Modification of PTFE nanopowder by controlled electron beam irradiation: A useful approach for the development of PTFE coupled EPDM compounds

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Abstract. Low-temperature reactive mixing of controlled electron beam modified Polytetrafluoroethylene (PTFE) nanopowder with Ethylene-Propylene-Diene-Monomer (EPDM) rubber produced PTFE coupled EPDM rubber compounds with desired physical properties. The radiation-induced chemical alterations in PTFE nanopowder, determined by electron spin resonance (ESR) and Fourier transform infrared (FTIR) spectroscopy, showed increasing concentration of radicals and carboxylic groups (–COOH) with increasing irradiation dose. The morphological variations of the PTFE nanopowder including its decreasing mean agglomerate size with the absorbed dose was investigated by particle size and scanning electron microscopy (SEM) analysis. With increasing absorbed dose the wettability of the modified PTFE nanopowder determined by contact angle method increased in accordance with the (–COOH) concentration. Transmission electron microscopy (TEM) showed that modified PTFE nanopowder is obviously enwrapped by EPDM. This leads to a characteristic compatible interphase around the modified PTFE. Crystallization studies by differential scanning calorimetry (DSC) also revealed the existence of a compatible interphase in the modified PTFE coupled EPDM.

Keywords: mechanical properties, PTFE nanopowder, EPDM, electron beam irradiation, compatibility

1. Introduction

Polytetrafluoroethylene (PTFE) finds an exceptional position in plastic industry due to its outstanding chemical and heat resistance, electrical insulation and its significantly low friction coefficient. These properties recommend PTFE for numerous and diverse applications [1]. Both elastomeric and thermoplastic fluoropolymers find a wide use especially in automotive applications such as seals, O-rings and gasket etc. [2]. It is also blended with other polymers or reinforced as a composite material for special purpose applications [3–5]. However, its inherently low adhesion and inert behaviour limit its dispersion and compatibility with other materials. Therefore, surface modification of PTFE to enhance its wettability and

compatibility is a prerequisite for its effective utilization in other compounds. New approaches were considered to surface modification of PTFE via different procedures [6–10]. Significant developments were also made both in the synthesis and manufacturing of new commercial fluorpolymers with improved mechanical properties [11–12]. However, electron beam modification provides a simple and effective method for modification of PTFE powder [13–20]. Recently, newly developed chemically coupled PTFE-PA compounds have opened a new way in producing high performance wear-resistant materials [21–23]. A new class of potential wear-resistant materials based on modified PTFE powder filled SBS, NBR and EPDM compounds were also produced [24]. Modified PTFE

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powder was specially utilized in NBR to expand its utility as wear-resistant material for sealing applications [25]. PTFE micropowders produced by emulsion polymerization are low-molecular weight fine coagulated powder commonly used as an additive in variety of applications [26–27]. In the previous study, PTFE coupled EPDM compounds were produced by reactive mixing of pre-modified PTFE nanopowder with EPDM [28]. In the present work the influence of dose-controlled agglomerate size, structural morphology and interfacial compatibility of PTFE nanopowder on the physical properties of the resulting modified PTFE-EPDM blends are presented. These investigations are of extreme importance especially in the development of new rubber compounds which require optimization of both the physical and tribological properties [29–30]. It has been shown that the desired physical properties can be achieved simply by controlled modification of PTFE nanopowder.

2. Materials and experimental

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. Algoflon L100X an emulsion grade received from Solvay Solexis S.p.A, Italy is an agglomerated white PTFE nanopowder with the bulk density and surface area of 0.25–0.44 g·cm⁻³ and 26 g·m⁻², respectively.

2.2. Modification of PTFE nanopowder

PTFE nanopowder was modified with absorbed doses of 20, 100, 200, 300, 400 and 500 kGy 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. The electron beam treatment was carried out in air and at room temperature with an absorbed dose of 2.5 kGy per pass and at an average dose rate of about 10 kGy/h. These treatment parameters were considered in order to avoid excess temperature rise which might favour deactivation of

the radical formation as well as to control agglomerate size and chemical structure via absorbed dose. Further information about the electron accelerator (ELV-2) facility can be found in [18].

