DEVELOPMENT AND CHARACTERIZATION OF PTFE NANOPOWDER-ELASTOMERIC COMPOSITES FOR TRIBOLOGICAL ALLPICATIONS

M. Sohail Khan[a*], D. Lehmann[a], G. Heinrich[a] and R. Franke[b]

[a] Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, D-01069 Dresden, Germany, khan@ipfdd.de

[b] IMA Materialforschung und Anwendungstechnik GmbH Dresden, Wilhemine-Reichard-Ring 4, D-01109 Dresden, Germany

ABSTRACT

The effect of the PTFE particles on the physical and tribological properties of EPDM rubber filled with non-irradiated and irradiated PTFE nanopowder has been investigated. The friction coefficient values of non-irradiated and irradiated PTFE filled EPDM composites decreased significantly compared to EPDM gum. The friction coefficient values also decreased with increasing PTFE loading. Non-irradiated PTFE-EPDM blends beside its significantly poor physical properties showed high wear resistance compared to the poor wear-resistant behaviour of higher irradiation dose PTFE filled EPDM having enhanced physical properties. Scanning electron microscopy of the PTFE powder suggested that radiation induced alterations are the key parameters in controlling both the physical and wear behaviour of PTFE filled composites. Radiation-induced chemical alterations in PTFE nanopowder characterized by electron spin resonance and FTIR spectroscopy showed increasing radical concentration and carboxylic groups (-COOH), respectively, whereas the mean agglomerate size decreased with increasing irradiation dose. The influence of these specific alterations on physical and tribological properties of EPDM is investigated.

1. INTRODUCTION

Polytetrafluoroethylene (PTFE), a highly crystalline polymer with melting temperature around 330 °C, possesses unique properties. Chemically inert, it has high chemical and heat resistance with upper service temperature around 260 °C [1]. It is usually blended with other polymers or reinforced as a composite material for special purpose applications [2-4]. For tribological purposes, PTFE and its fluoropolymers have found a wide use as a solid lubricant in different applications such as bushings. Although, it has unique low friction characteristics, it suffers from high wear rate because of its smooth molecular morphology [5]. For this reason, it is extensively used in conjunction with various kinds of fillers, thermoplastics and resins in order to exploit its inherent low friction characteristics and at the same time reduce its high wear rate behaviour [6-11]. Recently the development of chemically coupled PTFE compounds has opened a new route in producing enhanced wear resistant materials for high performance tribological applications [12-13]. In order to expand its utility in technical elastomers, a new class of modified PTFE filled SBS, NBR and EPDM compounds were produced which have the potential to be used as wear-resistant materials [14]. For this reason, modified PTFE micropowder were further utilized in a carbon black filled NBR recipe to obtain wear-resistant material for sealing applications [15]. However, a comprehensive investigation based solely on the friction and wear mechanism of PTFE coupled elastomers along with their physical properties in the mentioned studies has not been reported so far. Optimization between the tribological properties and physical properties is an important criteria in the development of new rubber compounds such as seal, gasket etc. Our preliminary investigations conclude that chemically coupled PTFE nanopowder in

EPDM enhances the physical properties [16]. However, the factors influencing the physical properties of the PTFE based EPDM might not hold true for their tribological properties. In this regard, the present work was designed specifically to provide an overview of the influence of the PTFE nanopowder on the physical and tribological properties of PTFE based elastomeric composites. The effect of PTFE loading, irradiation dose employed and PTFE dispersion in elastomeric composites containing irradiated PTFE, non-irradiated PTFE and without PTFE in EPDM is discussed.

2. EXPERIMENTS

2.1 Materials

Both EPDM (Buna EP G 6850) with ethylidene norbornene (ENB) content 7.7 wt%; ethylene content 51 wt%; Mooney viscosity, ML (1+4) at 125 °C, 60; ash content 0.2 wt%; specific gravity, 0.86; and peroxide (Perkadox 14-40 MB GR) were supplied from Lanxess Deutschland GmbH, Germany while coagent (R-20S/Saret 634C) was used from Sartomer, USA. PTFE nanopowder (Algoflon L100X) with a mean particle size and specific area of 17.7 μm and 26 g m^{-2}, respectively, was used as received from Solvay Solexis, Italy.

