

Plasma modified Polytetrafluoroethylene (PTFE) lubrication of α -olefin-copolymer impact-modified Polyamide 66

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Abstract

Tribological and mechanical properties of α -olefin-copolymer, impact-modified Polyamide 66, containing pristine and plasma treated Polytetrafluoroethylene (PTFE) micro-powders as solid-lubricants have been investigated. The PTFE powders were subjected to low pressure 2.45 GHz microwave plasma treatment with H_2 and NH_3 as the process gases to aid their dispersion in PA66. Formation of polar surface groups in conjunction with significant defluorination was observed for both H_2 (F/C atomic ratio 1.30) and NH_3 (F/C atomic ratio 1.13) plasma treated powders. The H_2 PTFE-impact modified PA66 composites exhibited a 25% increase in their impact energy absorption capabilities (25.0 J) than their pristine counterparts (20.0 J), **along with a significant reduction of the specific wear rate at higher p_v -values. At the p_v -value of 6 MPa.m/s, the specific wear rates for composites containing hydrogen plasma treated PTFE and nitrogen plasma treated PTFE were reduced by 33% ($0.7 \times 10^{-6} \text{ mm}^3/\text{Nm}$) and 50% ($0.6 \times 10^{-6} \text{ mm}^3/\text{Nm}$), respectively, as compared to pristine PTFE - α -olefin PA66 composites ($1.1 \times 10^{-6} \text{ mm}^3/\text{Nm}$); while showing similar coefficient of friction values.** The use of plasma functionalized PTFE powders thus provides a facile route for the production of impact modified PA66 compounds with significantly lower coefficient of friction and higher wear resistance for applications like bearings and sliding elements where impact strength as well as good tribological properties are required.

Keywords: Polyamide 66; Impact modification; Polytetrafluoroethylene (PTFE); Plasma treatment; Solid lubricants; Wear

1. Introduction

Polyamide 66 (PA66) possesses high stiffness, wear resistance and coupled with ease of processing makes it a widely used polymer in tribological engineering applications such as gears and bearings [1,2]. These excellent physical properties result from the presence of hydrogen bonds in molecular chains of the polyamide [3]. However, PA66 shows low notched impact strength and to improve its properties against stress concentration, impact modification of PA66 with polyolefin rubbers/elastomers is well known [4]. Recently, polyolefin elastomers have been introduced as a soft material that can be used as an efficient impact modifier [5–7]. The α -olefin-copolymer is a copolymer of ethylene and another α -olefin such as butane or octane and is produced using metallocene catalysts with narrow molecular weight distribution. As α -olefin-copolymer is a non-polar polymer and has poor miscibility with polar polymers such as polyamides, it is usually functionalised with low molecular weight polar groups on the polymer backbone. During the melt compounding of Polyamide 66 and maleic anhydride grafted α -olefin-copolymer, the amine groups of polyamide react with maleic anhydride to form a graft copolymer which increases the interfacial adhesion between the two phases. This leads to a chemical coupling across the interface during blending with the amine end groups of the polyamides, and to the formation of small particles in the polyamide matrix [7,8]. In fact, the Izod impact value of these modified compounds is more than one order of magnitude higher than for pristine PA66 [6]. Yu et al. have reported that the impact modification with elastomer/rubber is also beneficial for the friction and wear behaviour of these compounds [5], as the modification works as a surface lubricant. However, Chen et al. reported that polyolefin modification in polyamide 66 compounds are only able to form a discontinuous patchy transfer film on the steel counter surface, which causes inconsistent friction and wear rates [9]. Therefore, it is desirable to develop α -olefin-copolymer impact modified Polyamide 66 compounds in conjunction with solid lubricants like

Polytetrafluoroethylene (PTFE), which are able to form continuous friction films and thereby promoting a consistent tribological behaviour.

In the literature, the friction and wear behaviour of pristine nylons have been enhanced by using fillers and modifications [10–13] or by blending it with other polymers [14,15]. One of the predominant solid lubricants used with Polyamide 66 is Polytetrafluoroethylene (PTFE), which - due to its low coefficient of friction - is a well-known anti-adhesive material [16]. Significant amount of literature has been published on the influence of PTFE modification on polyamide and its compounds [17–20]. It was shown that PTFE decreases the coefficient of friction (CoF) and potentially also the wear rate, however, the mechanical properties of the compounds are reduced significantly. This reduction in the mechanical properties is largely due to the poor wettability and distribution of PTFE in the polyamide matrix. Polyamide-PTFE compounds are often produced via the melt mixing process, wherein the different surface energies of polar polyamide and non-polar Polytetrafluoroethylene results in its poor distribution in the polyamide matrix [21]. As a consequence, the friction and wear properties can vary in a wide range and are often poorly reproducible, even between samples of the same batch. The reported CoF and wear rates, especially when established as single point data, often do not reflect this inconsistent friction and wear behaviour. Furthermore, the presence of PTFE as a second phase weakens the mechanical properties of the compound. Therefore, a number of efforts have been made to alter the chemical structure of PTFE to incorporate functional groups *via* chemical etching, such as reduction with e.g sodium naphthalene [21,22] or electron beam irradiation of PTFE [23–25]. The incorporation of functional groups changes the polarity and therefore the surface energy of PTFE, which enables the formation of inter-molecular forces to the polyamide matrix [25]. PTFE can also be functionalized by the use low pressure microwave plasma and the method offers a versatile route to alter the surface of PTFE without affecting the bulk properties of the material [26]. It is easy to control

[26], environmentally friendly, and relatively low in cost [27]. The functionalization of PTFE sheets, films or sintered components is already well known and the authors have recently reported on the functionalization of PTFE powders using low-pressure microwave plasma and their possible use as a tribological filler in high temperature Polyethersulfone composites [28,29]. The available literature reveals that H₂ and NH₃ plasma treatment of PTFE leads to defluorination accompanied by the production of hydrocarbons, cross-linking, chain scission and, depending on the feed gas used, incorporation of oxygen- and nitrogen-containing groups [30–32].

In this work, PTFE micropowders functionalised via low pressure NH₃, H₂ microwave plasma treatment are used as a solid lubricant for enhancing the tribological properties of α -olefin-copolymer impact modified Polyamide 66. The compounds are further analysed using a host of characterization techniques such as mechanical testing, dynamic mechanical thermal analysis, X-ray photoelectron measurements and tribological measurements.

2. Experimental

2.1. Low pressure Microwave plasma treatment of PTFE powders

Commercially available PTFE micro powder TF9201Z (Dyneon™, Burgkirchen), with a specific surface area of 10 m²/g (ASTM 4567) and an average primary particle size of 6µm (ASTM 4464), was plasma treated in a “Nano” microwave plasma device (Diener electronic GmbH + Co. KG, Ebhausen, Germany). The plasma device is equipped with a rotary glass drum and is suitable for the treatment of polymer powders of up to 3 kg quantity at a time. The plasma treatment conditions used were similar to our previous works and are briefly described below [28,29]. A base pressure between 0.2-0.8 mbar was created using a rotary pump after loading the PTFE powder in the plasma chamber. Once the

desired base pressure was achieved, the process gas (H_2 or NH_3) was fed into the chamber and 2.45 GHz microwave plasma (270 W) excited using high voltage at the preferred working pressures. The gas flow and rotation rate of the glass drum were held constant to ensure uniform treatment of powders as they passed the excited plasma between the electrodes. The modified PTFE samples were then removed from the chamber and sealed in a plastic bag, at ambient laboratory conditions, for subsequent analysis and further use with α -olefin-copolymer impact modified Polyamide 66.

2.2 Preparation of α -olefin -copolymer impact modified PA66-PTFE compounds

The PA66-PTFE compounds were produced using commercially available α -olefin-copolymer impact modified PA66 and pristine, plasma modified PTFE powders. The impact modification of PA66 is typically achieved via the incorporation of 20% grafted α -olefin copolymer [33,34]. The α -olefin copolymer itself is composed of ethylene-1-butene copolymer grafted with maleic anhydride (trade name TAFMER MA7010) consisting of 67.9 wt% ethylene, 31.6 wt% butene and grafted with 0.5wt% maleic anhydride. In fact, the α -olefin-copolymer impact modified PA66 is considered as a two phase system, consisting of a hard phase (80% PA66) and a soft phase (20% α -olefin copolymer) and shows a density of 1.07 g/cm^3 with a melt volume-flow rate (MVR) of $3.84 \text{ cm}^3/10 \text{ min}$ ($275^\circ\text{C}/5\text{kg}$).