2.3. PTFE nanopowder characterization

The 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 contact angle measurements were performed on (1 mm thin, diameter 20 mm) PTFE discs with the help of OCA 40 Micro contact angle meter from DataPhysics Instrument GmbH, Germany. The rounded discs were prepared by compressing PTFE nanopowder at room temperature under a pressure of 1 MPa. Sessile drop method was performed to determine the wettability of PTFE discs modified similarly as discussed in section 2.2. The discs were used to obtain smooth and comparable surfaces for contact angle measurement.

The particles size and their distribution were determined with the help of the particle size analyzer, Sympatec HELOS HO367 from Sympatec GmbH Germany, 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 17.7 μm, respectively, as received from the supplier. Post and pre-irradiation structure morphology of the PTFE nanopowder modified to different absorbed doses were determined with the help of LEO 435 scanning electron microscope (SEM – acceleration voltage 20 kV) from LEO Electron Microscopy Ltd, England. SEM examination was also performed on the cryogenic surface fractured samples for the dispersion analysis of PTFE nanopowder in EPDM.

2.4. Specimen preparation

EPDM and 30 phr (parts per hundred of rubber) PTFE nanopowder were first pre-mixed in a Poly-

Lab Haake Rheomix internal mixer from Thermo Electron Corp, Germany for 5 minutes at 100°C and at a rotor speed of 50 rpm. Curatives including 7.5 phr coagent and 5 phr peroxide were added to the material on a two roll laboratory mill (Polymix 110L, Servitic, Germany) at room temperature. A constant friction ratio of 1.2 was maintained between the milling rolls. Approximately 2 mm thick sheets were drawn out from the mill and cured in a hot press (Fontune, Holland) under a pressure of 5 MPa at a temperature of 170°C up to their corresponding optimum cure time.

2.5. PTFE-EPDM blend characterization

Mechanical properties including tensile strength at break, percentage elongation at break and modulus at 300% elongation were carried out according to ISO 527 at a cross-head speed of 200 mm/min using tensile testing machine (Zwick, Germany). Hardness values were measured according to DIN 53505, using a Shore A Durometer. Indentations were made at several points for each specimen for the determination of the average hardness value. Differential scanning calorimetry (DSC) studies of the PTFE-EPDM composites were carried out using NETSCH DSC 204 from NETZSCH-Gerätebau GmbH, Germany to analyze the influence of absorbed dose on the compatibility and dispersion in EPDM from their crystallization studies. All experiments were performed under atmospheric conditions and at a heating rate of 10 K·min^{-1} above the melting temperature of PTFE up to 330°C. The results obtained were expressed as input energy versus temperature. Transmission electron microscopy (TEM) micrographs of the modified and non-modified PTFE filled EPDM were recorded on transmission microscope model EM910 from Carl Zeiss, Germany.

3. Results and discussion

3.1. Effect of modification on the molecular structure of PTFE

Figure 1 shows the ESR spectra of the modified and non-modified PTFE nanopowder. The ESR spectra show a systematic increase in the signal with increasing absorbed irradiation dose. Non-modified PTFE nanopowder produced no signal due to the absence of reactive free radicals. The
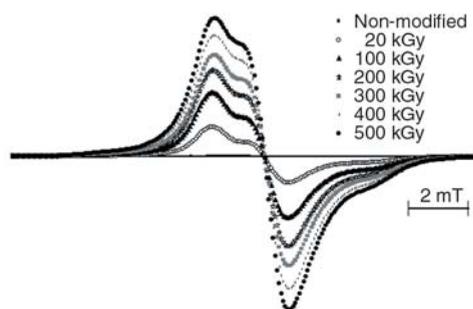
Figure 1. Electron spin resonance (ESR) spectra of PTFE nanopowder modified with differentabsorbed doses

