innoTRAC Journal
Volume 2 (2022), pp. 25-44
https://doi.org/10.14464/innotrac.v2i1.514

Tribological and mechanical properties of lubricant filled microcapsules in thermoplastic composites

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Received 30 June 2022; Accepted 30 July 2022; Available online 15 December 2022

ABSTRACT Polymeric materials with long lifetime and low frictional energy loss are frequently required for a broad range of applications. Microencapsulation of lubricating oils by in-situ polymerization (melamine-formaldehyde) and interfacial polymerization (polyurethane/polyurea) was used to obtain free-flowing powders, which can be used as additive for thermoplastic materials resulting in microcapsule-containing self-lubricating composites. The specific functionality of such composites is achieved via portioned and localised release of the lubricant in the areas of the interface, which experiences the highest degrees of stress and wear due to the friction. Friction-triggered on-demand release of the lubricating oil results in materials with higher wear resistance and potentially leading to new products with prolonged lifetime. In this study, different ratios of microcapsules were added in polyoxymethylene (POM) and polybutylterephthalat (PBT) matrices by using laboratory scale twin-screw extruder resulting in self-lubricating composite materials. The effect of such modification on the tribological and mechanical properties of the thermoplastic composites were investigated. Rotational ball on disc tests were used to investigate the wear loss and coefficient of friction for the composites with varied microcapsule concentrations. Tensile tests revealed decreased mechanical stability for the composites with higher microcapsule content regardless of microcapsule wall material composition. Addition of 5 wt.- % of encapsulated lubricant oil led to the substantial decrease of the frictional and wear coefficients. Further increase of encapsulated lubricant oil content to 10 wt.-% had a major decreasing impact on the mechanical properties, whilst the effect on the tribological performance was rather small.

KEYWORDS plastic, oil-filled-microcapsules, self-lubrication, tribology, wear, compounding, thermoplastic compound, functionalized compounds, POM, PBT

1. Introduction

Polymers and their compounds are often modified with functional fillers or additives to tailor the material properties to specific needs of an application. Due to their low cost,

ease of processing and low density, polymers are widely used in engineering applications [1]. The use of plastics in tribologically stressed components is specifically limited, especially at high speeds or heavy duty. High frictional forces may exceed the thermal load capacity and result in high wear and short lifetime of the component [2]. Plastics usually offer sufficient friction properties under dry running conditions. Besides the modification of the material, surface and design can be adapted to reach a lower frictional loss [3]. To improve the tribological properties, solid or liquid lubricant materials can be added. Solid materials like carbon nanomaterials, nanosilica, MO_2 or PTFE can be embedded in the polymeric matrix [4–12]. Today, the market range of solid additives with tribological effects is quite limited. The effect of friction reduction of solid materials is always lower than the one of an external lubrication [13]. The main advantage of self-lubricating plastics compounds is their low need of maintenance and the dramatically reduced wear. Therefore, they are predestined for use in components that are difficult to access, such as gear wheels in encapsulated structures. The direct incorporation of lubricating liquids in a polymeric matrix is strongly limited and brings difficulties in processing.

Micro encapsulated lubricants (i.e. oils or greases) represent a relatively new possibility as pseudo-solid additive for tribological applications. In recent years, several micro encapsulation technologies have been investigated. Shell materials alike melamin formaldehyde resin, polyurethane or polysulfone have been used to encapsulate various oils. Schoch et al. used melamin resin and polyurethane to encapsulate different commercial oils. They also demonstrated the micro encapsulation for oils with different chemical compositions. Additional additives in oils did not hinder the encapsulation process [14]. Therefore, the micro encapsulation process is accessible to a wide range of oils, available on the market today. Various research groups synthesized microcapsules for the usage in thermoset and thermoplastic materials [15]. During compounding, the microcapsule structures need to endure crack-free the thermal and shear stress of the compounding process. The desired release of the encapsulated oil-droplets is initiated by mechanical wear-damage at the surface of the part in the later application. The continuous release of small amounts of oil during the lifetime of the products offers an effective way to reduce frictional forces in the interface of the tribo-system.

The use of oil-filled microcapsules is predominantly described in epoxy resin-systems [16–22]. Guo et al. have encapsulated lubricant oil with poly(melamine-formaldehyde) and the resulting microcapsules were mixed epoxy-resins using different amounts [16]. Reaching a microcapsule concentration of 10 wt.-%, the coefficient of friction and wear decreased by 75 % and 98 %, respectively in comparison to the unfilled material. The work also shows, that a rising amount of microcapsules decrease the mechanical characteristics [16]. This could limit the use of microcapsules in some applications. Khun et al. investigated epoxy-based composites containing wax filled microcapsules and short carbon fibres (SCF) [18]. The results indicated that by additionally added SCFs the mechanical properties increased. Composites containing 10 wt.-% of microcapsules lead to lower friction and wear from up a level of 8 wt.-% SCF. The authors explain this with the 2.7 increased hardness of the material and the additional friction-reducing effect of SCF. [18]. The incorporation of oil-filled microcapsules in thermoplastic matrices has been

described for thermoplastic polyurethane (TPU), polypropylene (PP) and polybutylenterephthalat (PBT) [13,23–25]. Producing thermoplastic composites requires often higher thermal stability of the capsule wall than incorporating them in thermosets. For all these polymeric matrices, modified with capsules, a distinct decrease in tribological coefficient-values was measured in several tribological tests. Schoch et al. investigated polyglycol filled polyurethane microcapsules in POM. Rotating ball on disc tests showed a decrease of 70 % in COF and 84 % in wear volume. In their work, a systematic variation of capsules concentration has not been conducted to investigate tribological and mechanical properties. The quantity of publications on POM/microcapsules-composites is very low and only studied by the Schoch working group. This is remarkable, because POM is a widely used semi crystalline thermoplastic material for tribological applications and it's also being modified with solid state lubricants alike PTFE powder [12].

The aim of this study is to show the effect of microencapsulated food-grade oil using two different wall materials in engineered thermoplastics. The microcapsules were mixed, using a laboratory-scale compounder for POM and PBT with varying capsules concentrations. Based on rotating tribological steel ball on plate tests, the coefficient of friction and wear rates were evaluated. Mechanical properties were analysed using tensile tests (DIN EN ISO 527 at room temperature).

2. Methods

2.1. Materials

In order to also enable the possibilities of use in areas of food technology, a low-viscosity, appropriately qualified oil was chosen: "Food Lube R-5555" (Riedel Schmierstoffe, Germany) was encapsulated and used in the wall materials, mentioned above. This lubricant is based on synthetic oils and modified with PTFE. It is certified for food and pharmaceutical applications.

Distilled water was used in all experiments. The MF-prepolymer was provided by Ineos Melamines and is specified as a partial methylol etherified melamine resin with solid content of 85 wt.-% and a viscosity of 5,400 mPa·s, glycerol, Mowiol® 4-88 with Mw 31,000 (PVA), Polyvinylpyrrolidon with average mol wt 10,000 (PVP), Poly-[(phenylisocyanat)-co-formaldehyd] with average Mn ~400 (PMDI), 1,4-Diazabicyclo[2.2.2]octan (DABCO) and were purchased from Sigma Aldrich and used without further purification.