The PA66-PTFE composites were melt compounded on a co-rotating twin screw extruder, Coperion ZSK26 MCC with subsequent water bath cooling and pelletizing facilities. The temperature settings on the six zones of the barrel were chosen in the range of $260\text{-}285^\circ\text{C}$ with the die plate temperature of 280°C . For comparative purposes, and the impact modified PA66 is compounded with both pristine and plasma treated PTFE powders at 10 wt% loading. The formulation of the compounds and the corresponding sample names are shown in Table 1. Further preparation of samples for mechanical and tribological testing is described in the characterisation and testing section.

Table 1: Material designation and composition of various samples

Sample name	Composition
1-PA66-T0	Impact modified PA66 (80% Polyamide 66 + 20% α -olefin-copolymer)
2-PA66-T2	PA66 impact + 10% wt pristine PTFE (no plasma treatment)
6-PA66-H2	PA66 impact + 10% wt H ₂ plasma treated PTFE
28-PA66-NH3	PA66 impact + 10% wt NH ₃ plasma treated PTFE
31-PA66	PA66 (for comparison purposes)

2.3 Characterisation and Mechanical, Tribological testing

X-ray photoelectron spectroscopy (XPS) data were obtained on an AXIS Nova Spectrometer (Kratos Analytical Ltd., UK) having a monochromated Al K α X-ray source (excitation energy of 1486.6 eV) by pressing the PTFE powders onto a high-vacuum carbon tape using clean glass slides to provide a smooth surface for analysis. For binding energy calibration, the signal was calibrated to the F-C-F peak in the high-resolution C1s spectra at 292.8 eV or the F1s signal at 689 eV. Dynamic mechanical thermal analysis (DMTA) were carried out in tensile mode with a TA Instruments DMA 2980 at a frequency of 1 Hz, a heating rate of 10°C min⁻¹ and a temperature range of 30-200°C.

Standard tensile test bars, according to ISO 527 and dart drop test plates with dimensions of 60 mm x 60 mm, with a thickness of 2 mm were moulded on Krauss Maffei KM125-390 injection moulding machine. The moulding process temperatures were chosen in the region of 255°C to 280°C and the PA66-PTFE compounds were dried in a dessicant drier prior to the moulding process. Values from the tensile test according to DIN EN 527-2 were determined on a Zwick universal tensile tester Z020 (Zwick GmbH & Co. KG, Ulm). The melt volume-flow rates (MVR), according DIN ISO 1133, were generated on a Zwick Aflow plastometer by applying a temperature of 275°C and a load of 5kg. In order to investigate multiaxial impact behaviour of the compounds, an instrumented dart drop test was conducted according to DIN EN ISO 6603-2 on a high speed tester (Coesfeld GmbH, Dortmund). The

dart drop test measures the ability of the material to absorb energy before fracture. During the test, a dart with a diameter of 20 mm and a weight of 20.33 kg falls down on pneumatically fixed test plate. The dart is equipped with a load cell which measures the maximum force (F_m) encountered during the impact. The velocity of the falling dart is 4.4 m/sec and causes either plastic or elastic deformation, eventually leading to the failure of the material. The absorbed energy (E_m) is the integral of the area under the force displacement curve [35]. Charpy impact tests according to DIN 179-1 were conducted using a Zwick instrumented impact tester. The test was performed using a bar cut from the center of a multi-purpose specimen, notch type "A", and tested edgewise. The scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDAX, Oxford Instruments) analysis of the fracture surface was carried out using a Hitachi S3200 electron microscope at 1.5kV and the samples were sputtered with thin film of gold prior to imaging.

The tribological measurements including friction and wear data were obtained on a 4-station block-on-ring Atlas TriboTester at Tribologic GmbH (Kaiserslautern, Germany). The TriboTester is equipped with sensors, that enable time resolved tracking of friction, wear and counter body temperature. In this block on ring test according to ASTM G137 [36], the test friction and wear are generated by pressing a block-shaped test specimen against the outer circumference of a rotating bearing steel (100Cr6, 1.3505) ring, which was hardened to 60 HRC and ground to $R_a = 0.1 - 0.2 \mu\text{m}$. The test specimen were CNC milled from the inner section of tensile test bars. The injection moulded skin was removed during the machining in order to rule out effects that might originate from an uneven particle distributions in close-to-the-surface regions of the test specimen precursors (see cross sectional EDAX Fig. 1 in the supplementary information). The size of the contact area was 4 mm x 4 mm, for a nominal contact area of 16 mm². After machining all tribological test specimens were conditioned in a HPP 108 (Memmert GmbH, Germany) constant climate chamber according to ASTM D 618 [37] at 23

°C and 50 % relative humidity for at least 40 h. Directly before the start of each wear test, the corresponding polymer specimens as well as the steel counter bodies were thoroughly cleaned and degreased using petrol ether. In order to prevent a Hertzian contact between the initially planar test specimen and the curved steel ring, full conformal contact was established by introducing a thin strip of 1200 grit-sand paper into the contact and by subsequent grinding of the plastic test specimen until it has assumed the shape of the ring. The sand paper is removed and both the plastic and the metal ring are cleaned again with petrol ether. This procedure prevents the initial phase of the test to be flawed by the transition from line or Hertzian contact to full conformal contact. With high performance plastics, this alone can take several hours. The same is true for the wearing off of geometric errors like edge loading. Therefore, the breaking-in phase of the experiment is roughly limited to reaching thermal equilibrium, forming a transfer film (if so) and changes in surface topography (especially of surface roughness).

For PTFE, it is well known that the coefficient of friction decreases upon an increased in the load [38]. While high loadings may be the preferred usage of PTFE, low absolute CoFs would make it even more difficult to detect any potential difference between individual PTFE variants. Therefore the contact pressure was intentionally kept at rather low 2 MPa (= 32 N absolute load). It is a well-known effect that materials may exhibit similar friction and wear at a given $p\nu$ (where $p\nu$ is the product of contact pressure p and sliding speed ν) but start to yield different values for CoF and wear rate when the $p\nu$ values are increased. In order to examine the different PTFE variants at variable $p\nu$ -values, ν was incrementally increased from 1 m/s to 3 m/s in steps of 0.5 m/s while keeping p at 2 MPa (for the aforementioned reasons). The coefficient of friction μ was calculated by the measured friction force F_F and the applied normal force F_N according to $\mu = F_F / F_N$. The test specimen's height loss Δh was also tracked in a time resolved manner, which gives direct access to the linear wear rate w :

$$w = \frac{\Delta h}{\Delta t} \quad (1)$$

In this work, the thus defined linear wear rate w was obtained by ignoring the first 50 % of each data set. At speeds of 1 m/s this is due to the “breaking-in” that happens in the first stage of this first sliding speed segment. When the initial speed segment is over and sliding speed is increased to 1.5 m/s, more frictional heat gets dissipated and hence a new thermal equilibrium needs to be reached. During this the test specimen height loss signal is distorted by the thermal expansion of the polymeric test specimen as well as of all other components of the test setup. Therefore, evaluation according to Eq. 1 was delayed until friction and temperature have reached their new respective equilibrium values. As a general rule, this was simply done by ignoring the first 50 % of each sliding speed segment’s data set. On the second 50 % of the data set, the volume loss data – which is computed from the height loss data according to the utilized test specimen geometries – is approximated by a linear fit using the method of least squares. The linear wear rate is then computed from the slope of the resulting linear function. The specific wear rate w_s , was further calculated from w , using the applied contact pressure p and the sliding speed v , according to:

$$w_s = \frac{1}{pv} \cdot w \quad (2)$$

In order to ensure a reasonable statistical resolution of the test procedure, all friction and wear tests were done in octuplicate. Outlying observations were eliminated by standard procedures and arithmetic means, standard deviations and confidence intervals were computed from the outlier-free data samples.

