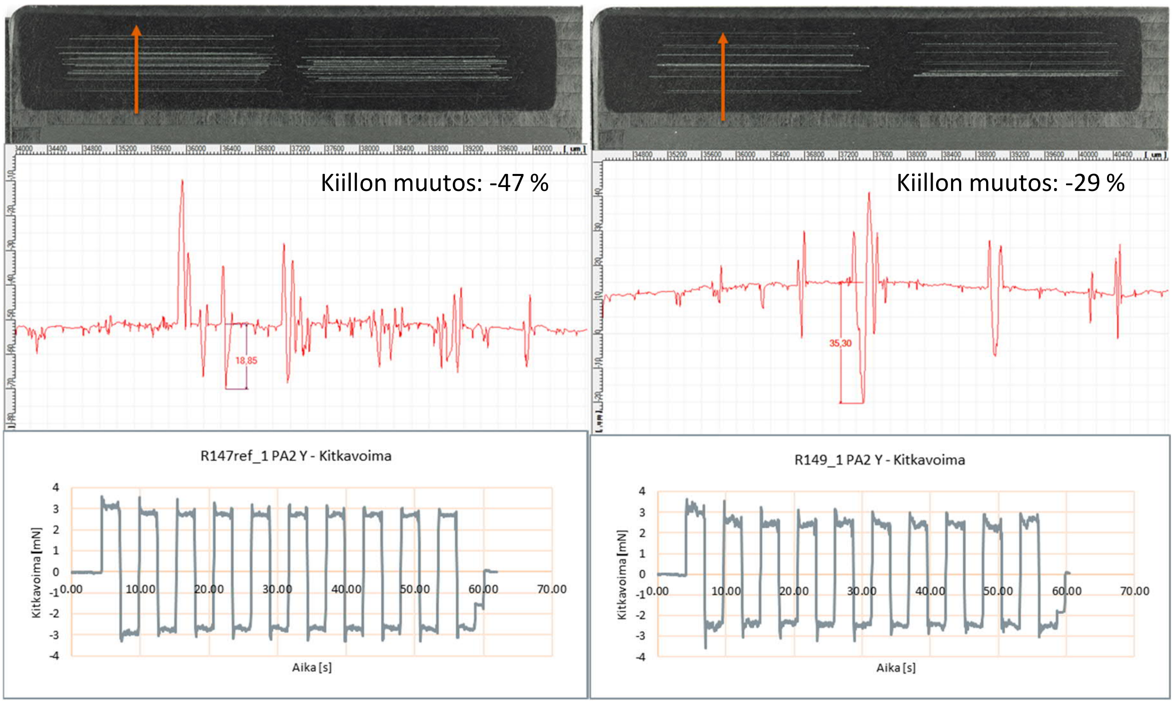
7.1 Scratch resistance of polyamides

Scratch resistance was evaluated by measuring the gloss change of the surface due to scratch testing. The gloss measurements were carried out prior and after the scratch testing and the change in gloss is presented in percentage values. The results for the glass fibre reinforced PA12 polymers, PA1010 and semi-aromatic polyamide compounds were measured on smooth surface, which was injection-moulded with the polished mould surface (PA2). The trends observed with the polished surfaces were similar also for the other surface textures.

Several additives were investigated with the polymer and some of them were found to increase scratch resistance of PA12 polymers. The addition of small amount of anti-scratching agent and the addition of glass beads gave the best results. Moreover, some other fillers and additives provided some improvement in scratch resistance, but the effect was not statistically significant. Figure 18 shows the surfaces of PA12-GF30 black sample, and PA12-GF30 black with anti-scratching agent performing well after scratch test. The 2D profile taken across the worn surface shows the higher amount of scratches on the surface of PA12-GF30 black compared to sample with anti-scratching agent. Also, the friction force measured during the test was higher for PA12-GF30 black.

Clearly, the antiscratching additives had a negative effect in PA12 matrix polymer. One interesting finding was that adding the black masterbatch into PA12 during compounding, provided better scratch resistance compared to commercial black PA12 polymer. In addition, the replacement of glass fibres with glass beads completely or partly, provided better scratch resistance.

The scratch resistance of PA1010 polymer was slightly improved by glass beads, but the electron beam cross-linking of PA1010 did not have a clear effect on scratch resistance. Semi-aromatic polyamide provided also reasonable scratch resistance.