Two different thermoplastic materials were chosen as matrix materials:

- Kepital F30-03 (POM copolymer, produced by Korea Engineering Plastics, Seoul, South Korea). This natural coloured and easy-flowing grade is developed for injection moulding applications
- PBT resin Toraycon 1200M, by Toray Industries (Tokio, Japan), also suitable for injection moulding processing.

Material properties (based on the material data sheet) of both polymeric materials are listed in Table 1**.**

Table 1: Thermal, rheological and mechanical properties of POM and PBT based on supplier's material data.

Material property	POM	PBT	Standard
Melt temperature / °C	165	224	ISO 11357
Melt-flow-rate; 2.16 kg (POM: 190 °C; PBT: 250 °C) /g·10 min^{-1}	27	21	ISO 1133
Density / kg·m^{-3}	1410	1310	ISO 1183
Stress at break / MPa	65	58	ISO 527 at RT
Elongation at break / %	25	>50	ISO 527 at RT

2.2. Synthesis of melamine resin and polyurethane microcapsules containing lubricant oil

MF microcapsules containing Food Lube were synthesized by in-situ polymerization (Figure. 1a). The synthesis process involved the preparation of the aqueous phase containing 0.12 g polyvinylalcohol (MW = 31,000 g·mol^{-1}) and 4 g MF-resin that were dissolved in 150 g deionized water. The organic phase (12 g Food Lube) was dispersed in the aqueous phase under mechanical stirring (rotor-stator type of a stirrer, Ultra-Turrax) at 5000 rpm and 60 °C. The pH was adjusted to pH 4 and the dispersion was stirred for 2 h at 60 °C and 350 rpm to complete polycondensation reaction. The capsules were separated from side products via filtration. The resulting wet cake was spread on the tray and dried on air for 48 hours.

PU Microcapsules containing Food Lube were prepared by interfacial polycondensation (Figure 1b). The oil phase (8 g Food Lube, 2 g PMDI and 6 g cosolvent) were dispersed in 50 g 1,5 wt.-% PVP solution containing 5 g glycerol under mechanical stirring (rotor-stator type of a stirrer, Ultra-Turrax) at 5000 rpm at room temperature. The suspension was further stirred with a glass blade stirrer at 500 rpm. 0,5 g DABCO dissolved in 5 g water were added to the suspension, which was further heated to 75 °C and stirred for another 2 hours for the completion of the interfacial polymerisation. The resulting wet cake was spread on the tray and dried on air for 48 hours.

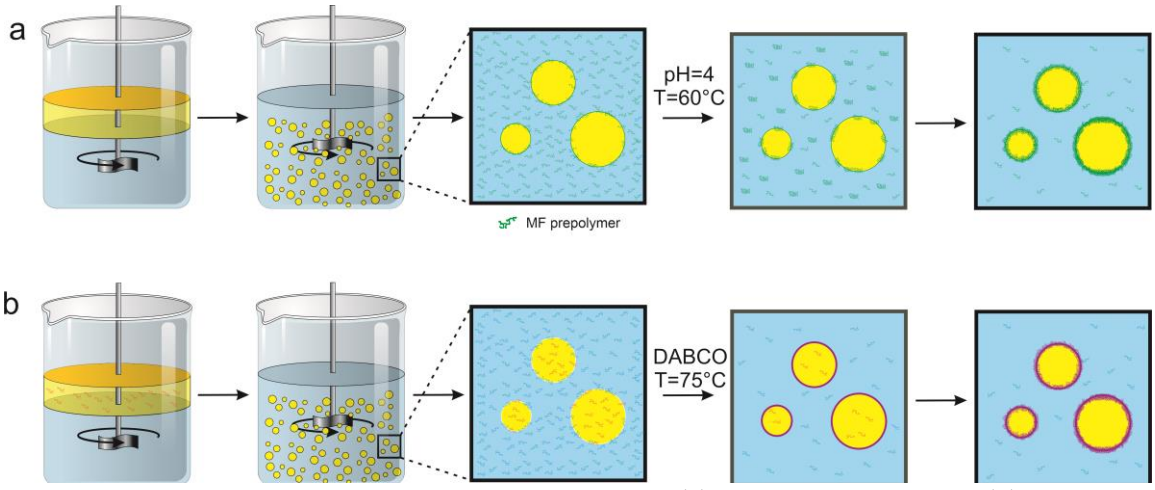

Figure 1: Scheme of the preparation of MF microcapsules (a) and PU microcapsules (b). The Food Lube lubricating oil shown in yellow colour is immiscible with water.

2.3. Preparation of self-lubrication thermoplastic composites

The microcapsule-loaded thermoplastic composites were prepared on a counter-rotating micro-conical twin screw extruder (HAAKE MiniLab II, Thermo Fisher Scientific, Germany). In this extruder, compounding with a low amount of material is possible. Nevertheless, in contrast to industrial co-rotating twin screw extruders, the material must be fed into the hopper as a premix. To enhance the mixing process, the polymer granules were milled on centrifugal mill (ZM 200, Retsch, Germany) to a polymeric powder. Before compounding, PBT was dried for 6 h at 80 °C in a convection oven to a residual moisture of 0.02 %. Subsequently, the polymeric and microcapsule powders were pre-mixed manually. The two capsule materials each have a specific oil content, so that although there are different proportions of capsules in the compound formulation, there is the same proportion of oil in the compound. The compositions of the samples are listed in Table 2.

Table 2: Sample composition for lubricant, polymer and capsules content.

Lubricant concentration / wt.-%	Polymer / wt.-%		Capsules / wt.-%	
	PU	MF	PU	MF
1	98.75	98.92	1.25	1.08
2	97.5	97.84	2.5	2.16
5	93.75	94.59	6.25	5.41
10	87.5	89.19	12.5	10.81
15	81.25	83.78	18.75	16.22
20	75	78.38	25	21.62

5 g of each sample composition were produced per batch. Several batches per capsule concentration were required to produce tensile bars and discs. A heated melt reservoir was used to transport the polymer melt out of the nozzle to a pneumatic laboratory injection moulding mechanism. Two different tools were used:

- Disc-form samples (diameter: d=25 mm; thickness: s=1.65 mm) were used for tribological test.
- Tensile rods (type DIN EN ISO 527-2 “5A”) were used for mechanical characterization.

The rotational speed of the screws was set to 100 rpm for both polymers. The machine settings for sample production were kept constant for each polymer type. Temperatures for each polymer are listed in Table 3.

Table 3: Machine temperatures for sample preparation.

Material	Extruder temperature / °C	Melt reservoir temperature /°C	Tool temperature /°C
POM	200	185	40
PBT	250	230	50

Although processing in the minilab is a laboratory method, experience has shown that it can be seen as an indicator for transfer to a larger scale such as the co-rotating twin screw extruder [14].

2.4. Characterization

Thermal stability

The thermal stability of the lubricant and microcapsules was investigated using TGA2 LF/1100/885 from Mettler with STARe Software. The weight of the specimen varied from 5 to 10 mg. All the measurements were performed under nitrogen atmosphere in aluminium oxide pan. The samples were heated with 10K·min^{-1} to 550 °C.

Scanning electron microscopy

The microcapsule powder and the processed polymer-microcapsule compounds were analysed via scanning electron microscopy (SEM) (Supra 40 VP, Carl Zeiss, Germany). SEM images of the compounds were made on fracture surfaces of the tensile test specimens.