2.2 Electron beam modification of PTFE powder

PTFE powder was irradiated with 20 kGy (low dose) and 500 kGy (high dose) of irradiation doses with the help of ELV-2 electron beam accelerator from Budker Institute of Nuclear Physics, Novosibirsk, Russia, installed at the Leibniz Institute of Polymer Research, Dresden. Irradiation was carried out in air at the room temperature. Irradiation dose of 20 kGy per pass were applied to avoid excess temperature rise which might favour deactivation of the radical formation. Further information about our irradiation facility can be found in [17].

2.3 PTFE nanopowder characterization

Number of free radicals was determined with the help of MiniScope MS200 electron spin resonance (ESR) instrument from Magnettech Limited, Germany. Spin numbers for each absorbed dose were calculated after four hours of electron treatment. Fourier Transform Infrared Spectrometer (FTIR) spectra were recorded on Vertex 80v (Bruker) FTIR spectrometer (4000 - 400 cm^{-1}, resolution = 2 cm^{-1}, 32 scans per measurement) in transmission mode on 10 μm thin PTFE foils to observe the chemical changes induced in PTFE nanopowder having exposed to different absorbed doses.

The mean agglomerate size was determined with the help of the particle size analyzer, Sympatec HELOS HO367 from Sympatec GmbH having a measuring range of 0.5/0.9-175 μm. The primary and mean agglomerate size of PTFE nanopowder was 70-80 nm and 17.7μm, respectively, as received from the supplier.

2.4 Measurement of physical properties

Tensile strength and percentage elongation at break were carried out according to ISO 527 at a cross-head speed of 200 mm/min using tensile testing machine (Zwick, Germany). Tear resistance was carried out according to DIN 53507 at a test speed of 100 mm/min. Hardness values were measured according to DIN 53505, using a Shore A Durometer. Indentations were made at several points for each specimen for the measurements of the average hardness values.

2.5 Friction and wear testing

A pin on disk test machine according to ASTM G 99 – 2005 (Implant Sciences) was used. A hardened carbon steel ball (German standard 100Cr6, 59±1 HRC, near AISI L3 steel) with a diameter of 5.0 mm and an initial surface roughness of Ra = 0.2 µm served as counterpart. The ball slides against the EPDM material. The polymer specimens are produced as plate with a square of (40 x 40) mm² and a thickness h = 2 mm. The plates are adhesive bonded to the steel plate. A sliding speed of v = 0.05 ms^{-1} is applied. The diameter of the rotation was 10 mm in each case. The tribological investigations were performed with a constant load of F_N = 1N over a testing time of t_B = 2 h. The tests were carried out at room temperature.

The wear scar shape was measured with a profilometer (Pertometer CONCEPT 6.2) at the end of each test. The shape was measured at four different locations. In each case the point was shifted around an angle of 90°. The wear volume was calculated with the assumption of a half circular area of the wear scar shape. The specific wear rate k is defined by the following equation:

$$k = \frac{W_V \ [mm^3]}{F_N \cdot s \ [N \cdot m]},$$

where W_V is the volume of the removed material, F_N is the normal load and s is the sliding distance. During the test, the coefficient of friction µ was recorded continuously. For a better comparison between the different types of materials, the average values of the friction coefficients [µ] at the end of each test are reported. It applies to all series that the mass wear loss of the counterpart ball was always below the detection limit of the scale with an accuracy of 0.1 mg.

2.6 Microstructure analysis of the EPDM-PTFE compounds

Scanning electron microscopic (SEM) analysis was performed on the wear scar after loading to observe the changes brought in by the counter-surface after repeated sliding and to assess the failure mechanism involved in wear of PTFE filled composites. SEM was performed with the help of LEO 435 scanning electron microscope (SEM - acceleration voltage 20 kV) from LEO Electron Microscopy Ltd, England.