3 Results and discussion

3.1 XPS analysis of NH₃ and H₂ plasma treatment on PTFE micro powders

As clearly observed in Table 2, both the H₂ and NH₃ plasma treatments were successful in modifying the surface of PTFE micro-powders by the action of plasma species resulting in defluorination. The wide energy survey spectra for pristine PTFE and NH₃, H₂ plasma treated samples (Figure 1(a)) only displayed peaks corresponding to carbon, fluorine and nitrogen/oxygen, indicating at the purity of the process. Significant changes in the peak shape of the C1s core level could be observed (Figure 1(b)) due to the addition of surface moieties and the defluorination effects of the plasma species. For pristine PTFE, only a single peak at binding energy of 292.2 eV, corresponding to -CF₂- bond could be observed which exhibited a narrow full width at half-maxima (FWHM) of 1.45 eV. Upon plasma functionalisation, an increase in the FWHM of this peak was observed (1.66 eV for H₂/10h/PTFE and 1.78 eV for NH₃/10h/PTFE), which can be attributed to the formation of new functional groups as well as chain scission [39]. With the use of H₂ as the process gas, hydrogen (C-H) and oxygen (C-O, C=O) functionalities were grafted on the PTFE surface leading to an increase in the O/C ratio. The presence of oxygen can be attributed to the removal of samples from the plasma device to the ambient environment and to the low-base pressure of the system during functionalisation process. Inagaki et al. have ascribed peak positions of 285.9–286.0, 287.6–287.9, 289.6–289.8, 293.5, and 294.9 eV, in H₂ treated PTFE surfaces to CH₂-CHF, CHF-CH₂ and C=O, CH(OR)-CHF, CF₂-CF₂, and CF₃-CF₂ groups, respectively [32]. According to Vandencastele [26], the small peak at 294 eV, at sample PTFE H₂/10h can be attributed to CF₃ components, produced via chain scission. As compared to pristine PTFE which displayed F/C ratio of 1.86, the hydrogen plasma led to a reduction in the F/C ratio to 1.30 (Table 2).

The C1s envelope of NH₃ plasma treated samples exhibits a considerable increase in the component at 285 eV, and can be ascribed to the formation of -C-C- and -C-H_x moieties [30,31]. Peaks located at 286.0, 288.2 and 291.9 eV can be ascribed to C-O/C-N and C=O, respectively. Similar to the case of

oxygen for H₂ plasma treated samples, we can assume that the oxygen observed for NH₃ treated samples is from the low base pressure of the system and exposure to ambient environment. The results of higher defluorination upon NH₃ treatment versus H₂ treatment are in accordance with results of Badey et al [40,41]. Further details on the defluorination mechanism can be found in our previous works [28, 29]. Using a method proposed by Khan et al [42], based on the calculation of carboxyl group as a measure of higher wettability, we have utilised XPS analysis to analyse the changes in PTFE upon plasma treatment. While the surface concentration of carboxyl groups for pristine PTFE was only 3.29% out of the total area under the C1s envelope, upon H₂ plasma treatment this value went up to 4.49% and reached a further value of 7.43% for NH₃ plasma treatment. Thus, both the NH₃ and H₂ plasma treatments are suitable for defluorination of PTFE and consequent attachment of nitrogen and oxygen polar moieties which can help in altering the surface energy of PTFE.

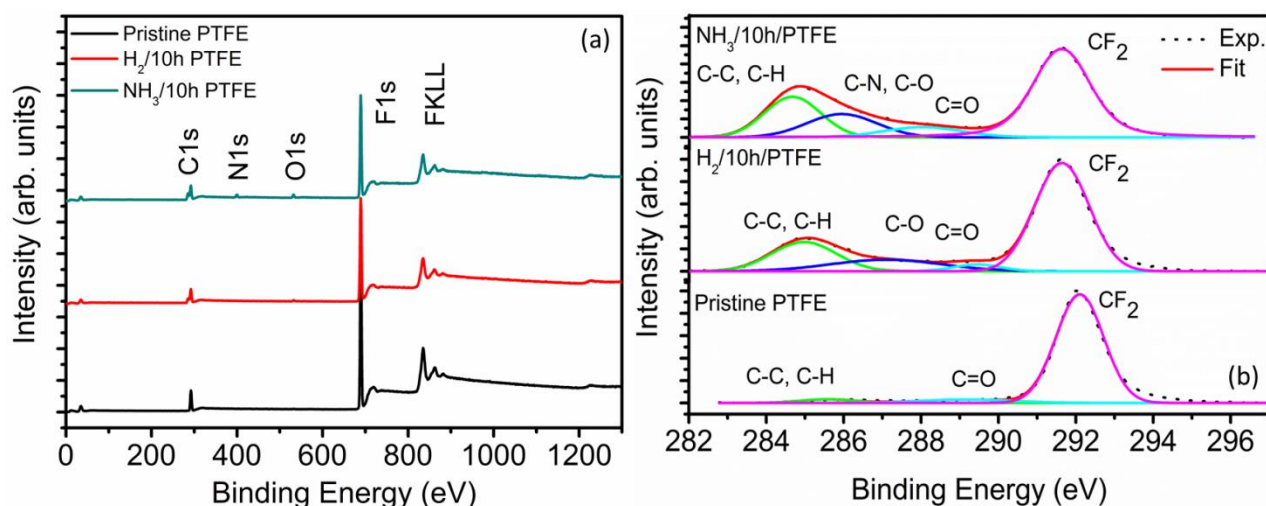


Figure 1: (a) Wide energy survey spectrum (WESS) and (b) deconvoluted core level C1s spectrum of pristine, H₂ and NH₃ plasma treated PTFE powders.

Table 2: Atomic percentages and elemental ratios of pristine and plasma treated PTFE powders

Sample	Atomic percentage [%]				Elemental ratios		
	C	F	O	N	F/C	O/C	N/C
Pristine PTFE	34.94	65.06	--	--	1.86	--	--
PTFE NH ₃ /10h	44.85	50.81	1.66	2.68	1.13	0.04	0.06
PTFE H ₂ /10h	43.11	56.04	0.85	--	1.30	0.02	0.00

3.2. Mechanical and tribological properties of PA66-PTFE compounds

3.2.1. Tensile and flow properties:

Table 3 shows the values obtained from the tensile test according to DIN ISO 527 and the MVR flow test values according to DIN ISO 1133. It can be clearly observed that the impact modification of PA66 significantly decreases both the Young's modulus as well as tensile strength. While, commercially available PA66 (sample 31-PA66) exhibits a Young's modulus of 3.5 GPa and a tensile strength of 90.0 MPa; upon impact modification the corresponding values are reduced to 1.76 and 44.0 MPa, respectively. This dramatic drop in the mechanical properties can be ascribed to the formation of a two-phase system in impact modified PA66. Due to the significant difference in the surface energies of Polyamide and α -olefin copolymer, there exists only weak interfacial interaction between the two phases leading to the lower mechanical properties. Upon impact modification, the tensile strain at break increases from 7% to 58%; while the viscosity increases significantly due to the rubber modification. The effect of addition of pristine PTFE on the Young's modulus and tensile strength of the PA66-PTFE compounds is small; with the tensile strength reducing from 43.6 MPa (for impact

modified PA66, 1-PA66-T0) to 39.9 MPa (10 wt% pristine PTFE, 2-PA66-T2) and the corresponding Young's modulus decreasing from 1.76 GPa to 1.74 GPa, respectively.