Capsule size distribution

Laser Diffraction particle size analysis was used for the determination of the average microcapsule diameter using LS 13 320 SW (Beckmann Coulter). Low angle forward light scattering with optional PIDS (polarization intensity differential scattering) technology was used.

Tribology

The tribological investigations were performed on a rotational ball-on-disc setup at norm conditions (23 °C, 50 % rel. humid.). As counter body a 100Cr6 steel ball with a radius r of 3 mm and a roughness of Ra 0.032 µm was used. Normal load F_N and linear speed of rotation was kept constant at 10 N and 50 cm·s^{-1}. Each compound (n=3) was tested over a distance S of 5 km and a track radius R of 8 mm. Microscopical analysis on the steel ball did show any wear phenomena. The wear loss of the analysed tribological system is only described by the width s of the wear track of the polymer part. The wear track width of the polymer discs was measured at 5 positions via light-microscopic images for each of the 3 samples. The calculation of the wear volume V_{wear} has been done according to ASTM G99-17. Equation (1) was used to determine the specific wear rate w_s given by equation (2).

$$V_{wear} = \frac{\pi \cdot s^3 \cdot R}{6r} \qquad \text{Equation (1)}$$

$$w_s = \frac{V_{wear}}{F_N \cdot S} \qquad \text{Equation (2)}$$

Mechanical properties

The influence of the microcapsules on the mechanical properties were characterised based on tensile test (Z010, Zwick/Roell, Ulm, Germany) according to DIN EN ISO 527. The strain was measured using a multiXtens-system. The specimens were tested with a speed of 50 mm·min^{-1} (Young's modulus at 1 mm·min^{-1}) and a pre-force of 1 N. Young's modulus, stress at break, and elongation at break were tested and analysed.

3. Results

3.1. Microcapsules

In figure 2, the microcapsules of MF and PU are shown in scanning electron microscopy. MF microcapsules are nearly spherical, the diameter of most of the capsules is about 20-30 µm (Figure 3), however smaller particles also can be observed. The PU microcapsules are slightly bigger (with dimeters about 30-50 µm (Figure 3) and not spherical showing some concavities on the surface. These concavities are often observed for the capsules obtained by interfacial polymerisation and are not the result of capsule damaging during isolation or characterisation.

a) MF-microcapsules b) PU-microcapsules

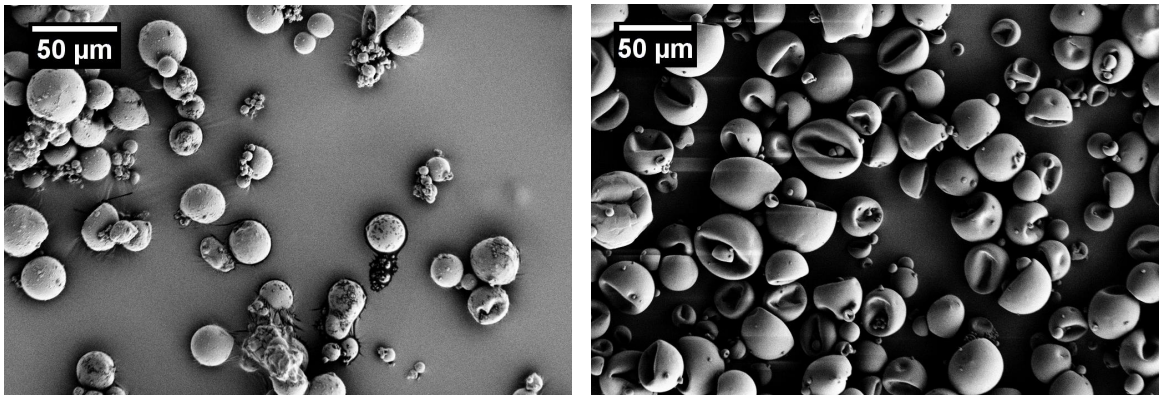

Figure 2: SEM images of a) MF microcapsules and b) PU microcapsules.

The particle size analysis (Figure 3) confirms the results of the SEM analysis and demonstrates that SEM images can be considered representative. Thus, both types of capsules show rather broad particle size distributions with the small fraction of particles with diameters below 5 µm, which were also observed in SEM. The particle size distribution maxima are around 20 µm and 30 µm for MF and PU microcapsules, correspondingly.

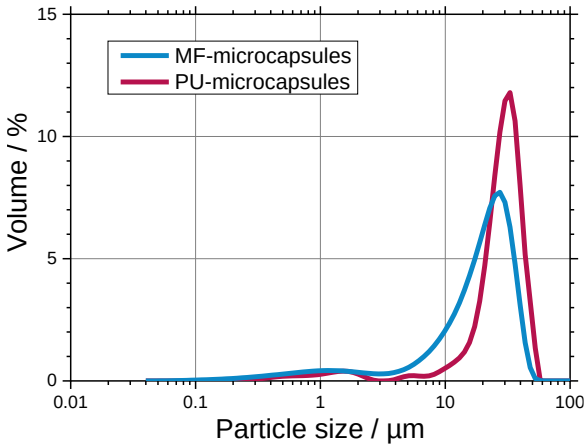

Figure 3: Particle size distribution of MF and PU microcapsules.

Thermogravimetric analysis (TGA) was used to determine the thermal stability of the microcapsules under inert atmosphere. It can be seen (Figure 4) that Food Lube itself has an outstanding thermal stability. Almost no thermal decay can be observed until ca. 340 °C. The slight weight loss (ca. 2 wt.-%) below 120 °C can be attributed to the loss of moisture, that is probably the result of storage of samples in open pans at ambient humidity before characterisation. Due to their excellent thermal stability both types of microcapsules were considered promising candidates for the integration into the chosen polymer matrixes by extrusion.

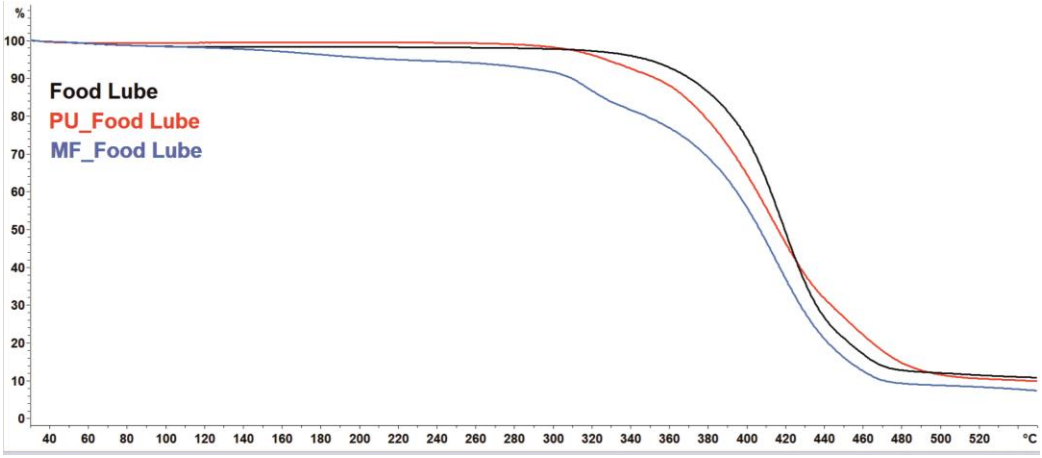

Figure 4: Thermogravimetric analysis of Food Lube, MF microcapsules and PU microcapsules.