3. RESULTS AND DISCUSSION

3.1 Effect of modification on the molecular structure of PTFE

Electron treatment generates persistent reactive free radicals and functional groups on the surface due to degradation of PTFE nanopowder by chain scission. Figure 1 visualizes the radiation induced degradation of PTFE in the presence of air. It has been reported that PTFE undergoes C-F and C-C scission during energy rich electron modification process. C-F scission results in secondary radicals while C-C scissions produce primary free radicals. These free radicals react with atmospheric oxygen to yield stable perfluoroalkylperoxy radicals. Besides these peroxy radicals, carbonyl fluoride groups are also formed which hydrolyses in the presence of atmospheric moisture to form carboxylic acid groups (-COOH). Chemical changes introduced in PTFE after exposure to electron treatment were monitored by FTIR spectroscopy. Figure 2 shows several new bands in the infrared spectrum of modified PTFE. The peak at 1884 cm^{-1} was identified with carbonyl fluoride groups (-COF) while 1810 cm^{-1} are free and 1777 cm^{-1} are associated carboxylic acid groups (-COOH).

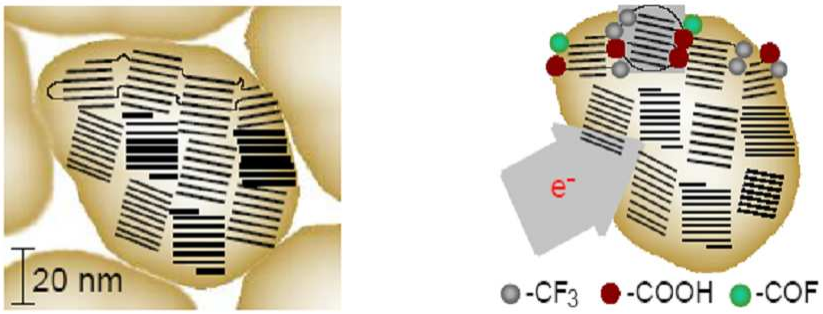

Figure 1. Radiation induced degradation of high molecular weight PTFE nanopowder

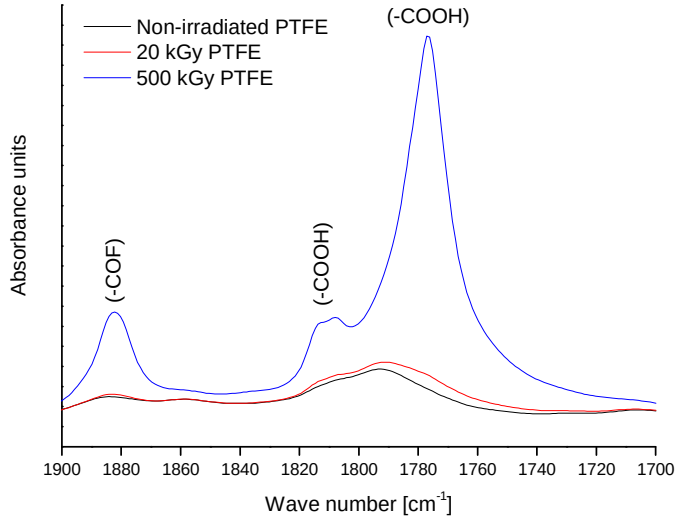

Figure 2. Infrared spectra (1900-1700 cm^{-1}) of PTFE nanopowder modified to different irradiation doses in comparison to non-irradiated PTFE

3.2 Friction and wear behaviour

The friction coefficient (μ) and the specific wear rate (k) of the EPDM gum and PTFE filled composites as a function of PTFE loading are shown in Figure 2. It is seen that the friction coefficient decreased for all the PTFE filled composites compared to EPDM gum. A gradual decrease in the friction coefficient can be observed with increasing PTFE loading for both the irradiated and non-irradiated filled vulcanizates. The friction coefficient decreased from 2.1 in case of EPDM gum to almost less than 1.0 for 50 phr PTFE filled vulcanizates. However, at constant PTFE loading the friction coefficient is weakly dependent on the irradiation dose. This could be due to the formation of a thin PTFE transfer film at the interface of the counter-surface. The existence of transfer film

is common for PTFE filled compounds. This transfer film mechanism generally leads to the similar friction values. The specific wear rate values compared to EPDM gum decreased for all the PTFE filled vulcanizates except for 500 kGy (high dose) PTFE filled vulcanizates, which showed the weakest resistance to wear with increasing PTFE loading.

