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Chemical Bonded PA66-PTFE-Oil Composites as Novel Tribologically Effective Materials: Part 2

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Abstract. Polytetrafluoroethylene (PTFE) exhibits excellent non-stick properties and a very low coefficient of friction under tribological stress, but it is incompatible with almost all other polymers. In the first part of this study we presented the generation of the novel tribological material based on unsaturated oil, radiation-modified PTFE (MP1100) and Polyamide 66 (PA66). To get a better understanding of the chemical properties and chemical composition of the compounds, the PA66-MP1100-oil-cb (chemical bonded) compounds were examined by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). In this part, the mechanical properties of the compounds are compared with plain PA66 and PA66-MP1100-cb. The tribological investigation was carried out using the Block-on-Ring tribometer. It was found that the mechanical properties of PA66-MP1100-oil-cb with 20 wt.% MP1100-oil-cb only show slight differences compared to PA66, but the tribological properties of the compounds have been significantly improved through chemical coupling between the three components. Finally, the amount of the compound that was deposited on the surface of the steel disc counterpart was analyzed after the tribological testing.

1. Introduction

PTFE offers excellent tribological properties in a wide temperature range (-250 °C to +260 °C). However, PTFE exhibits poor mechanical properties and has low adhesion to metal surfaces [1]. Contrary to the chemical stability of PTFE, it is highly sensitive to high-energy radiation. Compared with PTFE, polyamide has got very good mechanical properties on one hand, but it has a high coefficient of friction against steel on the other hand. PTFE itself can be modified by using high-energy radiation to obtain persistent perfluoroalkyl (peroxy) radicals and functional groups (-COF and -COOH) [2, 3]. There are two approaches to link radiation modified PTFE to other polymers. One method is the modification via persistent peroxyalkyl radicals and the other route is using the generated functional groups (COOH and COF). The persistent perfluoroalkyl (peroxy) radicals can be used to form the covalent bond with other polymer/monomers via radical addition reaction [4]. The COOH- functional groups of radiation modified PTFE can be used to create a covalent bond with polyamide by transamidation reaction, at the same time the compatibility between radiation modified PTFE and the



polyamide can be improved [5]. In this study, four olefinic oil-types were used, which contain at least one C=C double bond and different functional end groups, and as radiation modified PTFE, MP1100 was used. The olefinic oil molecules can be covalently bonded to MP1100 via radical reactions, and the oil functional end groups can generate a variation in affinity to the metal surface. The manufacture and characterization of the compounds based on MP1100, selected oil-types and PA66 were presented in the first part of this study [7]. Here, to illustrate the influence of oil on the mechanical properties of the PA66-MP1100-oil-cb compounds, the mechanical and tribological properties of PA66-MP1100-oil-cb were investigated and compared to the reference materials (PA66-MP1100-cb and origin PA66). For the mechanical testing, the compound was injection molded to multipurpose test specimens according to ISO 3167 standard, and subsequently tensile stress, strain at break, the modulus of elasticity, the tensile strength, and the Charpy notched impact strength were tested as well. For the tribological testing, the material extrudates were processed by injection molding and were manufactured in pins with a width of 10 mm and a working length of 3 mm afterwards. Finally, the tribological behavior of the compounds was investigated by block-on-ring rig test.

2. Experimental and Methods

2.1. Materials and reactive extrusion

The materials were processed in two steps. During the first step the four different oil types [Methyl oleate (MO), Oleyl alcohol (OA), Oleic acid (OES), and Oleyl amine (OAMIN)] were chemical bonded to radiation modified PTFE (MP1100, Chemours, US) through solid-phase reactive extrusion by using HAAKE Rheomex PTW 16/25 twin-screw extruder (Thermo Fisher Scientific, Germany). MP1100 is radiation modified PTFE emulsion polymer and was used how it was available. The ratio of MP1100/oil was 10/90 wt%. The maximum processing temperature was 170°C. After the first extrusion, the MP1100-oil-cb compound was cooled, pulverized and then used to couple with PA66 (Technyl A205F, Solvay). Here the MP1100-oil-cb and PA66 were dosed in a ratio 20/80 wt% and processed by Leistritz ZSE 27 Maxx twin-screw extruder (Leistritz Extrusionstechnik GmbH, Germany) in melt. The process temperature was 330 °C. Theoretically, the final sample contains 80 wt% PA66, 18 wt% MP1100 and 2 wt% oil

2.2. Injection Molding

In order to determine the mechanical properties and tribological properties of the compounds, multipurpose test specimens (according to ISO 3167 standard method) on one hand, and semi-finished products were prepared by injection molding (Allrounder 420 C, Arburg, Germany) at 350 °C on the other hand.