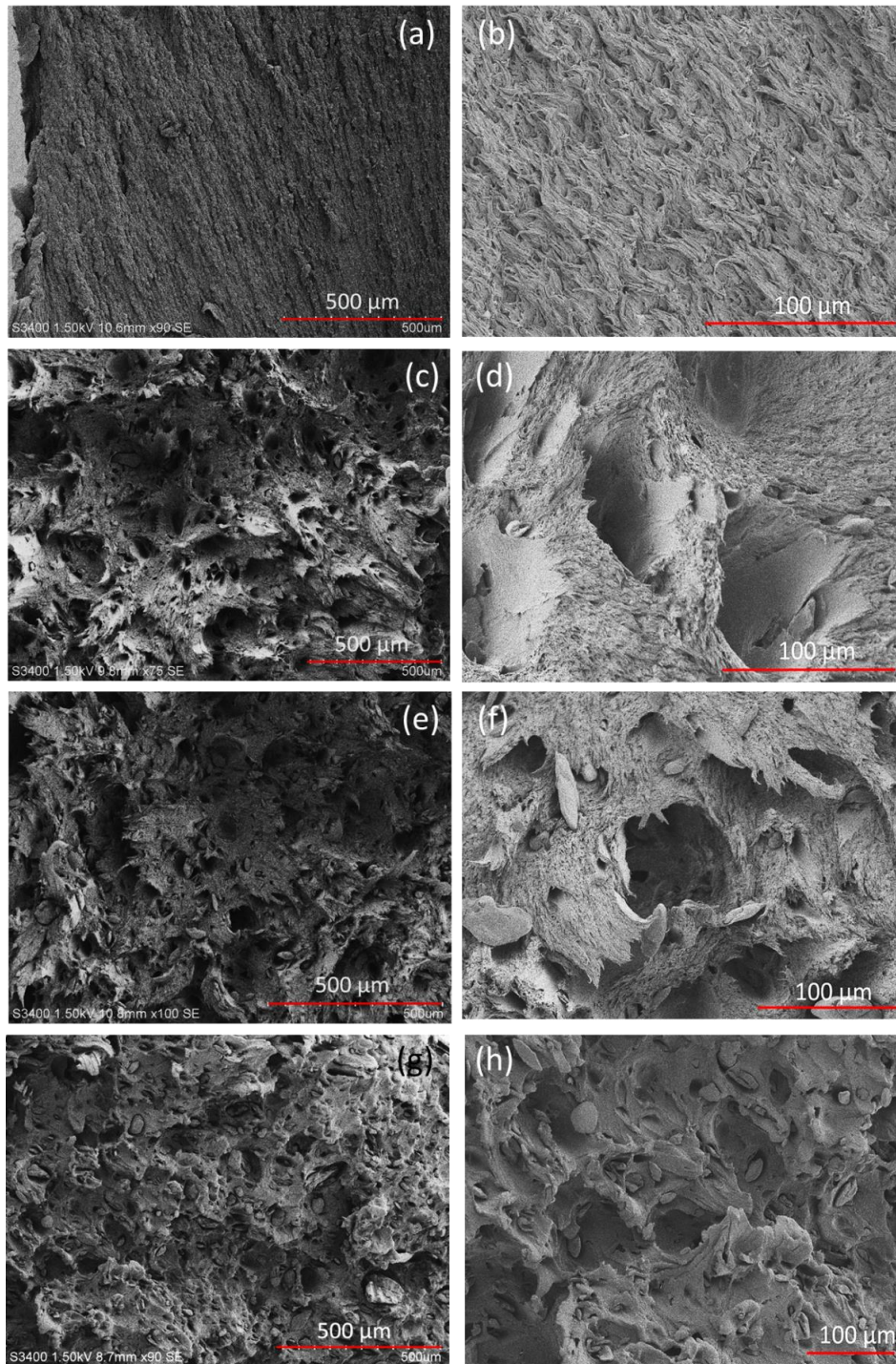


Figure 2: SEM analysis of the fracture surface of (a, b) 1-PA66-T0, (c, d) 2-PA66-T2, (e, f) 6-PA66-H2 and (g, h) 28-PA66-NH3 samples.

Table 3: Mechanical and melt volume flow properties of PA66 and PTFE-PA66 compounds.

Sample name	Young's modulus (MPa)	Tensile strength (MPa)	Tensile strain at break (in %)	Strength Charpy Notched test (kJ/m²)	MVR range (360°C / 10 kg cm³ / 10 min)
	ISO 527-1/2	ISO 527-1/2	ISO 527-1/2	ISO 179-2-1eA	ISO 1133
31-PA66	3.500	90.00	7.00	12.00	136
1-PA66-T0	1.758	43.63	57.84	32.00	3.84
2-PA66-T2	1.744	39.92	45.07	17.20	3.30
6-PA66-H2	1.758	40.18	46.60	12.90	3.34
28-PA66-NH3	1.733	41.45	38.28	15.40	3.98

This decrease in the tensile strength can be attributed to the low friction nature and soft behaviour of PTFE filler between the PA66 layers which do not resist the stretching/tensile force but rather assists in it leading to a reduction in the tensile strength and elongation [12]. The values of tensile strength and Young's modulus for plasma treated PTFE composites are quite similar to that of pristine PTFE-impact modified PA66 composites. For same percentage of addition of PTFE, the plasma modified PTFE powders do not show any significant improvement in the tensile properties as compared to the pristine PTFE powders for the composites. Franke *et al.* showed that the e-beam functionalisation (in the presence of oxygen) of PTFE powders induced carboxylic groups on the PTFE surface, which in conjunction with the high shear rates encountered in the melt mixing helped in the uniform distribution of PTFE in the PA matrix [21,24]. This is accompanied by formation of chemical bonding via the trans-amidation reaction leading to an enhancement in the mechanical and tribological properties of the compounds [21,24]. In our case, the number of potential amine groups, reacting with the incorporated functional groups of the PTFE, is already limited due to the total modification content of 30 wt% (20 wt% α -olefin copolymer and 10 wt% PTFE). During the impact modification process with grafting of an α -olefin copolymer by means of maleic anhydride, some amine groups have already

reacted with the maleic anhydride coupling agent [43,44] and therefore are not able to react with the functional groups present on the plasma treated PTFE and therefore the intended improvement in the tensile properties does not emerge completely [21,24]. **Figure 2 (a-h)** shows the SEM images of the fracture surface for pristine and plasma modified impact modified PA66 compounds. For impact modified PA66 samples, plastic deformation and fibrillation of the PA66 matrix is the dominant mechanism which leads to the failure of the material. The rubber modification provides sites to induce multiple crazing and shear yielding which can effectively diffuse the fracture energy throughout the polymer matrix [45]. During the tensile testing, the interface between the PTFE particles and the impact modified PA66 matrix plays a key role for crack initiation and propagation. For pristine PTFE compounds (2-PA66-T2), there exists no chemical interaction between the polymer matrix and the PTFE particles and the tensile force experienced during the testing leads to a separation between the filler material and the matrix which can lead to the extracting of the soft filler phase as observed in **Fig. 2(c, d)**. While the fracture mechanism is still dominated by the plastic deformation of the PA66 matrix, the extraction of PTFE particles (**Fig. 2(d)**) also plays a significant role in lowering the tensile strength of the compounds at the interface. In the case of plasma treated PTFE compounds, it was observed that the distribution and de-agglomeration of PTFE particles in the matrix was significantly better, especially for NH₃ plasma treated PTFE powders. For both the H₂ and NH₃ plasma treated PTFE impact modified compounds, the tensile failure was still caused by the conjunction of plastic deformation and extraction of PTFE particles from the matrix. However, due to the improved dispersion of the PTFE particles, the extraction of the PTFE particles for NH₃ plasma treated sample was not as severe and the de-agglomeration ensured that the fracture energy was distributed all across the surface (**Fig. 2 g, h**).

As compared to pristine PA66, the α -olefin modified PA66 shows significantly higher viscosity, which can be attributed to the rubber modification. The PTFE micro-powders are well known additives for improving the melt flow properties of thermoplastic resins, however, the addition of PTFE to impact modified PA66 did not reveal any appreciable change in the flow properties of the compounds. The addition of pristine PTFE showed slightly anomalous behaviour in which 10wt% addition of PTFE enhanced the viscosity ($3.30 \text{ cm}^3/10 \text{ min}$) and the subsequent increase to 20wt% lowered the viscosity ($3.72 \text{ cm}^3/10 \text{ min}$). The addition of both H_2 and NH_3 plasma treated PTFE powders did not led to any significant improvements in the melt flow properties with the NH_3 treated samples (28-PA66-NH3) showing nearly the same MVR values as compared to the pristine PTFE addition.