(a) (b)

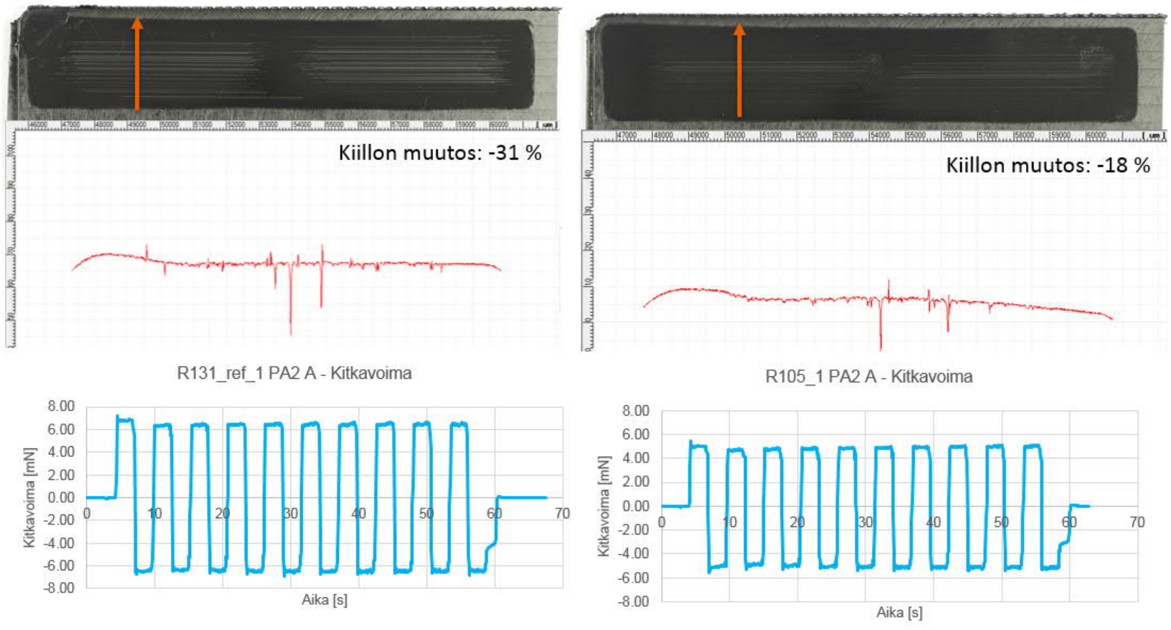
Figure 18. Image of the scratched surface, 2D profile across the scratches, and the friction force measured during the tests of (a) PA12-GF30 black sample, and (b) PA12-GF30 black with anti-scratching agent.

7.2 Scratch resistance and tear strength of TPU-based polymers

7.2.1 Scratch resistance

Scratch resistance was evaluated by measuring the gloss change also for the TPU samples. Scratch resistance of TPU was found to improve by the additives: oil and high molecular weight polysiloxane copolymer. The common nominator for these additives is that they both are mobile molecular additives, which potentially migrate to the very surface of the TPU material. Figure 19 shows the surfaces of TPU and TPU with high molecular weight polysiloxane copolymer, after the scratching test. The pictures of the worn surfaces show clearly the difference of the two surfaces, the surface with high molecular weight polysiloxane copolymer additions showing fewer and less visible scratches compared to neat TPU material. In addition, the friction force is lower for the TPU with high molecular weight polysiloxane copolymer addition. The results showed the correlation of scratch resistance with the hardness of the TPUs.

According to the preliminary experiments electron beam crosslinking with cross-linking agent did not improve the scratch resistance. The cross-linked TPU-samples had in fact slightly lower hardness (Shore A75-76) as compared to the non-crosslinked reference (ShA 78-79). Moreover, upon the EB cross-linking, the tear strength of the TPU had reduced roughly by 5%.



(a) (b)

Figure 19. The picture of the scratched surface, 2D profile across the scratches, and the friction force measured during the tests of (a) TPU, and (b) TPU with addition of high molecular weight polysiloxane copolymer.

7.2.2 Tear strength and hardness of TPU-based polymers

The results of tear strength tests showed that the effect of fillers and additives depends on the type of the TPU matrix. The tear strength of TPU (01) filled with silanized hemp fibres was improved significantly by hemp and cellulose microfiber loading. The addition of hemp fibre to TPU increased the tear strength values 70 to 100% and the hardness increased up to about 80 Shore A, as shown in Figure 20.