3.2. Sample preparation

Up to a lubricant concentration of 10 wt.-%, the sample preparation was done with constant process parameters using POM and PBT. For higher lubricant concentrations, oily surfaces of the moulds and polymeric samples occurred. A non-destructive compounding of the microcapsules is a main requirement for scale-up fabrication. The released oil hinders the comparability of the different samples. Therefore, tribological investigations were performed with maximal lubricant concentration of 10 wt.-%.

Figure 5 shows the fracture surfaces of POM and PBT samples containing PU and MF microcapsules. The investigated samples did show any capsules agglomeration. Microcapsules were distributed uniformly along the investigated sample surface. Ruptured microcapsules shells have been detected mainly at the MF-microcapsules compounds. It is very difficult to make statements about the extent to which sample preparation has influenced the result.

a) POM 10 % PU capsules b) PBT 10 % MF capsules

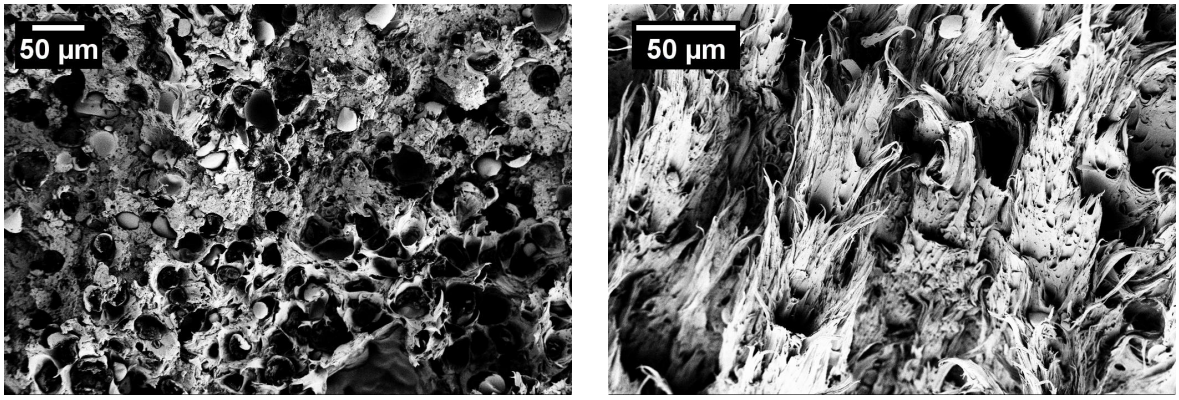

Figure 5: SEM images of thermoplastic composites of a) POM/ 10 % PU-capsules and b) PBT/10 % MF-capsules. The images show the surfaces of fractured tensile bars.

3.3. Tribological properties

POM

Figure 6 shows the coefficient of friction during the tribological tests for a) MF-microcapsules and b) PU-microcapsules, both blended in POM. Capsule filled samples show initially lower COF-values compared to the unfilled reference samples. Independent of the capsule wall material, the COF index increases with test length at 1 and 2 % lubricant concentration. The COF of the unfilled sample and samples with a lubricant concentration of 5 wt.-% and 10 wt.-% show only smaller changes of COF during the tribological tests. No influence of the wall material on the COF was found.

a) MF-microcapsules b) PU-microcapsules

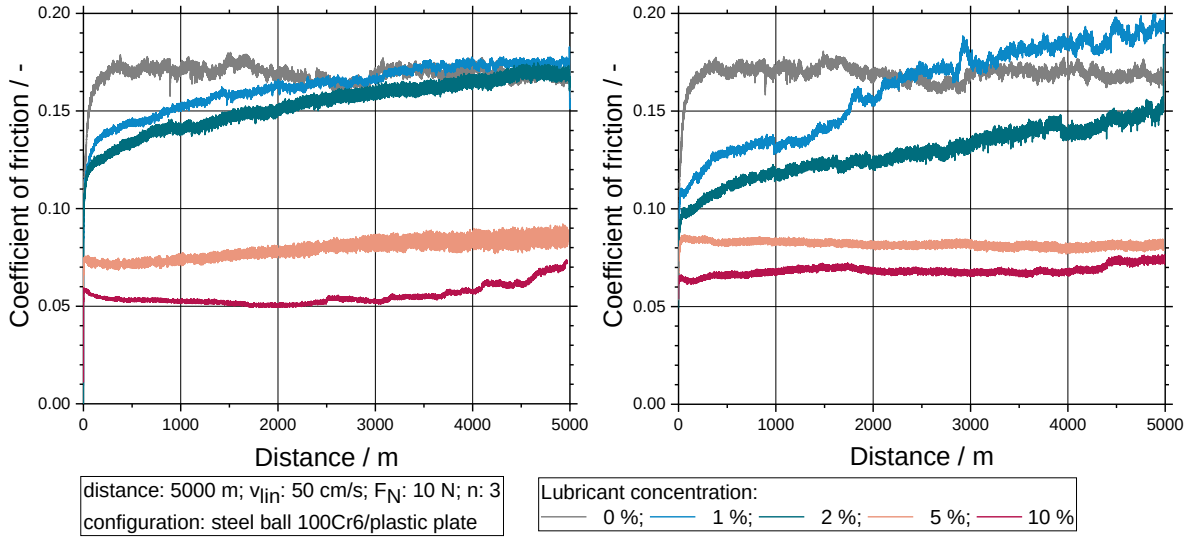

Figure 6: Coefficient of friction over sliding distance of a) MF and b) PU filled POM-samples with varying lubricant concentration in steel ball on plate configuration.

The mean values of COF and specific wear volume from rotational-tribological investigations are presented in Figure 7. The values represent the average values over the entire

frictional test. Samples with a lubricant concentration of 1 and 2 % have smaller mean COF compared to the unfilled sample, due to initial reduced COF values. The capsule wall material does not have any influence on the mean COF-values. Increasing lubricant concentration lead to a decrease of the COF. Compared to the unfilled sample (COF: 0.169 ± 0.011), the addition of 10 wt.-% encapsulated lubricant results in 67 % (MF-COF: 0.055 ± 0.002) and 59 % (PU-COF: 0.068 ± 0.002) lower COF-values.

The specific wear rate from the tribological analysis of the samples are shown in Figure 7 b. Samples with a lubricant concentration of 1 and 2 wt.-% and a PU capsule wall showed an increased wear volume compared to the unfilled sample. With increasing lubricant concentration, the specific wear volume was decreasing. An influence of the capsule wall material on the wear properties of the samples hasn't been detected. The addition of 10 wt.-% of microcapsules lead to a reduction of wear in the tribological test of 49 % (MF) and 51 % (PU) compared to the unfilled sample.