3.2.2. Impact behaviour:

Figure 3(a) shows the force-time diagram for the impact modified PA66 and pristine, plasma treated PTFE-impact modified PA66 compounds. While the impact modified PA66 (sample 1-PA66-T0) shows a typical ductile fracture behaviour, the addition of PTFE, both pristine and plasma treated, changes this to ductile brittle behaviour, as observed in the abrupt loss of values after having reached the values of maximum force (F_m). All curves with PTFE modification follow this trend. As observed clearly from Figs. 3(a, b), the incorporation of pristine unmodified PTFE only marginally lowers the maximum force (F_m) and energy absorption (E_m) values. While the pristine impact modified PA66 (1-PA66-T0) exhibits a maximum force of 3.7 kN and an energy absorption of 26.4 J; the corresponding values for pristine PTFE-impact modified PA66 (2-PA66-T2) are 3.3 kN and 20.8 J, respectively. However, the addition of plasma treated PTFE seems to provide a beneficial effect to the multi-axial impact behaviour. In fact, both the F_m and E_m values for H_2 (6-PA66-H2) are higher than that of pristine PTFE-impact modified PA66 samples. While the pristine PTFE-impact modified PA66

compound (2-PA66-T2) exhibits a maximum force of 3.35 kN and an energy absorption of 20.8 J; the corresponding values for H₂ plasma treated PTFE-impact modified PA66 samples are 3.57 kN and 25.0 J, respectively. The F_m and E_m values for NH₃ plasma treated PTFE-impact modified PA66 samples (28-PA66-NH3) are only marginally higher than those of the pristine PTFE-impact modified PA66 samples. Although the value of maximum force (F_m) and energy absorption (E_m) of the compound containing the hydrogen treated PTFE (6-PA66-H2) does not completely reach the values of compound 2-PA66-T0, we have to take into consideration that the total modification content (soft phase) of the PTFE containing compounds is 30 wt%, and therefore 10 wt% higher than the pristine impact modified compounds. This beneficial effect can be attributed to the incorporation of the functional groups in the PTFE modification. The higher surface energy of the plasma modified PTFE enables a better dispersion in the polyamide-rubber-matrix and therefore promotes improved multi-axial impact behaviour. As observed in Table 3, upon the addition of α -olefin-copolymer to PA66, the notched impact strength of impact modified PA66 test increased sharply from 12.0 kJ/m² to 32.0 kJ/m² which can be attributed to the addition of elastomer which prevents crack propagation in compounds during the impact [34,43,46]. The addition of 10 and 20 wt% pristine PTFE to the impact modified PA66 reduces the notched impact strength significantly to 17.20 kJ/m² and 11.50 kJ/m², respectively, due to the formation of a three-phase system of elastomer, PA66 and PTFE. While the addition of H₂ and NH₃ plasma treated PTFE powders reduced the notched impact strength, the change in this strength was much smaller for NH₃ plasma treated samples as compared to H₂ plasma treated samples. In fact, the NH₃ plasma treated samples retained nearly 90% of the notched impact strength (15.90 kJ/m²) as compared to the addition of pristine PTFE powders, which can be attributed to the possible interactions between the amide groups of polar PA66 and functional nitrogen polar groups on plasma treated PTFE. As discussed earlier, during the impact modification process, some amine groups have

already reacted with the maleic anhydride coupling agent and are therefore not able to interact significantly with the functional groups on PTFE, leading to the reduction in the interaction and hence the intended improvement in notched impact strength does not emerge completely [21,24].

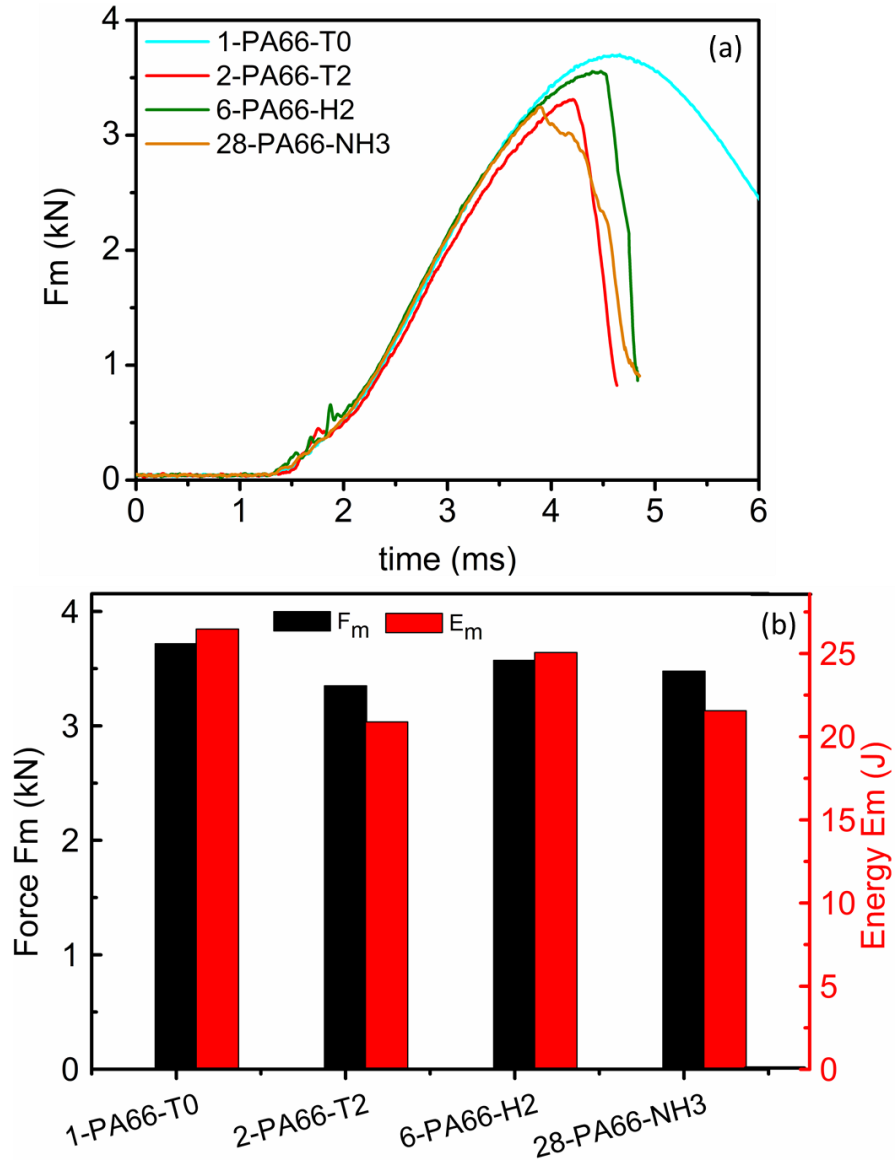


Figure 3: (a) Force displacement curves of impact modified compounds; (b) Total energy (E_m) and maximum force (F_m) values obtained from the dart drop test of PTFE-PA66 samples.