With the cellulose fibre filler it was possible to increase the tear strength by 20 to 60 % for different compounds and the hardness was slightly under 70 Shore A. Polyester and polyamide fibres also increased the hardness in the case of this TPU grade, but they had less significant effect to the tear strength compared to hemp and cellulose fibres. High molecular weight polysiloxane copolymer additive was also added into this compound to improve the scratch resistance.

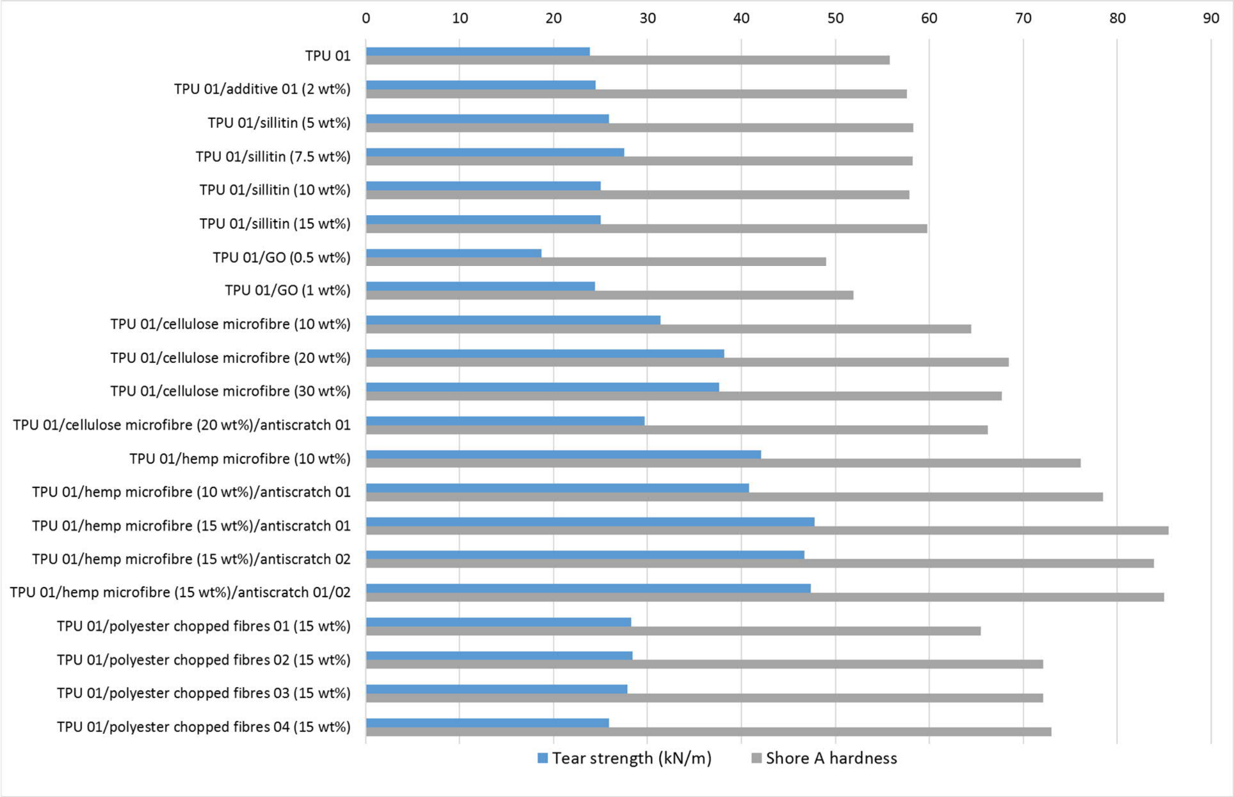


Figure 20. Tear strength and Shore A hardness of the TPU batch 01 compounds and reference samples.

In the TPU matrix of batch 02, the tear strength was increased by about 30 % with 10 wt% addition of hemp fibre (
Figure 21). The hardness was also increased of these compound up to about 80 to 85 Shore A. The compound with the high molecular weight polysiloxane copolymer antiscratch additive provided slightly lower values. The addition of antiscratch additives into TPU grade did not change the tear strength nor the hardness. Nanoclay and Sillitin were found to decreased the tear strength of TPU compounds.