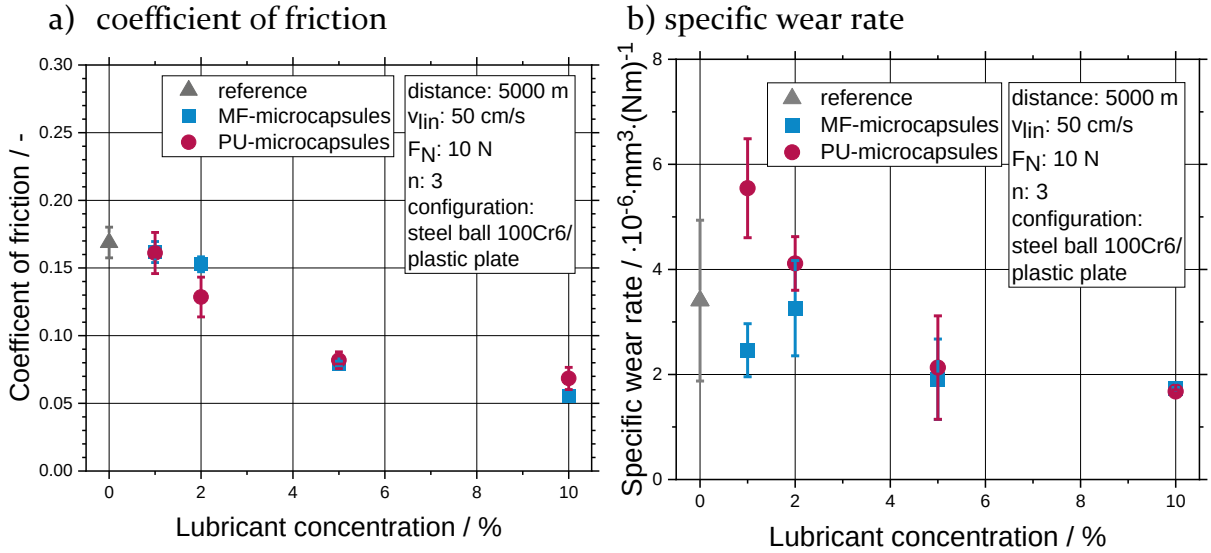

Figure 7: a) Mean values of the COF and b) specific wear rate of lubricant filled POM samples in rotational tribological tests. Samples were prepared with MF and PU microcapsules with varying capsule content.

Figure 8 displays microscope images of the wear tracks after the tribological test. The non-additivated sample (a) showed grooves in the wear track and accumulations of plastic wear debris on the borders of the wear track. By adding microcapsules (b, c & d) the wear tracks were less visual in contrast to the reference (a). Microcapsules were detected visually in the wear track and beneath the entire surface of the sample. Grooves are less developed, and the wear tracks showed smoother surfaces.

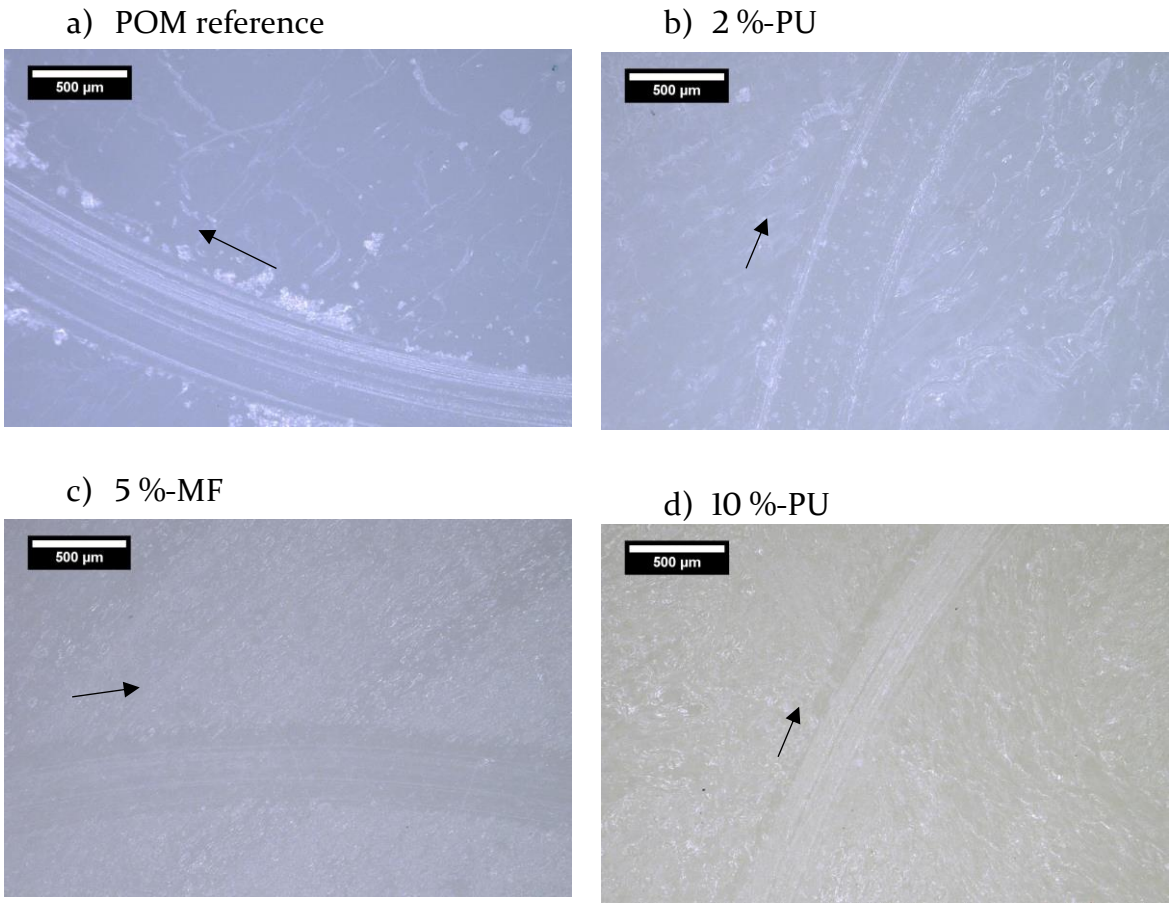

Figure 8: Optical microscope images of POM wear tracks. Shown samples: a) unfilled POM reference, b) 2 %-PU, c) 5 %-MF and d) 10 %-PU. Arrows indicate the direction of ball-movement.

PBT

Figure 9 shows the friction curves for PBT-samples with varying lubricant concentration. The compounding of small amounts of encapsulated lubricant had a strong impact on the frictional behaviour of the samples and decreases the COF to a large extent. For the investigated sliding distance, the microcapsule filling provided nearly constant COF-values. Higher deviations could be detected for the unfilled sample and the 1 wt.-% additivated samples. Regarding the capsule shell material, no differences were detected.