2.3. Mechanical testing

For the mechanical testing, tensile tests were carried out according to the standard testing method DIN EN ISO 527-2/1BA/1-50 (ZwickRoell 1456 universal testing machine, Germany). The notched impact bending test and the Charpy notched impact strength tests were carried out according to the DIN EN ISO 179/1EA standard using a ZwickRoell pendulum impact tester 4J.

2.4. Tribological testing.

Tribological investigations of the compound materials were carried out on a block-on-ring test rig. Figure 1 shows a scheme of the test configuration. For the experiments, rectangular pins with a nominal contact surface of 10 x 3 mm² were manufactured from the respective compounds. The pins were pressed onto the rotating steel disc, whereby a new disc was used for each measurement. The steel disc made of

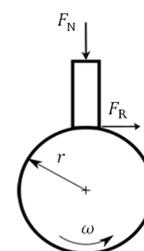


Figure 1: Scheme of tribological testing.

16MnCr5, which was hardened (60 HRC) and ground in the axial direction at a 3D arithmetical mean roughness of $Sa = 0.2 \mu\text{m}$, has a diameter of 80 mm and a width of 13 mm.

After the pins and the steel discs were manufactured, they were cleaned in an ultrasonic bath (using cyclohexane, isopropanol and acetone) and dried under the ambient condition in the laboratory. The tests were carried out at constant nominal pressure ($p = 5 \text{ MPa}$) and constant speed ($u = 0.3 \text{ m/s}$) for 5 h (approx. 6 km). The wear of compounds was determined by measuring the mass wear after the experiments.

3. Results and discussion

3.1. Results of mechanical testing.

Figure 2 shows that the compound PA66-MP1100-cb has got a significantly higher E-modulus compared to the original PA66. It is supposed that this behavior is due to the chemical bonding between the components and the very good breaking down and distribution behavior of the MP1100 particles in the PA66 matrix. Furthermore, according to the literature [6], the crystalline proportion of the compounds was increased through the reactive extrusion and injection molding process. The compounds with chemical bonded oil (PA66-MP1100-OA-cb, PA66-MP1100-MO-cb, PA66-MP1100-OES-cb, and PA66-MP1100-OAMIN-cb) generally have got lower elasticity values than original PA66 and the PA66-MP1100-cb. This is in fact due to the two steps extrusion process. In the first extrusion step, it was expected, that the bonding between oil molecules and MP1100 proceeds by radical reactions selectively. However, PA66-MP1100-OAMIN-cb compound showed the lowest modulus of elasticity in contrast to the other types of PA66-MP1100-oil-cb at the end. This is due to the fact that the NH_2 -end-group of oleyl amine has reacted with the carboxylic group of the MP1100 during the first extrusion step too, resulting in a much higher coupling degree between OAMIN and MP1100, how it was detected by FT-IR-spectroscopy. During the second extrusion step of with PA66 in melt, there are only less or no $-\text{COOH}$ functional groups of MP1100 still available for the chemical reaction that led to a very low bonding of PA66. So, the MP1100-OAMIN-cb is mainly physically distributed in the PA66 matrix. The reactive compounding of PA66 with 20 wt% of MP1100 has reduced the tensile strength values by approximately 10% in the opposite to the plain PA66. The chemically bonded PA66-MP1100-oil-cb compounds with several oil types show only a slight additional decrease effect of the tensile strength (Figure 2) compared to PA66-MP1100-cb.