Figure 22 shows the tear strength and Shore A hardness of the TPU batch 03. The antiscratch additives did not change the tear strength and hardness of TPU but nanoclay decreased the tear strength.

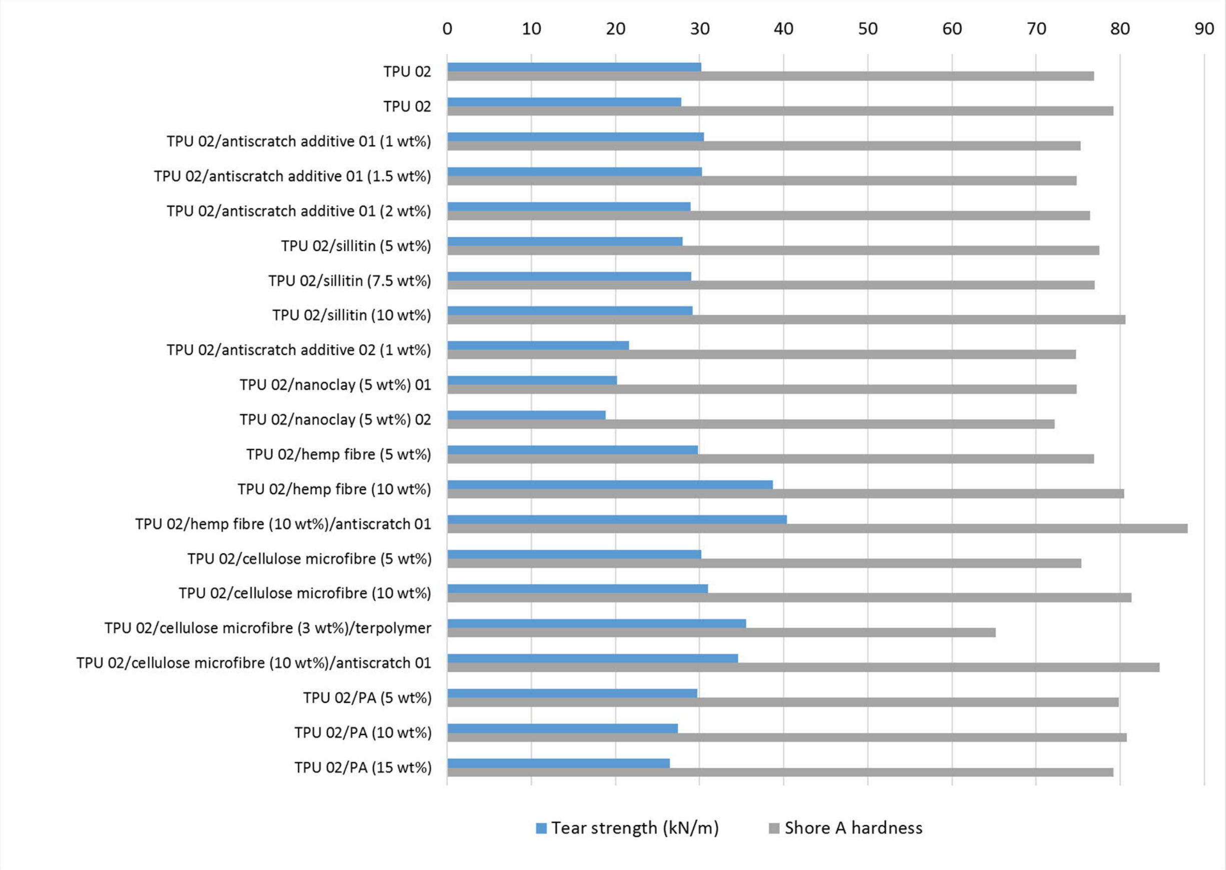


Figure 21. Tear strength and Shore A hardness of the TPU batch 02 compounds and reference samples.