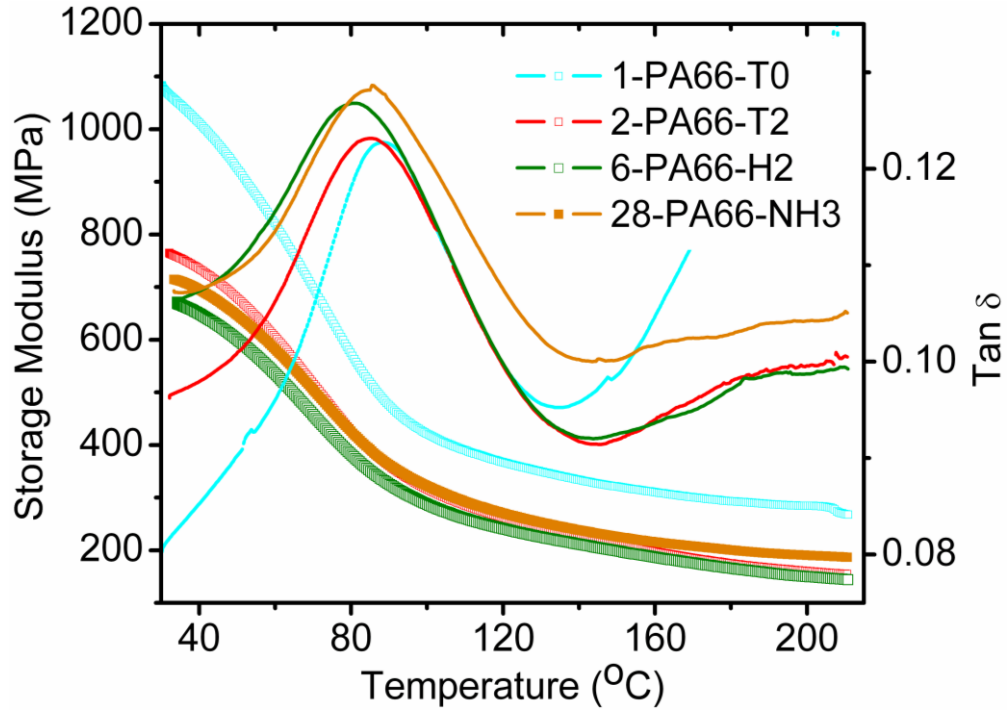


Figure 4: Plots of storage modulus and $\tan \delta$ versus temperature for impact modified PA66 and its composites with pristine and plasma treated PTFE powders.

Figure 4 shows the dynamic storage modulus and loss tangent versus temperature for various PTFE impact modified PA66 composites. It can be clearly observed that the addition of PTFE reduces the storage modulus, E'' , for both rubbery and glassy regions. This reduction in the storage modulus can be ascribed to the addition of “soft” PTFE material in conjunction with the presence of the α -olefin elastomer. Now, the dynamic modulus indicates the inherent stiffness of the material under dynamic loading. In the region where the dynamic modulus-temperature curve has an inflection point, the $\tan \delta$ goes through a maximum, which essentially is the glass transition (T_g) temperature region. Consequently, the pristine impact modified PA66 showed a T_g of 88.40°C which was reduced to 85.10°C for addition of 10wt% pristine PTFE and to a further 81.20 °C with the addition of 10wt% H₂ plasma treated PTFE. Similar effects have also observed by Zeynali et al. [47] However, the addition

of NH₃ plasma treated PTFE to the impact modified PA66 was able to reverse this trend by enhancing the T_g to 85.40 °C, which is quite close to the values observed for the addition of pristine PTFE. We believe that the presence of hydrogen bonding and possible interaction between the amine groups of PA66 with the polar groups of NH₃ treated PTFE increase the hindrance of the main chain motion of PA66. This increased hindrance results in the relaxation peak of PA66 being shifted back to higher temperatures, resulting in the increased T_g as well as higher value of tan δ, as compared to pristine and H₂ plasma treated PTFE composites [12]. The trend was replicated in the storage modulus as well wherein the NH₃ plasma treated PTFE composites showed higher storage modulus in the glassy as well as rubbery regions as compared to H₂ plasma treated composites.

3.2.3. Tribological behaviour of PA66-PTFE compounds:

Now, as mentioned earlier, the tribological behaviour of the samples was studied in octuplicate due to the limited repeatability of friction and wear tests, especially at higher $p\nu$ values. Figure 5 shows typical examples of the measured curves (for 10 wt% pristine PTFE- α -olefin PA66), including loss in height, Δh , coefficient of friction, μ , and the temperature change, ΔT at $p\nu$ values of 2, 4 and 6 MPa.m/s, respectively. It should be noted that the curves represent average values obtained from the all valid individual curves, i.e. all curves not belonging to values designated to be outlying. At the beginning of all five speed segments (only three shown for the sake of brevity), the (average) height loss rate is negative because of the thermal expansion of the specimens and the test setup. When the corresponding thermal equilibrium is reached, thermal expansion stops and the height loss rates become positive. As mentioned earlier in section 2.3, the first half of each segment was not utilised for data extraction purposes (see Fig. 6). In fact, during the second half of each segment, no significant

changes in friction, wear and temperature values could be observed, which we consider to be the proof of having chosen sufficiently long test durations for every segment.

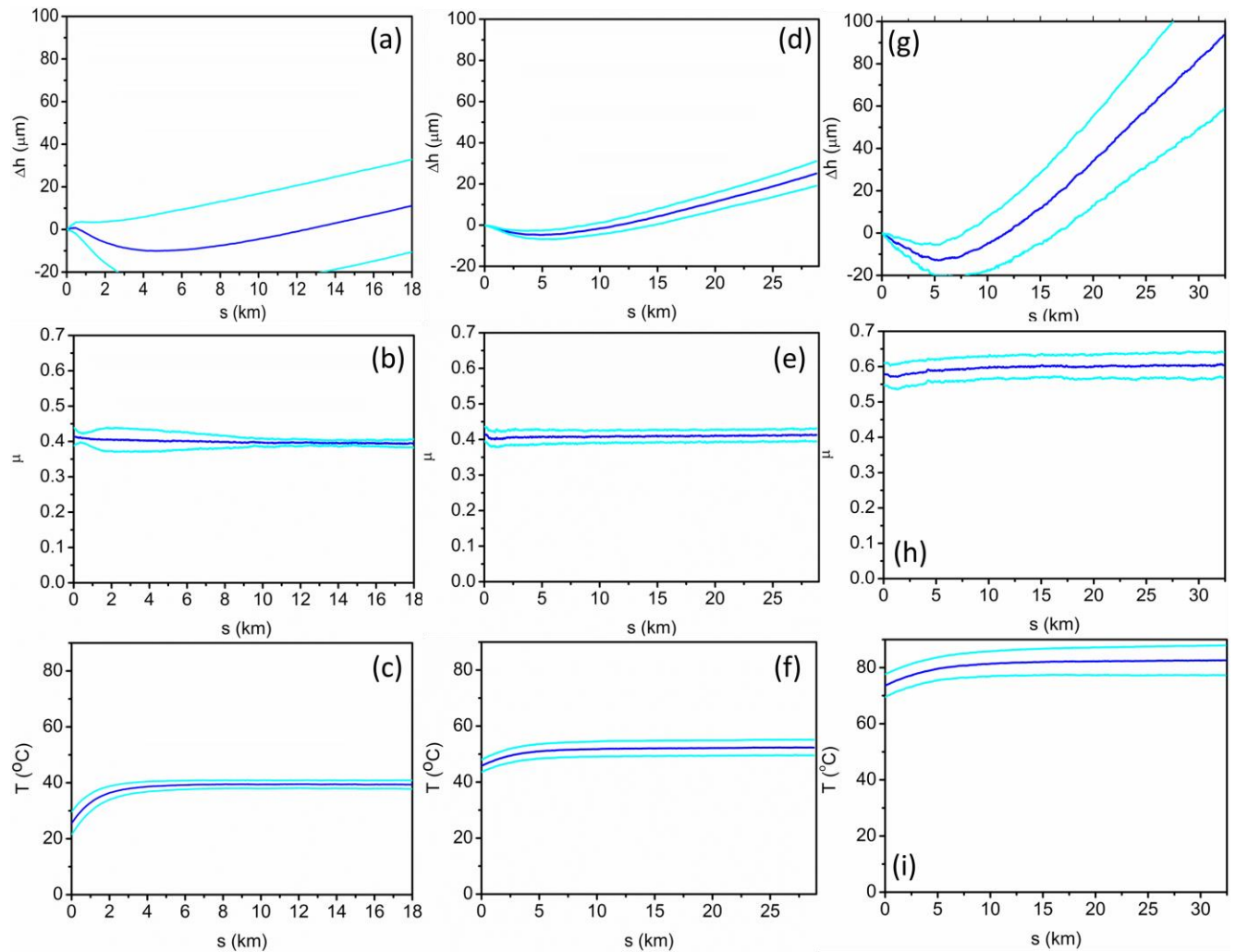


Figure 5: Average curves (dark blue) of test specimen height loss (top), CoF (middle) and counter body temperature (bottom) and upper and lower boundaries (light blue) of the corresponding confidence intervals. From left to right sliding speed increases from 1 m/s to 3 m/s in steps of 1 m/s.