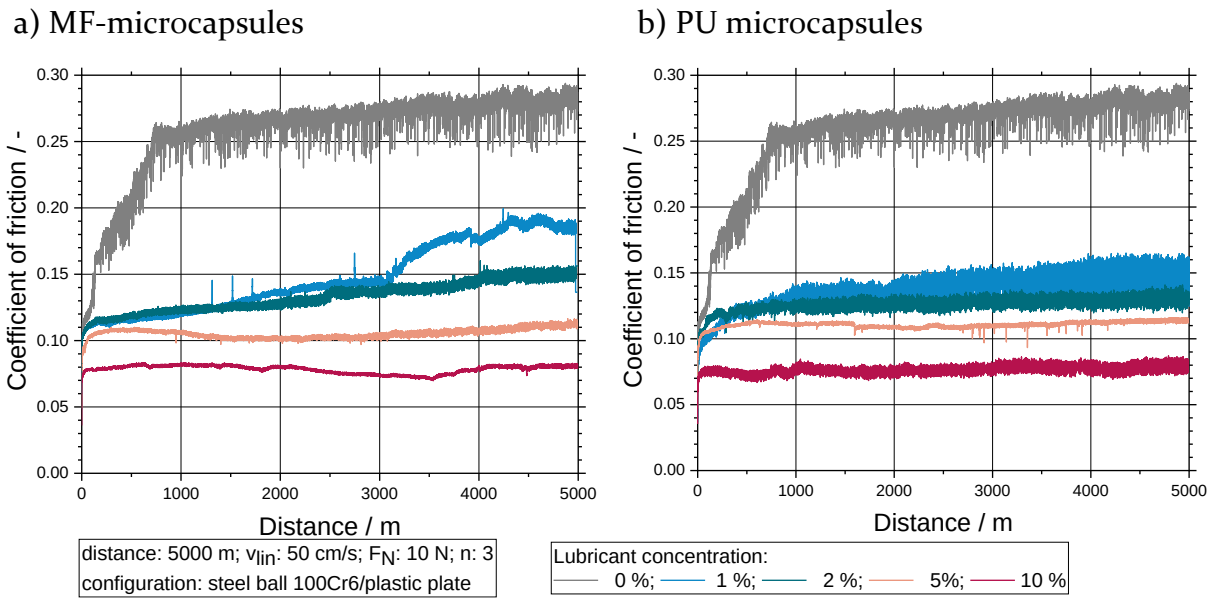

Figure 9: Coefficient of friction profile of a) MF and b) PU microcapsule filled PBT samples with varying lubrication concentration.

Figure 10 a) summarizes the mean COF-values over the investigated sliding distance of 5 km. Small amounts of capsule content already had a big impact on the tribological performance. A 1 wt.-% amount of lubricant results in a coefficient of friction of 0.14. With increasing the lubricant concentration, a further decrease of COF was detected. Compared to the unfilled reference (COF: 0.258 ± 0.011), a lubricant concentration of 10 wt.-% leads to a reduction of COF of 70 % (MF-COF: 0.078 ± 0.004; PU-COF: 0.076 ± 0.001).

The corresponding specific wear rates are displayed in Figure 10 b). The wear reductions were found to be smaller for smaller amounts of lubricants compared to the COF-reductions. The sample with 1 wt.-% of PU-microcapsules has a wear rate five times lager then the corresponding unfilled sample. This could be explained by sample inhomogeneities from the batch process. At a lubricant concentration of 10 wt.-% the wear rate of MF and PU microcapsules are nearly equivalent. Compared to the unfilled sample an additivation of 10 wt.-% of lubricant leads to a wear rate reduction of 58 % (MF) and 59 % (PU).

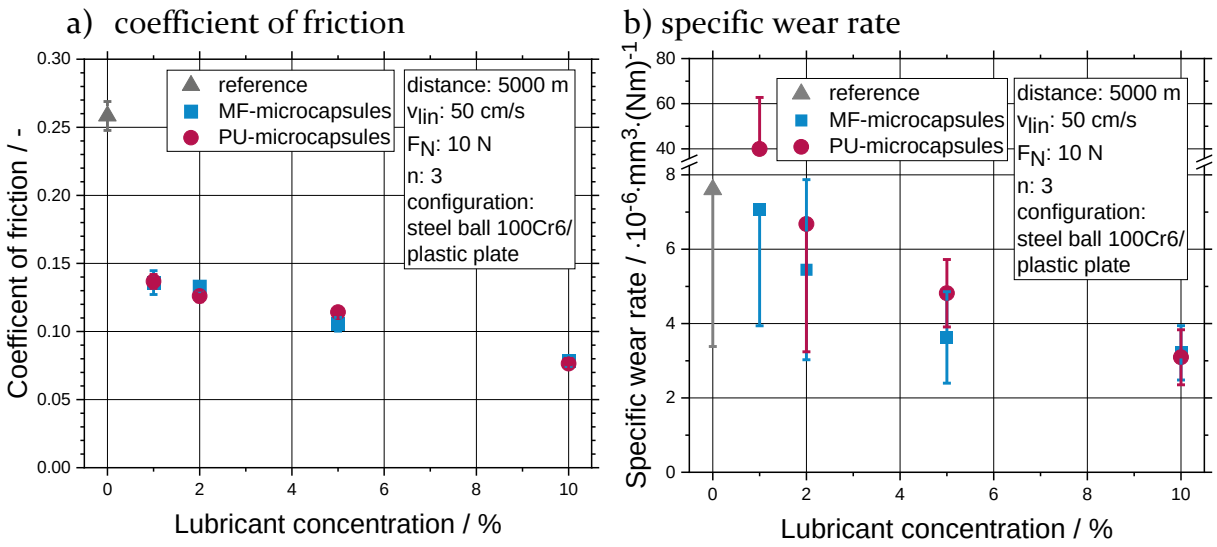

Figure 10: a) mean coefficient of friction and b) specific wear rate of different MF and PU microcapsule filled PBT samples.

In Figure 11 optical microscope images of the wear tracks are shown. The tribological stressed area of the unfilled sample (a) shows a multitude of fine grooves. Especially for samples with a smaller amount of lubrication, sections of the wear tracks showed stronger deformations. With increasing lubrication concentration, these phenomena (shown in Figure 11 b) occurred less frequently. The sample with a lubrication concentration of 10 wt.-% (c) had a smooth wear track and showed only a small tendency to build up grooves and wear debris.

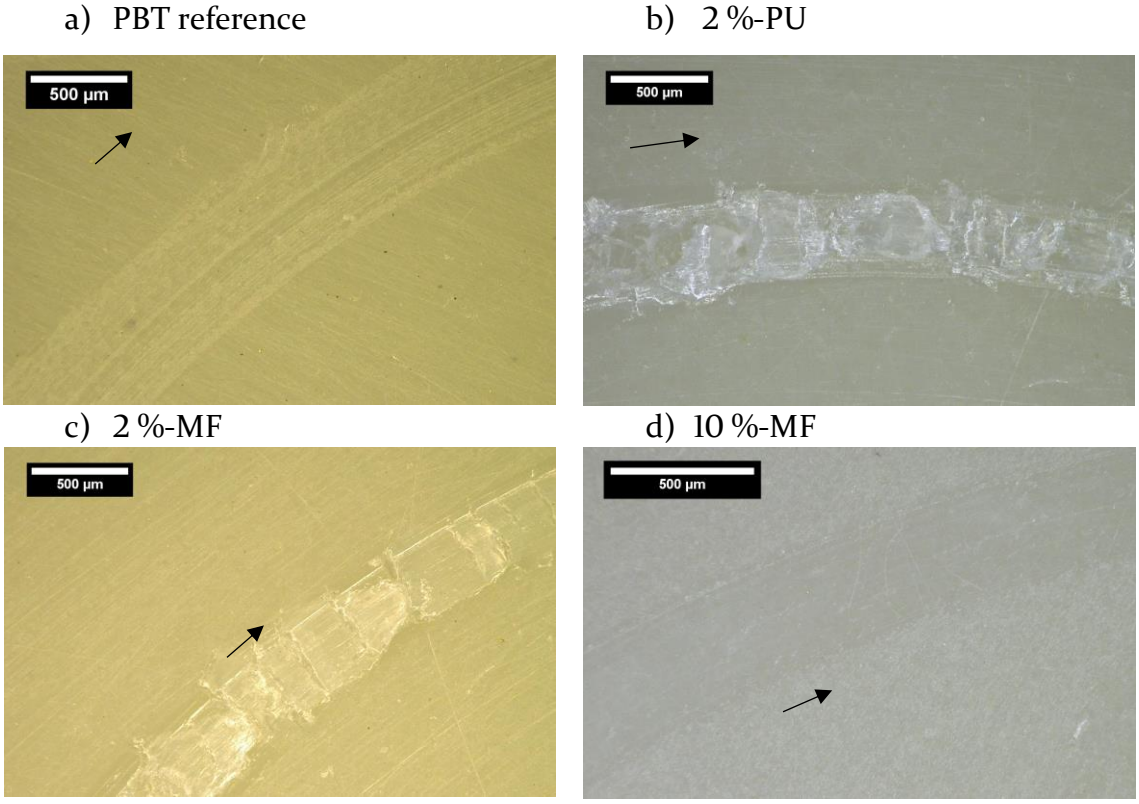

Figure 11: Optical microscope images of PBT wear tracks. Shown samples: a) reference, b) 2 %-PU c) 2 %-MF and d) 10 %-MF capsules. Arrows indicate the direction of rotating ball-movement.