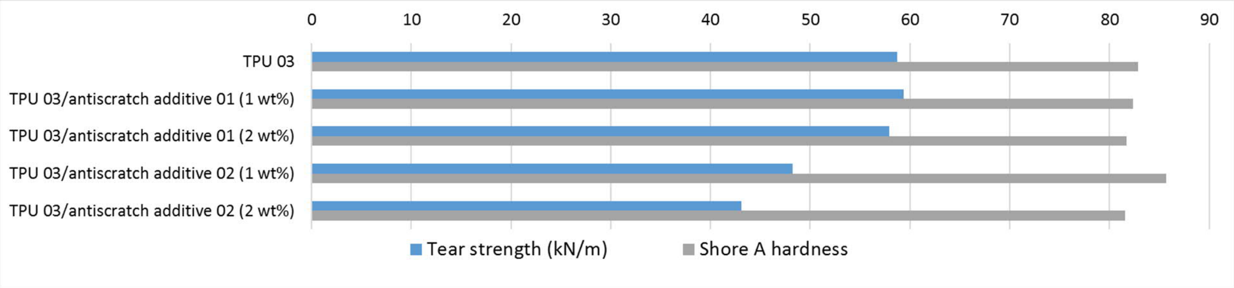


Figure 22. Tear strength and Shore A hardness of the TPU batch 03 with antiscratch additive and reference sample.

8. Discussion

DURPOL project had two different directions in the development of polymers, one being the development of abrasive wear and scratch resistant hard polymers that would have reasonable modulus for demanding applications. The other direction was to develop the tear strength and scratch resistance of TPU compounds. In both cases, also the cost of materials was one criteria that was taken into account. E.g. for applications requiring wear resistance, PEEK polymer shows good combination of wear resistance and high modulus. However, the price of PEEK is extremely high, which restricts the use of the material in many applications. One target in polymer development was also to develop hard, wear resistant polymer compounds that can be processed with injection moulding technique, which is well suited for mass production and capable to produce products with complex shapes. Figure 23 describes the different objectives related to development of abrasive wear resistant polymers for demanding applications.

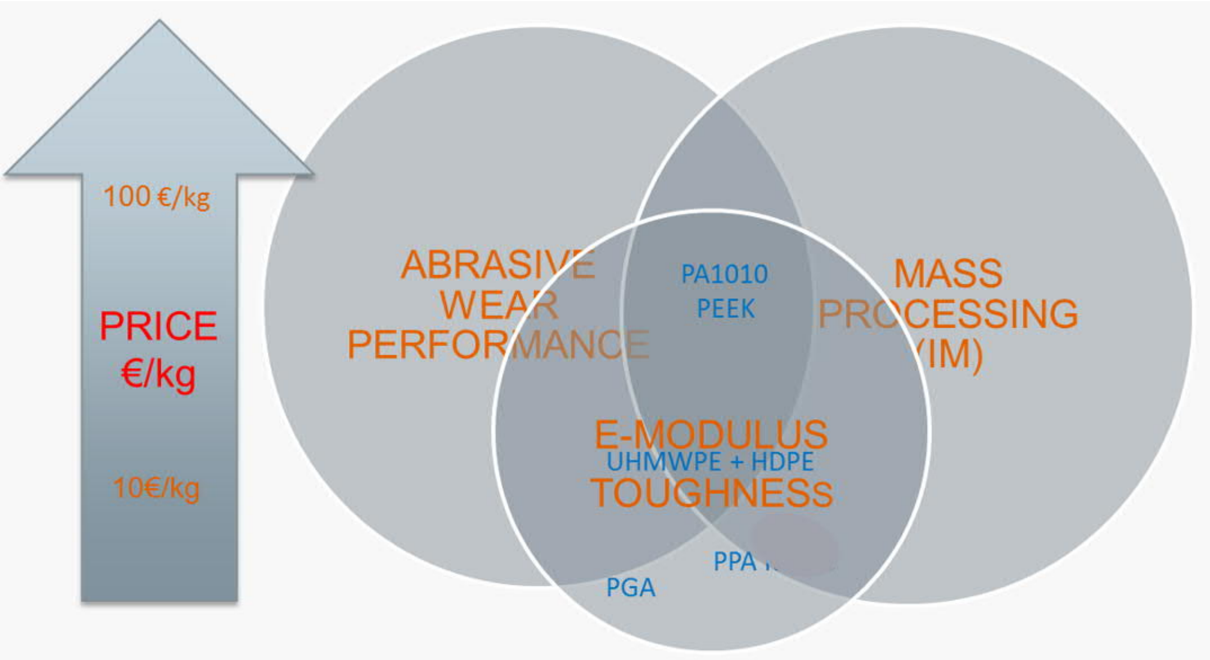


Figure 23. The different aspects related to polymer development for abrasive wear applications in DURPOL project.