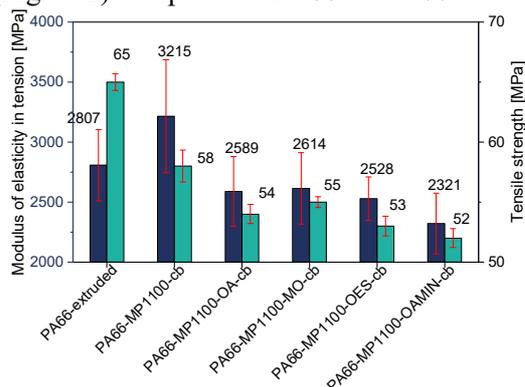


Figure 2: Modulus of elasticity in tension and tensile strength.

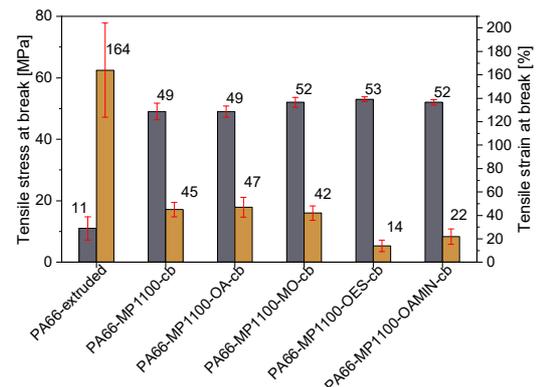


Figure 3: Tensile stress at break and tensile strain at break.

Figure 3 shows the result of tensile stress at break. It is obvious that in the case of PA66-MP1100-cb, the value is four times higher than the value of plain PA66. The samples with chemical bonded oil (PA66-MP1100-OA-cb, PA66-MP1100-MO-cb, PA66-MP1100-OES-cb and PA66-MP1100-OAMIN-cb) did not change the tensile stress at break compared to PA66-MP1100-cb. It is assumed that the oil content (2 wt%) is too low compared to PA66 and MP1100 (80 wt% and 18 wt%) to get a further significant effect. On the other hand, the values of tensile strain at break have drastically decreased

(approximately 70%) when PA66 was compatibilized with MP1100 (approximately 70%). Concerning the various oil types, it was found that for PA66-MP1100-OA-cb and PA66-MP1100-MO-cb, there was almost no sign of any influence of chemical bonded oil on the tensile strain at break. Hypothetically it can be assumed that there is a transamidation reaction between excess Oleic acid and PA66, so that the probability that MP1100 reacts with PA66 could be reduced. The result is that the compatibility between MP1100 and PA66 is lower with the presence of Oleic acid, so the tensile strain at break is reduced compared to the other oil-modified compounds.

In case of Charpy notched impact strength (Figure 4), the compound PA66-MP1100-cb has the highest value, and this is approx. 40% more than the value of plain PA66. As realized before in other combinations this behavior should be the result of chemical bonding as well as the much better breaking down of MP1100 aggregates and distribution of MP1100 particles in the PA66 matrix. The Charpy notched impact strength of the other compounds in the presence of more or less bonded oil are lower than those of PA66-MP1100-cb as the oil interferes with the compatibilization between PA66 and MP1100. The Charpy notched impact strength values decrease in the following order: PA66-MP1100-cb>PA66-MP1100-OA-cb>PA66-

MP1100-MO-cb>PA66-MP1100-OAMIN-cb>PA66-MP1100-OES-cb.

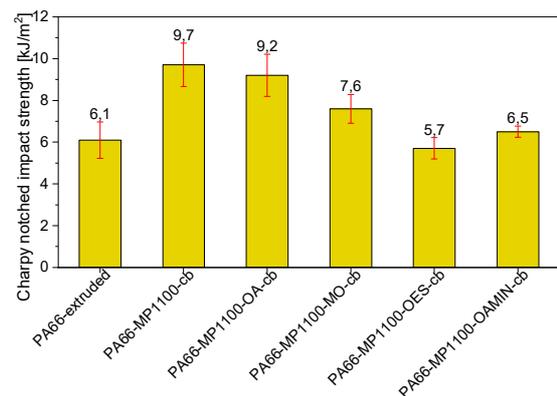


Figure 4: Charpy notched impact strength.