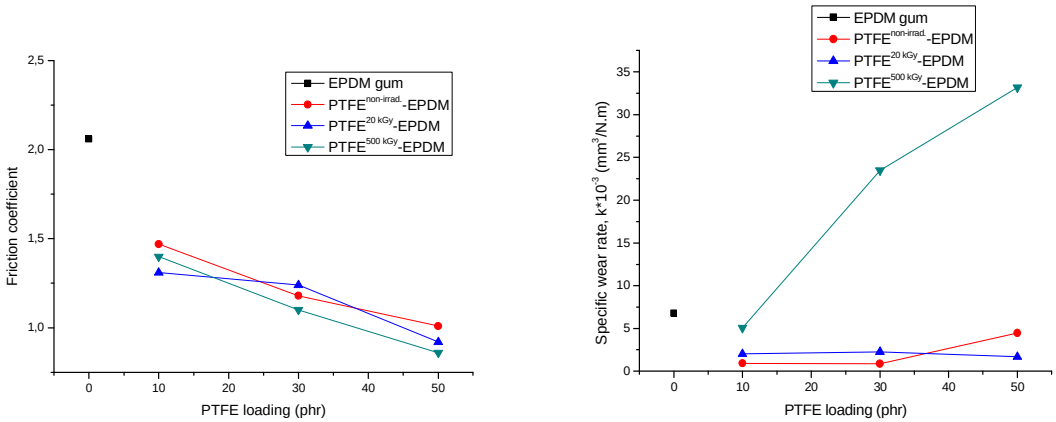

Figure 2. Friction coefficient (a) and specific wear rate (b) as a function of PTFE loading for EPDM gum, non-irradiated and irradiated PTFE filled vulcanizates

However, both 20 kGy PTFE and non-irradiated PTFE filled EPDM show almost similar and reduced specific wear rate for all PTFE loadings.
Table 1 shows the effect of irradiation dose on the radical concentration and the mean agglomerate size of PTFE powder. The highest irradiation dose of 500 kGy has the highest radical concentration and the smallest mean agglomerate size. For a slightly 20 kGy irradiation dose, the agglomerate size is reduced from 17.7 μm for non-irradiated PTFE powder to 4.24 μm. Non-modified PTFE nanopowder has extremely low radical concentration due to the absence of reactive free radicals. Radical concentration increased with irradiation dose while on the other hand the mean agglomerate size of the PTFE powder is decreased due to chain scission of the high molecular weight PTFE powder as shown in Figure 1.

Table 1. Effect of the different irradiation doses on the mean agglomerate size and radical concentration of irradiated PTFE.

Radiation dose (kGy)	Mean agglomerate size, x_{50} (μm)	Radical concentration (spin numbers/g)
0	17.7	3.15 E+15
20	4.24	6.48 E+17
500	3.67	2.04 E+18

Figure 2 (a) shows that the friction coefficient for various PTFE filled composites is weakly dependent on the mean agglomerate size. It is reasonable to consider that PTFE based composites generally exhibited a low friction compared to unfilled EPDM gum and their friction is almost independent of the agglomerate size and structural changes due to irradiation. However, in general these factors play an important role in the wear behaviour of the different filled systems [6, 18, 19].

Although, PTFE itself is known to have no wear-reducing capability, SEM analysis of these PTFE nanopowder indicates that the strong influence of the irradiation dose on the mean agglomerates size and structural changes are the key factors in controlling the wear behaviour of PTFE filled EPDM. Enhanced wear abrasion resistance of the bigger agglomerates is prominent in case of the non-irradiated PTFE filled EPDM. The wear-reducing action of the comparatively smaller PTFE agglomerates is poor in case of 500 kGy PTFE filled EPDM composite.

3.3 Analysis of the wear mechanism

SEM morphologies shown in Figure 3 have been performed on the wear scars of (a) 20 kGy and (b) 500 kGy PTFE filled composites to investigate the possible wear mechanism involved in their wear abrasion. The surface of the 20 kGy PTFE filled vulcanizate indicates the presence of large PTFE agglomerates. The large agglomerates appear to have been firmly embedded within the matrix. The worn track surface shows that these large PTFE agglomerates have been excessively abraded by the counter-surface. The binding of these large PTFE agglomerates is due to their physical locking in the EPDM matrix making it difficult for the counter-surface to remove them from the surface as compared to smaller PTFE agglomerates which become easily detached.