In the application cases where the material has no special requirements for strength or stiffness, the lowest wear can be gained with the soft elastomers (e.g. TPU). However, when the TPUs were modified e.g. by preparing TPU-PA blends to increase the modulus, the wear of the developed material increased. Concerning the neat polymers, PA1010 exhibits lower wear compared to PEEK, and also HDPE is on a similar level in abrasive wear compared to PEEK, but the modulus of these polymers is clearly lower compared to PEEK, around 2 GPa and 1.2 GPa, respectively. The PA compounds were generated by using different fillers to improve the modulus of PA1010. Indentation modulus and tensile modulus of PA1010 was increased by electron beam crosslinking and by compounding with silanized fillers. Addition of silanized 15 wt% Glass flakes, 15 wt% Halloysite nanotubes increased the indentation modulus from the 1.9 GPa range to 2.3 GPa level while retaining the abrasive wear resistance of the PA1010 polymer. Crosslinking is known to improve significantly the mechanical properties of polyamides and their composites (PA66 and PA6) in elevated temperatures (up to > +100°C) and it is therefore highly recommended in applications where the temperature rises above the glass transition.

Semi-aromic polyamide polymer was also investigated in the project. The material has high modulus combined with reasonable wear resistance, but the polymer is brittle. The attempt was to toughen it by blending with UHMWPE or PA polymers. The lowest abrasive wear was achieved by PA soluble plasticizer additions in semi-aromatic polyamide.

For the PE polymer the development routes adopted was to make HDPE/UHMWPE blends. UHMWPE polymers typically have high wear resistance, but it is not possible to process them by injection moulding techniques. In DURPOL project, we succeeded in generating injection mouldable compatibilized UHMWPE/HDPE blends. In addition, different fillers were used in the blend to improve the performance on the blend. The UHMWPE/HDPE with fillers, such as γ-Al_2O_3, graphene oxide and fumed silica provided improved abrasive wear resistance, but the modulus was slightly reduced. Addition of glass flakes increased the modulus, but the wear performance remained on the same level as for HDPE. Increase of modulus was also achieved with ultrafine precipitated calcium carbonate (PCC), interestingly reducing also the abrasive wear.

Crosslinking of HDPE has been reported to improve the mechanical strength, elastic moduli, surface hardness at ambient temperature and to significantly reduce creep (and likely also hinder the stress relaxation), particularly at elevated temperatures, typically 80-100°C or even at higher temperatures, where the cross-linked HDPE retains some material integrity while the non-cross-linked material is already melted. The changes in the mechanical properties are typically dependent on the irradiation dose. Moreover, cross-linking has been reported to enhance the wear performance of UHMWPE. Therefore, it is anticipated that better retention of abrasive wear resistance and possibly somewhat higher modulus at elevated temperatures can be achieved by the electron beam crosslinking of UHMWPE/HDPE blend. In our preliminary studies with UHMWPE/HDPE blend with nanofillers, the cross-linking indeed raised the room temperature EIT indentation modulus by roughly 15%. The observed abrasive wear resistance measured at ambient room temperature was similar, and typically slightly worse compared to the non-cross-linked reference blend. This could be explained either by mild degradation by the irradiation, or by the higher structural modulus of the cross-linked material - indeed a similar effect was observed in the UHMWPE/HDPE blend with micron-sized fillers and having higher modulus. However, some of the preliminary results with the UHMWPE/HDPE nano-compound are encouraging enough to support irradiation cross-linking processing in the real industrial product development cases.

The selected polymers that were studied or developed in DURPOL project are collected in Table 5. As presented in the table, the properties of polymers have no direct correlation to abrasive wear, but the wear resistance is a combination of several material properties providing low abrasive wear performance for demanding applications.

As can be observed, several polymer composites had abrasive wear volumes below the reference values of 20 mm^3 (for low load level) and 40 mm^3 (for high load level). In addition, the modulus of the developed polymer composites was increased with selected fillers. These polymers with improved performance can be selected for different applications requiring abrasive wear resistance.