3.4. Mechanical Properties

POM

Results of the tensile tests are shown in Figure 12. The incorporation of lubricant filled microcapsules in POM resulted in decreased tensile stress at break. With increasing lubricant concentration, the tensile strength steadily reduced. The mixing of 10 wt.- % of lubricant oil resulted in stress at break of 37.8 ± 2.3 MPa (MF) and 36.9 ± 0.5 MPa (PU). The reduction of tensile strength was less for PU-microcapsules compared to MF-capsule wall material. Investigations on the influence of the microcapsules on the elongation at break are shown in Figure 12 b. For all the samples, higher standard deviations were measured. Due to the high standard deviations, elongation at break took place around 15 % for all samples.

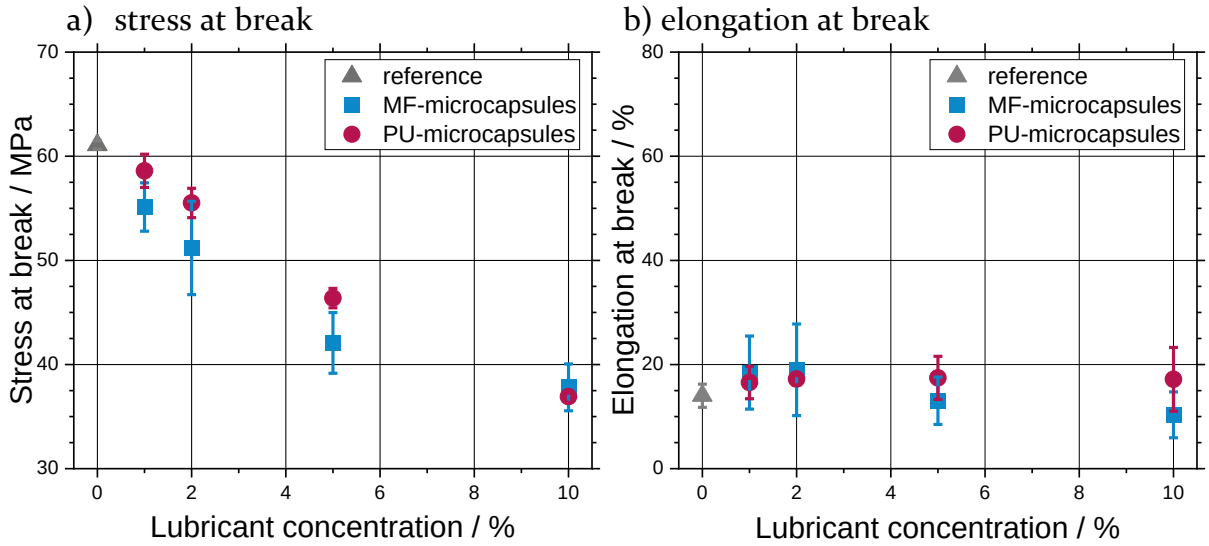

Figure 12: Stress at break and elongation at break of POM with varying encapsulated lubricant concentration.

PBT

Mechanical properties of microcapsule filled PBT are shown in Figure 13. The incorporation of microcapsules leads to decreased stress at break (Figure 13 a). With increasing lubricant concentration, tensile strength decreases. The reduction of tensile strength is less, when MF-microcapsules are used. By incorporation of 10 wt.-% of lubricant tensile strength is 23 % (MF) and 31 % (PU) lower compared to unfilled PBT. The results for elongation at break are displayed in Figure 13 b. The unfilled PBT shows a high deviation in the elongation at break value. Lubricant containing PBT show a tendency of breaking at lower elongation rates. The amount of lubricant and the type of capsule wall material used have no influence on the elongation at break level.

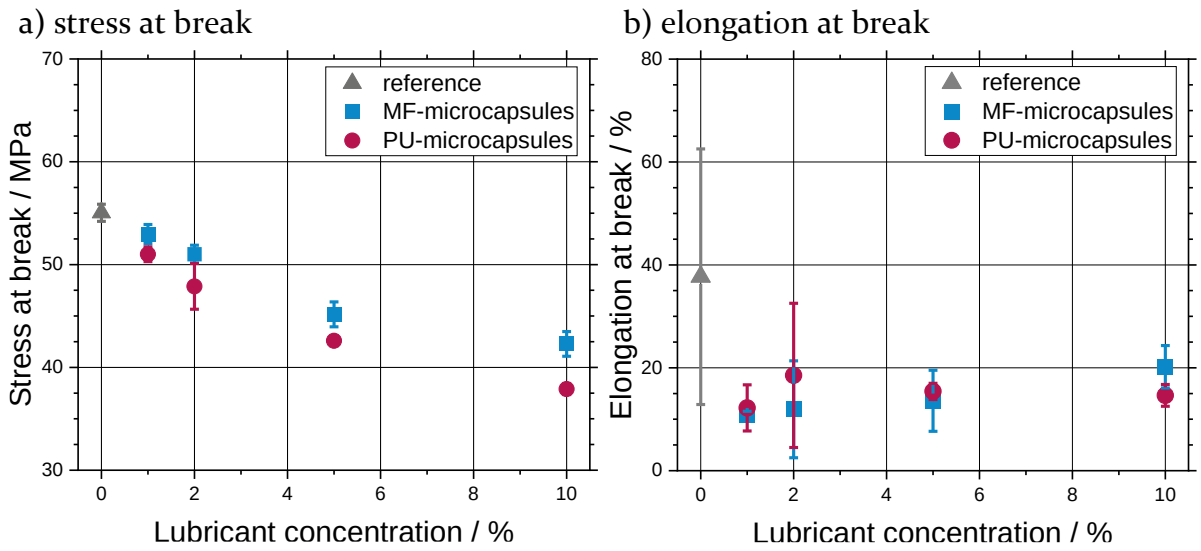

Figure 13: Stress at break and elongation at break of PBT with varying encapsulated lubricant concentration.

In the following the results of the study are summarised: compounding experiments with these two types of microcapsules with varying capsule content were conducted on a laboratory scale twin-screw extruder. The sample preparation with the engineering thermoplastics POM and PBT showed no leakage of oil up to a lubricant concentration of 10 wt.-%.