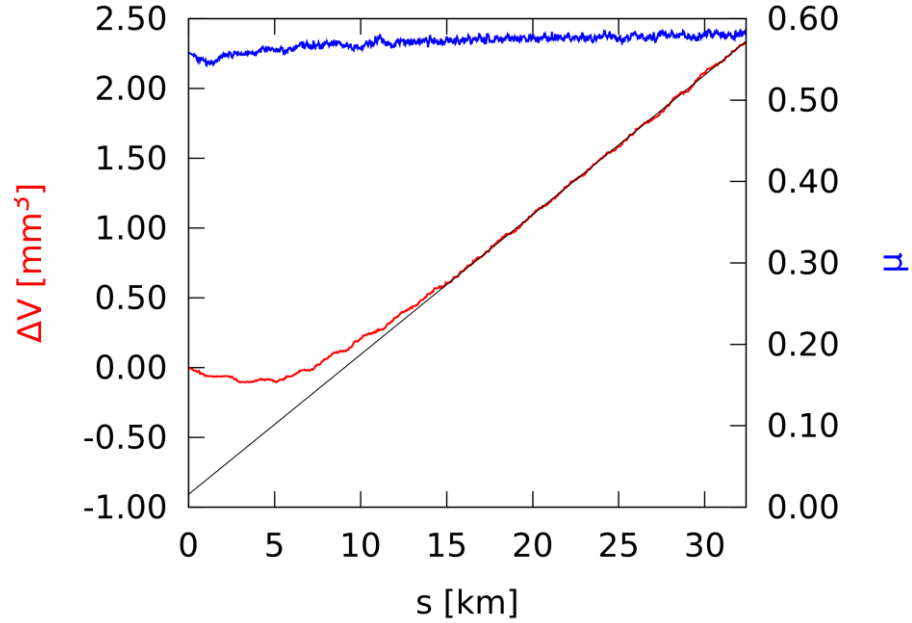


Figure 6: Typical example of the time resolved tracking of volume loss ΔV (red) and coefficient of friction μ (blue) of a selected polymeric test specimen (1-PA66-T0 at 3m/s), as well as the linear fit (black) in the second half of the experiment.

Table 4: Linear and specific wear rate of the investigated materials as a function of sliding speed.

Sample		31-PA66		1-PA66-T0		2-PA66-T2		6-PA66-H2		28-PA66-NH3	
Speed	pv	w_t	w_s	w_t	w_s	w_t	w_s	w_t	w_s	w_t	w_s
[m / s]	[M Pa · h]	[$\mu\text{m}/\text{h}$]	[$10^{-6} \text{mm}^3/\text{N m}$]	[$\mu\text{m}/\text{h}$]	[$10^{-6} \text{mm}^3/\text{N m}$]	[$\mu\text{m}/\text{h}$]	[$10^{-6} \text{mm}^3/\text{N m}$]	[$\mu\text{m}/\text{h}$]	[$10^{-6} \text{mm}^3/\text{N m}$]	[$\mu\text{m}/\text{h}$]	[$10^{-6} \text{mm}^3/\text{N m}$]
1.0	2	10±1	1.4±0.1	7±1	1.0±0.1	4±1	0.6±0.1	4±1	0.6±0.1	4±1	0.6±0.1
1.5	3	15±2	1.4±0.2	9±2	0.8±0.2	6±1	0.6±0.1	6±1	0.6±0.1	5±1	0.5±0.1
2.0	4	22±4	1.5±0.3	11±2	0.8±0.1	8±2	0.6±0.1	7±2	0.5±0.1	6±1	0.4±0.1
2.5	5	50±6	2.8±0.3	24±4	1.3±0.2	12±3	0.7±0.2	10±2	0.6±0.1	9±2	0.5±0.1
3.0	6	215±	10.0 ±1	50±9	2.3±0.4	24±4	1.1±0.2	16±3	0.7±0.1	12±2	0.6±0.1

Table 5: Coefficients of friction of the investigated materials as a function of sliding speed

Sample		31-PA66	1-PA66-T0	2-PA66-T2	6-PA66-H2	28-PA66-NH3
Sliding speed	pv	CoF	CoF	CoF	CoF	CoF
[m / s]	[MPa · m/s]	[1]	[1]	[1]	[1]	[1]
1.0	2	0.52 ± 0.02	0.41 ± 0.02	0.35 ± 0.01	0.40 ± 0.02	0.34 ± 0.02
1.5	3	0.57 ± 0.02	0.42 ± 0.02	0.34 ± 0.02	0.40 ± 0.02	0.35 ± 0.02
2.0	4	0.61 ± 0.04	0.43 ± 0.02	0.36 ± 0.02	0.41 ± 0.02	0.35 ± 0.01
2.5	5	0.72 ± 0.05	0.57 ± 0.03	0.39 ± 0.02	0.42 ± 0.03	0.37 ± 0.02
3.0	6	0.82 ± 0.06	0.64 ± 0.05	0.40 ± 0.03	0.44 ± 0.02	0.40 ± 0.03

Table 6: Counter body temperatures of the investigated materials as a function of sliding speed.

Sample		31-PA66	1-PA66-T0	2-PA66-T2	6-PA66-H2	28-PA66-NH3
Sliding speed	pv	Counter body temperature [°C]	Counter body temperature [°C]	Counter body temperature [°C]	Counter body temperature [°C]	Counter body temperature [°C]
[m / s]	[MPa · m/s]					
1.0	2	61 ± 2	40 ± 1	41 ± 2	44 ± 2	40 ± 2
1.5	3	65 ± 2	47 ± 2	46 ± 1	49 ± 2	45 ± 1
2.0	4	70 ± 2	55 ± 2	49 ± 3	53 ± 3	49 ± 2
2.5	5	82 ± 3	71 ± 6	56 ± 3	58 ± 4	55 ± 3
3.0	6	108 ± 5	88 ± 7	62 ± 3	65 ± 4	61 ± 5

Tables 4-6 show the numeric results extracted from the observed curves, i.e. the linear (w) and specific (w_s) wear rates (Table 4), the coefficients of friction (Table 5) and the counter body temperatures (Table 6) for the various applied sliding speeds. All numbers represent 95%-confidence intervals, composed of arithmetic mean and 95 %-confidence. As can be seen from Table 4 and Figure 7(a, b), pristine PA66, i.e. without any impact or friction modifier, exhibited rather high friction and wear

values. Up to 2 m/s (= 4 MPa m/s), its specific wear rate amounts to nearly $1.4 \times 10^{-6} \text{ mm}^3/\text{Nm}$ and rises quickly when the speed, v , is increased further. The increase in the $p\nu$ values beyond 4 MPa m/s causes the specific wear rate to nearly double its value from $1.5 \times 10^{-6} \text{ mm}^3/\text{Nm}$ to $2.8 \times 10^{-6} \text{ mm}^3/\text{Nm}$ and thus can be considered to be the critical $p\nu$ value for the investigated pristine PA66 (Fig. 7(a)). The CoF of neat PA66 starts out at 0.52 at 1 m/s which is higher than the usually reported span of 0.25 – 0.40 for PA66 vs. steel in pin on disc or thrust washer tests [48, 49]. This discrepancy is a frequently observed by the authors for the utilized block on ring test method [9] and it is especially characteristic for the specific combination of tribometer and steel counter body that has been used for the tests. With increasing sliding speeds, the CoF increases even further until it reaches 0.82 at 3 m/s (Figure 7(b)). This increase of friction with increasing sliding speed can also be observed for the other investigated materials. This behavior is in good agreement with values reported by Biswas and Kalyani [38]. The observed high CoFs of neat PA66 resulted in counter body temperatures of up to 108 °C at 3 m/s.