For the development of soft polymers with tear resistance and scratch resistance, the TPU composites with cellulose microfibre and hemp fibre reinforcements combined with the “soft touch” were developed. These new materials were processed without plasticizers using commercial mineral filler additives. The tear strength of soft TPUs was improved up to 95% by the addition of 10-15 wt% silanized hemp fibres and also significantly (53%) by the addition of 20 wt% silanized cellulose microfibres.

The scratch resistance of TPU was found to improve by the high molecular weight polysiloxane copolymer and specified oil as additives. The scratch resistance of hard polymer PA12-GF30 was increased by nano and micron sized fillers, the addition of small amount of anti-scratching agent and the addition of glass beads gave the best results.

The agent used for assisting the electron beam crosslinking was clearly not optimum for the TPU grade used in this study. However, according to literature and the crosslinking service provider, there exists also successful applications for electron beam crosslinking of TPU. Those applications usually require specialty crosslinkable TPU grades. However, according to the first experiences, more work on this field would be clearly worthwhile.

Table 5. The comparison of Notched Charpy Impact Strength, Young's Modulus, Tensile strength and abrasive wear values of selected polymers studied and developed in DURPOL project. The values in brackets represent the values received from the data sheets.

	Notched Charpy Impact Strength[kJ/m]	Young's modulus	Tensile strength	Wear volume	
		[GPa] *	[MPa]	[mm^3]	
				19N	45N
Semi-aromatic PA 01	1.4 ± 0.2	- (4.7)	- -99	13.8	52.0
Semi-aromatic PA 02	1.6 ± 0.2	4.4 ± 0.5 (4.7)	- -99	13.6	45.3
PEEK	4.2 ± 0.2	3.6 ± 0.2 (4.0)	94.4 ± 0.3 -98	19.9	37.2
PGA	2.0 ± 0.5 (2.2)	- (7.6. flex mod.)	- -117	25.4	25.2
PA1010	4.6 ± 0.4	1.3 ± 0.02 (1.7)	45.7 ± 0.2 -54	17.0	24.7
HDPE intermediate viscosity	113 ± 2 (P)	0.69 ± 0.08 (n.a.)	24.3 ± 0.7 -22	19.7	34.1
Selected DURPOL compounds (1 mm/min strain rate for the E-modulus)					
PA1010 /GB (20 %)	2.8 ± 0.5	- 2.3 (DMA)	-	16.5	30.1
UHMWPE/HDPE/GO(0.5 %)	80 ± 20 (P)	0.62 ± 0.05	22.9 ± 1.6	16.2	26.8
UHMWPE/HDPE/SiO_2(5.8%)	-	0.72 ± 0.04	21.2 ± 0.5	16.6	24.8
UHMWPE/HDPE/GO industrial scale	79 ± 22 (P)	0.38 ± 0.04	20.9 ± 1.7	17.1	23.3
UHMWPE/HDPE/GF(15%) /GO industrial scale	40 ± 6 (H)	1.03 ± 0.02	25.2 ± 1.5	26.1	36.5
UHMWPE/HDP/UFPCC(25%) industrial scale	54 ± 12 (H)	1.01 ± 0.01	21.6 ± 0.9	21.0	33.9
UHMWPE/HDPE/GF(15%) industrial scale	48 ± 16 (H)	0.83 ± 0.07	24.5 ± 1.7	20.8	29.5

9. Conclusions

The following conclusions can be made based on the research work carried out in DURPOL-project.

- UHMWPE/HDPE blends, PA1010 based nano- and microcomposites were formulated. Of the studied fillers, 15 wt% loading of silanized 1 µm GF was ideal in raising the tensile modulus of the UHMWPE/HDPE blend significantly. Abrasive wear resistance of the UHMWPE/HDPE composite materials outperformed PEEK. Electron beam crosslinking raised slightly the E-modulus and had a minor effect on the abrasive wear resistance.
- Indentation modulus and tensile modulus of PA1010 was significantly (+30%) increased by electron beam crosslinking and by compounding with silanized fillers. However, the cross-linked materials had higher abrasive wear.