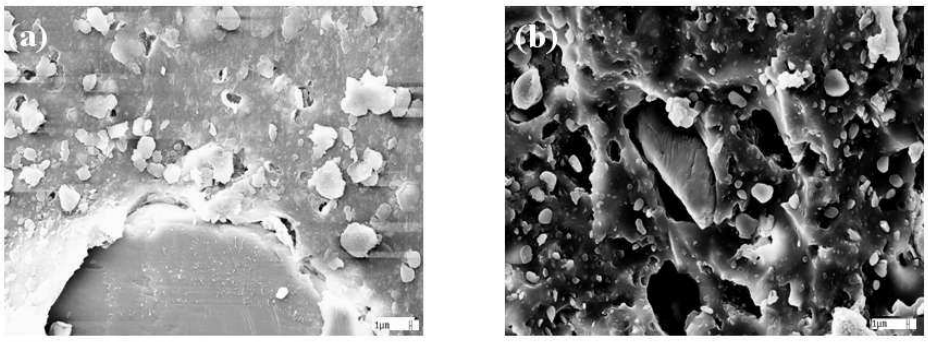

Figure 3. Scanning electron micrographs showing the worn surfaces of: (a) 20 kGy PTFE filled EPDM; (b) 500 kGy PTFE filled EPDM.

For 500 kGy PTFE filled EPDM with smaller particles, the load supporting action is diminished. The worn topography of these materials resembles those of the EPDM gum except for the presence of the small PTFE agglomerates. This suggests that the mode of deformation for these materials have occurred in the deep regions of the soft matrix or at the interfaces between the matrix and small particles. No load supporting action and wear resistance of the small PTFE particles itself have been observed in such case. This indicates that the soft matrix itself suffered from severe wear.

3.4 Physical and wear properties relationship

Figure 4 shows the physical properties of 30 phr PTFE filled vulcanizates in comparison to EPDM gum. Although, 500 kGy irradiated PTFE in EPDM significantly enhanced the tensile strength at break, elongation at break and tear resistance, it deteriorated the hardness of the filled composites. It is interesting to note that hardness Shore A of 500 kGy PTFE filled vulcanizate and EPDM gum is the same as indicated