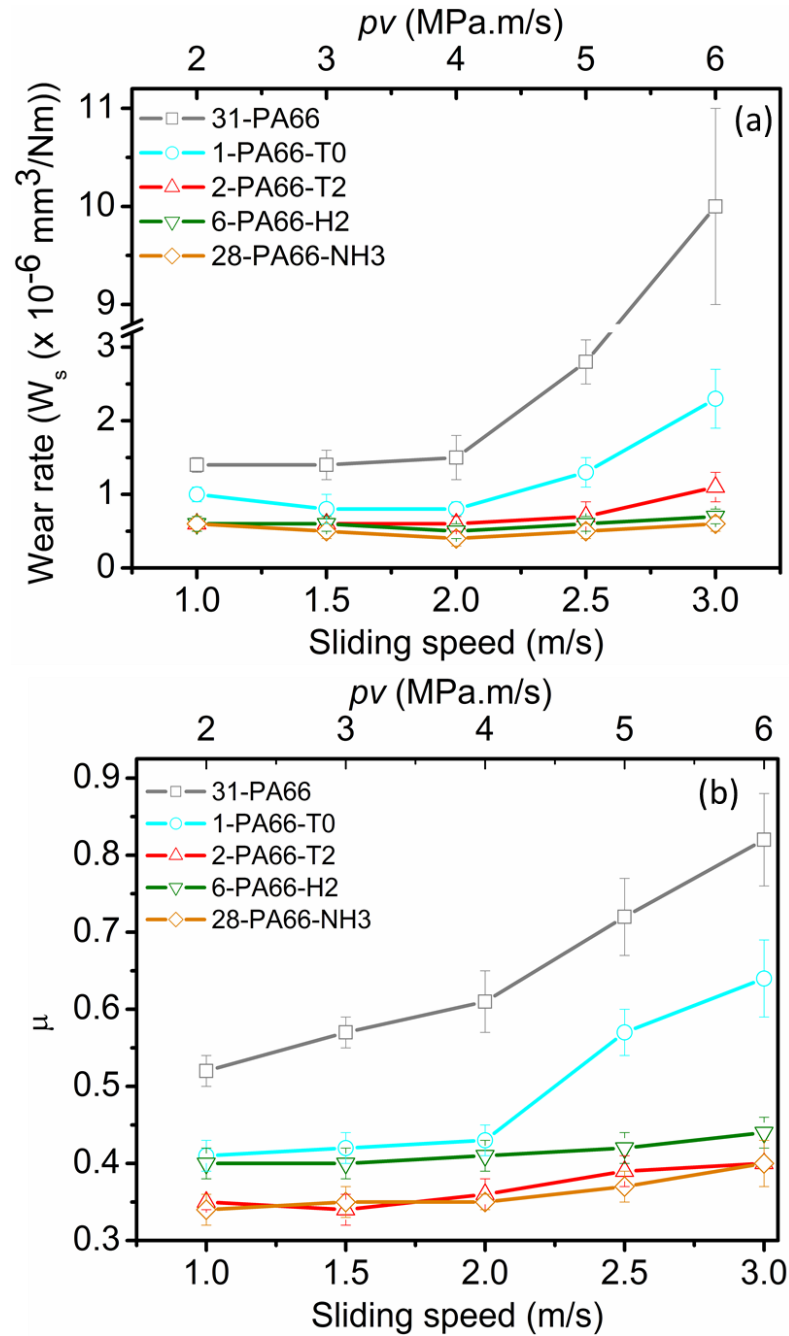


Figure 7: (a) Specific wear rate for pristine and composite samples as a function of sliding speed, (b) variation of coefficient of friction as a function of sliding speed.

The addition of the impact modifier (α -olefin copolymer) not only significantly reduces the wear rate but also increases the limiting pv to 5 MPa.m/s, beyond which the specific wear rate nearly doubles

when increasing v from 2.5 m/s to 3.0 m/s, i.e. by 20 % (Fig. 7(a) and Table 4). The values of coefficient of friction (Table 5, Fig. 7(b)) were also reduced significantly by the addition of the impact modifier – on average by 25 % – which also resulted in significantly lower counter body temperatures (see Table 6). Based on the existing literature reports, temperature has a huge and significant impact on the wear behavior of unreinforced plastics. The authors attribute the observed reduction in wear and the increase in limiting pv , primarily to the 25 % reduction of friction and therefore to the lower generation of frictional heat. It has been observed previously by Chen et al, that polyolefin modification in polyamide 66 compounds are only able to form a discontinuous patchy transfer film on the steel counter surface, which causes inconsistent friction and wear rates [9]. Similar observations of higher CoF values and temperature rise for pristine PA66 as compared to impact modified PA66 has also been reported by Yu et al. [5]. Now, the introduction of 10 wt.% pristine PTFE to the impact modified material led to a further reduction of wear rate by about 40 % from $1.0 \times 10^{-6} \text{ mm}^3/\text{Nm}$ to $0.6 \times 10^{-6} \text{ mm}^3/\text{Nm}$ (for 2 MPa m/s, see Table 3). Again, when increasing v beyond 2.5 m/s the specific wear rate increases significantly, however not by 100 % as for the PTFE-free but impact modified material but ‘only’ by about 50 %. At 1 m/s only a rather small reduction of the coefficient of friction is observed – from 0.41 to 0.35 - when adding pristine PTFE to the impact modified PA66. However, the PTFE is able to significantly abate the overproportional increase in friction and temperature that is observed for neat and impact modified PA66 at higher sliding speeds (see Table 4-6). As regards the wear rates, the specific wear rate are nearly constant around $0.6 - 0.7 \times 10^{-6} \text{ mm}^3/\text{Nm}$ until speeds of 3 m/s are reached, where it significantly increases to $1.1 \times 10^{-6} \text{ mm}^3/\text{Nm}$. Now, as compared to the pristine PTFE, the addition of plasma modified PTFE – H_2 - or NH_3 -treated – does not result in further significant reduction of the coefficient of friction. As reported in our prior work, the plasma treated PTFE exhibits a lower contact angle [28] and thus can exhibit improved adhesion properties with the

PA66 matrix. In fact, the coefficient of friction of composites containing plasma treated PTFE is therefore slightly higher (for H₂ plasma treated) or similar (for NH₃ plasma treated) than as compared to the reference sample containing pristine PTFE (Fig. 7(b)). Bismarck et al. have observed similar increase of coefficient of friction for short term plasma treatment of LDPE [50]. However, both the plasma treated PTFE powders were able to reduce wear at the highest applied sliding speed, i.e. 3 m/s (6 MPa.m/s). For both the plasma treated impact modified PA66 compounds, the specific wear rates varied between 0.5 to 0.7 x 10⁻⁶ mm³/Nm with the variation always being within the boundaries of the confidence interval. Hence the limiting $p v$'s of these materials amount to 6 MPa m/s, at least, which is a notable improvement over pristine PTFE, whose PA66 composite yields a limiting $p v$ of 5 MPa m/s. However, to further probe these interactions and how the plasma treatment of PTFE powders affects the formation of the friction film during the run-in and steady state conditions [51], further analysis using techniques such as XPS needs to be carried out as a function of sliding distance and will be the subject of future work.

4. Conclusions

The α -olefin copolymer modified Polyamide 66 compounds containing pristine and plasma treated PTFE were mechanically and tribologically evaluated and benchmarked against pristine Polyamide 66. The PTFE micropowders were plasma treated using low-pressure NH₃ and H₂ microwave plasma technique resulting in the successful incorporation of polar surface moieties. The H₂ plasma treated PTFE-impact modified PA66 composites exhibited a 25% increased energy absorption capabilities (25.0J) than their pristine counterparts (20.0 J). Although the coefficient of friction is slightly increased by the plasma treatment of the PTFE modification, the treatment has proven to be beneficial for the specific wear rates at higher $p v$ -values and, connected to this, to increase the limiting $p v$ of PA66

filled with 10 % PTFE. At a $p\nu$ -value of 6 MPa m/s, the specific wear rate could be reduced by about 33% for the composite containing hydrogen plasma treated PTFE and by about 50% for the composite containing ammonia treated PTFE (as compared to pristine PTFE). Therefore, despite being limited in scope, we consider our friction and wear tests to support the assumption that the incorporation of functional groups via plasma treatment can be an effective and efficient route enhancing the tribological properties of PA66.

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