- Toughening of semi-aromatic polyamide was achieved by blending with toughening agent and PA1010, or by the addition of soluble sulphonamide plasticizer. The high modulus was retained but the good abrasion resistance of the neat polymer was compromised.
- Tear strength of soft TPUs can be enhanced up to 95% by the addition of 10–15 wt% silanized hemp fibres and also significantly (53%) by the addition of 20 wt% silanized cellulose microfibres.
- Scratch resistance of PA12-GF30 was increased by nano and micron sized fillers and e-beam crosslinking.
- Scratch resistance of TPU was found to improve by the high molecular weight polysiloxane copolymer and specified oil as additive.
- PGA has quite a good wear resistance both in low and high loads in sand abrasion test.

10. Summary

The thermoplastic polymer compounds and polymer composites for enhanced abrasive wear resistance were based on commercially available polymers, compounded with micron-sized and nanosized fillers. PA1010, HDPE UHMWPE were used as base polymers in the DURPOL compounds. Thermoplastic polyurethane (TPU) compounds with enhanced tear and scratch resistance, and glass fibre reinforced polyamide 12 (PA12) were also developed for enhanced scratch resistance.

The abrasive wear resistance of polymers was evaluated by sand abrasion tests. The tests followed the standard ASTM 65-04 concerning the overall test setup, except the loading conditions were varied. The polymer wear was determined as the weight loss. For the scratch resistance evaluation, the reciprocating scratch testing was performed on VTT REC tester. The influence of the scratches on the appearance of the polymer surface was measured with a gloss meter and 2D profilometry. For evaluation of tear resistance of TPU materials, the specific test samples were processed by injection moulding and y stamping to specific form. The samples were tested according the ISO 34-1 standard (Method B). The polymers were also characterised by optical microscopy and SEM. The indentation measurements were used to determine the plane stain modulus, indentation modulus and indentation hardness. Atomic force microscopy, DSC and DMA analysis, tensile tests and Charpy tests were also carried out for selected samples.

In the application cases where the material has no special requirements for strength or stiffness, the lowest wear can be gained with the soft elastomers. However, when the TPUs were modified e.g. by preparing TPU/PA blends to increase the modulus, the wear of the developed material increased. Concerning the neat polymers, PA1010 exhibits lower wear compared to PEEK, and HDPE is on a similar level in abrasive wear, but the modulus of these polymers is clearly lower compared to PEEK, around 2 GPa and 1.2 GPa, respectively.

The PA compounds were developed by using different fillers to improve the modulus of PA1010. Addition of silanized 15 wt% Glass flakes, 15 wt% Halloysite nanotubes increased the indentation modulus from the 1.9 GPa range to 2.3 GPa level, while retaining the abrasive wear resistance of the PA1010 polymer. Indentation modulus and tensile modulus of PA1010 was also increased by electron beam crosslinking.

The semi-aromatic polyamide polymer was also studied in the project. The material has high modulus combined with reasonable wear resistance, but the polymer is brittle. It was toughened by blending with UHMWPE or with PA, providing similar or slightly higher level of wear compared to neat semi-aromic polyamide. The lowest abrasive wear was achieved by PA soluble plasticizer additions in semi-aromic polyamide.

For the polyethylene the development routes adopted was to make HDPE/UHMWPE blends. UHMWPE polymers typically have high wear resistance, but it is not possible to process them by injection moulding techniques. In DURPOL project, we succeeded in generating injection mouldable UHMWPE /HDPE blends with the addition compatibilizing agents. In addition, different fillers were used in the blend to improve the performance on the blend. The UHMWPE/HDPE with fillers, such as γ-Al_2O_3, graphene oxide and fumed silica provided improved abrasive wear resistance, but the modulus was slightly reduced. Addition of Glass Flakes increased the modulus, but the wear performance remained on the same level as for HDPE. Increase of modulus was also achieved with ultrafine precipitated calcium carbonate (PCC), interestingly reducing also the abrasive wear.

In our preliminary studies with UHMWPE/HDPE with nanofillers, the electron beam cross-linking raised the room temperature E_{IT} indentation modulus by roughly 15%. The observed abrasive wear resistance measured at ambient room temperature was similar, and typically slightly worse compared to the non-crosslinked reference blend. This could be explained either by mild degradation by the irradiation, or by the higher structural modulus of the cross-linked material, a similar effect was observed in the UHMWPE/HDPE blends with micron-sized fillers, and thereby having higher moduli.

For the development of soft polymers with tear resistance and scratch resistance, the TPU composites with cellulose microfibre and hemp fibre reinforcements combined with the “soft touch” were developed. These new materials were processed without TPU plasticizers.