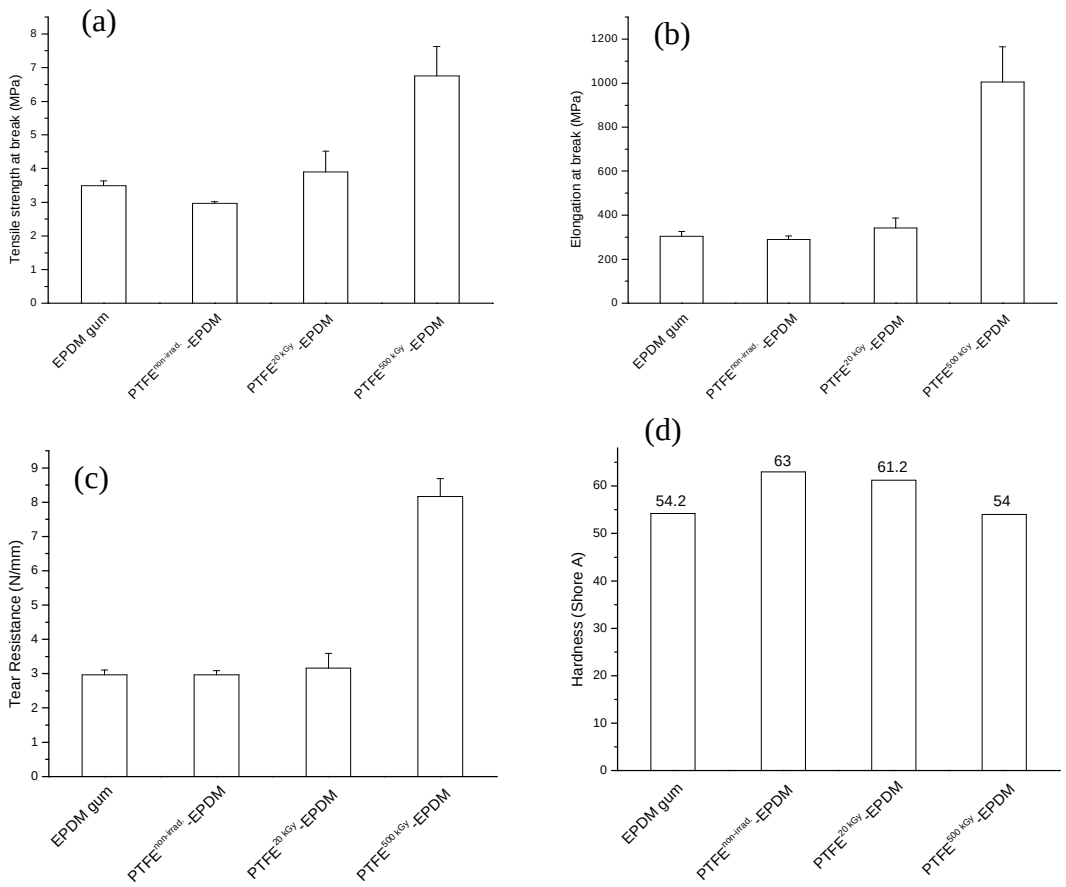

Figure 4. Physical properties of 30 phr PTFE filled vulcanizates in comparison to EPDM gum

in Figure 4 (d). Both of these materials suffered from tremendous materials loss by the sharp asperities of the counter-surface. In order to investigate relationships between wear and mechanical properties, no correlation has been found for specific wear rate against tensile strength at break, elongation at break or tear resistance except hardness. The specific wear rate decreased with increasing hardness. The use of higher irradiation dose PTFE in EPDM reduced the hardness and increased the specific wear rate of the vulcanizate. Beside this, numerous other successful correlations of wear rate with various physical properties such as tensile strength, elongation and hardness for various kind of polymer composites have also been made in the past [19-23]. These investigations have explicitly concluded that the key in developing any such correlations is strictly dependent in unambiguously identifying the dominating properties of the materials which control and inhibit wear. Similar is the case of 500 kGy PTFE filled vulcanizates where indentation of the hard and sharp asperities resulted in high wear rate. However, it is important to realize that in general the frictional properties of rubber-like materials beside sliding speed, temperature and normal load also depend on the typical surface characteristics of the load counter-face [24]. The results and data showed in the present work are valid only for the load and sliding speed of 1.0 N and 5.0 cms^{-1}, respectively.

As seen in Figure 4 (d), except for hardness, all the mechanical properties of the irradiated PTFE filled vulcanizates improved with the use of irradiated PTFE powder in

EPDM. Thus, 500 kGy PTFE filled EPDM showed low friction coefficient but has high specific wear rate (k). It suggests that the achievement in tribo-performance was at the cost of the most of the mechanical or tribo-properties. Non-irradiated PTFE filled composites showed lower (k) values but has extremely poor tensile strength at break, elongation at break and tear resistance. In this work both beneficial and detrimental effects of the factors influencing the physical and tribological properties of the PTFE filled vulcanizates have been reported. Thus, with increasing irradiation dose, though physical properties increased substantially, it was at the cost of deterioration of the hardness of the vulcanizate and wear performance.

4. CONCLUSIONS

The friction coefficient and wear rate could be reduced by the use of PTFE nanopowder as a friction modifier additive in EPDM gum. Radiation induced changes in PTFE nanopowder effects both the physical and tribological properties of the host vulcanizates. Hardness of the material and agglomerates size played an important role in reducing the wear rate of the PTFE filled elastomer composites. Non-irradiated PTFE with comparatively larger agglomerate size resist wear by providing the load support. Large size agglomerates physically embedded in the matrix are effective in reducing the wear but have almost no effect in enhancing the physical properties. Irradiated PTFE agglomerates having smaller mean agglomerate size enhances the physical properties due to compatibility and dispersion with EPDM but suffers from high wear rate due to low hardness of the vulcanizates.

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