The tribological characterization of the produced parts showed decreased wear and frictional values. By increasing lubricant concentration, the effect of lowering tribological values are more distinct. The selection of capsule wall material has only a small influence on tribological performance. Higher deviations between MF and PU capsule walls occurs regarding mechanical values. Here, PU microcapsules show higher mechanical properties with POM as matrix material. In PBT decrease of mechanical properties with MF-microcapsules was less pronounced.

4. Discussion

The investigations showed that it is possible to encapsulate additivated food grade oil with MF and PU microcapsule wall materials by in-situ polymerization (MF-capsules) and interfacial polymerization (PU capsules). MF-capsules have a nearly spherical shape and the morphology of the PU shells showed concavities. The concavities are believed to be the result of uneven cross-linking of the polymer on the still liquid droplet interface, which leads to the tensions and shape deformation before and during the capsule solidification process.

MF microcapsules show nearly gradual loss of mass until 300 °C (about 8 % in total), after which complete thermal decomposition of the microcapsules takes place in a 2-step process between 300 °C and 500 °C. The weight loss below 300 °C is attributed to the evaporation of residual water (about 2 %) and post-condensation of melamine resin [26]. The post-condensation of the MF capsule walls at the temperatures between 120 °C

and 200 °C is believed not to lead to the mechanical disruption of the microcapsules, but to their further cross-linking and densification. The first decomposition step starting at ca. 310 °C is assigned to the MF shell decomposition, which is further accompanied by the evaporation of the capsule core material. Interestingly, the decomposition of the Food Lube in this case happens at lower temperatures than of the Food Lube in non-encapsulated state. This can be attributed to the higher available surface area in case of the microencapsulated material and corresponding faster kinetics of evaporation.

PU microcapsules showed no weight loss up to ca. 300 °C. The stepwise weight loss above 300 °C is assigned to the decomposition of PU shell followed and further accompanied by the evaporation of Food Lube. The PU microcapsules appear to be slightly more thermally stable than MF microcapsules, which can be attributed to different moisture content, different thermal decomposition patterns for polymers used as the shell materials and different microcapsule size [27]. Besides the thermal properties, mechanical properties of the microcapsules are of great interest of the different shell materials. These values can be used to better predict the fracture behaviour in processing and later application.

The leakage of oil in the composite preparation at higher capsule concentrations could have been initiated by higher shear forces on the capsules. The observed phenomena of higher stability and less oil-release during the sample preparation of PU capsules at higher concentrations can be explained, based upon a higher stability of the PU capsules. Keller and Sottos investigated the mechanical stability of microcapsules used for self-healing polymers [28]. They showed that the capsule size has a significant effect on failure strength and that smaller capsules can withstand higher loads. Even if PU capsules have a larger diameter, they showed higher stability in the compounding process. This could be explained by the higher wall thickness of the PU-capsules. At scale-up production conditions, higher capsules concentrations can be added through enhanced process engineering. Schoch et al. compounded lubricant filled microcapsules by adding the capsules to the molten polymer via side-feeder close to the nozzle of a twin-screw extruder [14].

Tribological investigations on microcapsule/POM composites showed an effective reduction in friction and wear values for lubricant concentration above 5 wt.-% up to 67 % and 51 % respectively. At lower lubricant concentrations, higher wear rates were detected for PU-microcapsule-filled samples. This might be explained by sample inhomogeneities or insufficient release of oil. By raising the lubricant concentration from 5 wt.- % to 10 wt.-%, friction and wear coefficient were only reduced to a small extend. The application of 5 wt.-% of microcapsules represents an effective amount to enhance the tribological performance of POM compounds. Mechanical values derived from microcapsules/POM composites tensile tests showed decreased mechanical values whilst increasing the lubricant concentration. Microcapsules create defects within the matrix and lead to earlier mechanical failure. Even though the capsule content is higher at the same amount of lubricant concentration for PU-capsules-composites, the reduction of stress at break is smaller. This can be explained by a stronger adhesion of the PU capsules to the POM matrix.

Tribological investigations of microcapsules/PBT composites revealed a strong decrease in the coefficient of friction even at low lubricant concentrations. At low lubricant concentrations, wear induced defects were detected and the analysed wear-rate showed higher deviations. We assume that there is a decrease in wear defects and deviations when samples with increased surface quality are produced. Mechanical characterization of microcapsule/PBT composites showed decreasing tensile strength with increasing amount of lubricant. For the same lubricant concentration, MF-microcapsules show higher tensile strength compared to PU-microcapsules. This can be caused by the higher concentration of PU-capsules to generate the lubricant concentration, required. Moreover, the compatibility of MF-shell and the PBT-matrix can be stronger compared to PU-capsules. Investigations of neat capsule wall materials in PBT and POM are required, to investigate the connection strength in greater detail.

Compared to the claimed mechanical properties of the plastic producers (Table 1), the samples produced in this work show slightly smaller values for POM and PBT. This can be attributed to the smaller standard sample geometries and the production on a laboratory scale. As the lubricant content increases, the influence of the matrix plastic used decreases. With a lubricant concentration of 5 and 10 wt.-% stress at break is at a comparable level for the plastic matrices used. The elongation at break values for both plastic types show very similar results. The addition of microcapsules leads to an elongation at break of between 10-20 %, regardless of the type and proportion of microcapsules. In further studies the effects of additional reinforcing fillers are of great interest in POM and PBT. Several studies have shown that mechanical values increase and the COF decreases when carbon fibres or inorganic fillers are added [13,17,18,29,30].

Under the chosen tribological conditions, unfilled POM shows lower tribological values than unfilled PBT. In contrast to POM, even a small proportion of microcapsules has a high impact on the tribological properties of PBT. With increasing capsule concentration, the differences in tribological values between POM and PBT compounds become smaller. However, the values of the POM composites remain lower than those of PBT for all concentrations. Under these sliding conditions, POM/microcapsule composites are to be preferred.

Further tribological tests are mandatory to evaluate the effectiveness of lubricant filled microcapsules in thermoplastic engineered materials. Investigations in different tribological systems and test conditions are of great importance to get deeper insights in the tribological behaviour of the composites. Comparative tribological tests with different internal lubricants can show under which conditions the respective use of lubrication additives is most suitable. Scale-up production are of importance to generate a higher sample quality and to investigate the injection moulding behaviour of microcapsule filled composites.

5. Conclusion

In this study, two capsule shell materials (melamin-formaldehyde resin and polyurthane resin) were used to generate lubricant filled microcapsules. Sample production of POM

and PBT composites were performed by micro-twin-screw extruder. Up to an oil concentration of 10 wt.-%, no leakage of oil was detected. Mechanical properties revealed decreasing mechanical properties with increased lubricant concentration. Tribological characterization showed that lubricant filled microcapsules can effectively decrease the friction (-70 %) and wear values (-58 %). Taking mechanical properties into account, a capsule concentration of 5 wt.-% offered sufficient friction and wear reduction in POM and PBT. Test results of the two different types of microcapsules showed only small deviations in their tribological and mechanical behaviour and are both suitable for tribological applications. Further tribological investigations are required to extend the understanding of the friction and wear behaviour of the rarely investigated lubricant-filled microcapsules in thermoplastic materials.

Acknowledgement

This research is financially funded by the German Federal Ministry for Economic Affairs and Climate Action (BMWK) via the German Federation of Industrial Research Associations (AiF) as part of the program for the promotion of joint industrial research (IGF) (project-ID: 210707 BG).

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