3.2. Result of tribological testing

Figure 5 shows the curve of the coefficient of friction (COF) and the disc temperature (ϑ_{Steel}) of PA66-MP1100-OES-cb in contact with the steel disc, as an example for the PA66-MP1100-oil-cb materials. The temperature was measured approximately 2 mm below the contact surface, which means that the recorded temperature is lower than the current contact temperature. For each compounds, three measurements were carried out. It can be seen that up to a sliding distance of approx. 1 km, the coefficient of friction and the temperature increase rapidly in the running-in phase. Afterwards, the coefficient of friction gradually decreases again and reaches a more or less constant value after a sliding distance of approx. 4 km. This behavior of the coefficient of friction can be attributed to the temperature dependency of the material parameters of the compounds, which influences the adhesive and the deformation parts of the friction forces.

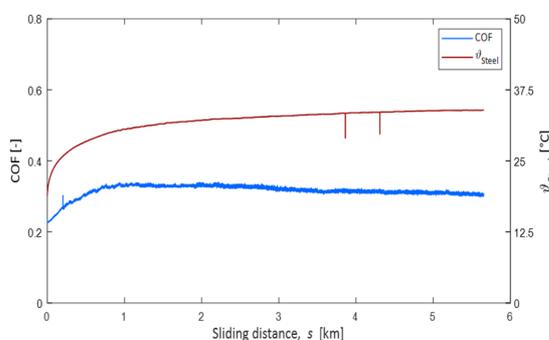


Figure 5: Characteristic behavior of the coefficient of friction and the temperature of PA66-MP1100-OES-cb

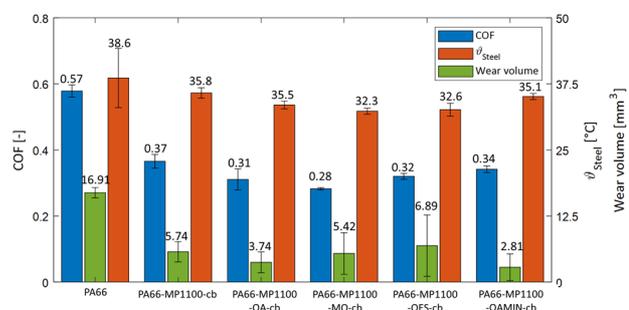


Figure 6: Influence of oil type on the friction behaviour of the PA66-MP1100-oil-cb compounds

Figure 6 shows the influence of four oil types on the friction behavior of PA66-MP1100-oil-cb and the heating of the counter body. The values of the coefficient of friction and temperature shown below

correspond to the mean value of the coefficient of friction from a running distance of 5 km upwards, see Figure 5. Additionally, Figure 6 shows the volume wear of the compounds, calculated with the determined loss of mass at the end of the respective tests using the determined density of the compounds from Table 1. It can be seen that in the load range investigated, the oil type methyl oleate shows a more favorable friction behavior in contact with the steel disc.

Table 1: Density of the compounds

Compound	PA66	PA66-MP1100-cb	PA66-MP1100-OA-cb	PA66-MP1100-MO-cb	PA66-MP1100-MO-cb	PA66-MP1100-OAMIN-cb
Density (g/cm ³)	1,1355	1,2470	1,2435	1,2519	1,2472	1,2515

4. Summary and Outlook

Although only 2 wt% of oil is chemically bonded in PA66-MP1100-oil-cb, its effect is visible in their mechanical properties. The elasticity of the compound with chemically bonded oil is generally lower compared to PA66-MP1100-cb, especially for the compound with oleyl amine (reduce approx. 28%). The Charpy notched impact strength values of the compounds decreases in the following order: PA66-MP1100-cb>PA66-MP1100-OA-cb>PA66-MP1100-MO-cb>PA66-MP1100-AMIN-cb>PA66-MP1100-OES-cb.

The friction behavior of chemically bonded PA66-MP1100-oil is generally better than for PA66-MP1100-cb, among them the compound containing methyl oleate shows the best result.

In the future works:

- We strive for single-step reactive extrusion for the producing of the compounds.
- We use other oil types containing phosphate functional groups to increase the affinity of the compound to the metal surface.
- The influence of the transferred tribo-film on the steel disc will be investigated in the steel/bronze contact.

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