increase in signal indicates that the radical concentration is increased with increasing absorbed dose or modification. 500 kGy irradiated PTFE nanopowder having the highest spin numbers shows the highest number of radical concentration. Electron beam treatment generates persistent reactive free radicals and functional groups on the surface due to degradation of PTFE nanopowder by chain scission. Figure 2 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 [31–32]. 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 hydrolyse in the presence of atmospheric moisture to form carboxylic acid groups (–COOH). The complete reaction mechanism can be found in [33]. Chemical changes introduced in PTFE after exposure to electron treatment were monitored by FTIR spectroscopy. Figure 3 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} associated carboxylic acid groups (–COOH).
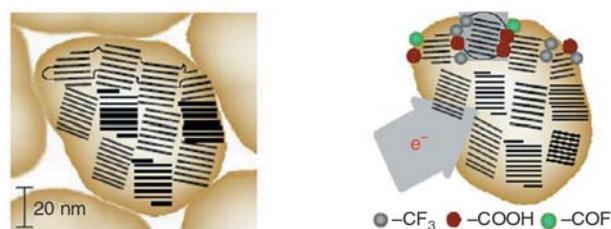
Figure 2. Radiation induced degradation of high molecular weight PTFE nanopowder
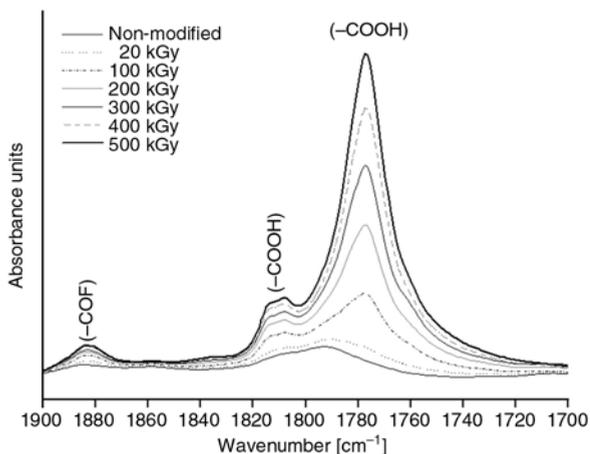
Figure 3. Infrared spectra (1900–1700 cm⁻¹) of L100X (nanopowder) after modification by different absorbed doses in comparison to non-modified PTFE
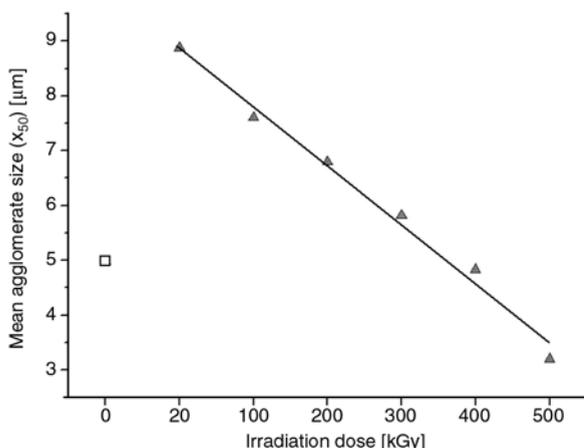
Figure 4. Mean agglomerate size of PTFE nanopowder as a function of absorbed dose (Empty box indicates non-irradiated while filled triangles indicates irradiated PTFE nanopowders)

Figure 4 shows the influence of absorbed dose on the mean agglomerate size of PTFE nanopowder. It can be seen that mean agglomerate size of PTFE nanopowder decreased systematically with absorbed irradiation dose. It suggests that mean agglomerate size of PTFE nanopowder can be controlled via absorbed dose. The decrease in agglomerate size is due to chain scission of PTFE nanopowder. High molecular weight PTFE is reduced to low molecular weight PTFE. The highest absorbed dose of 500 kGy shows the smallest mean agglomerate size. The mean agglomerate size delivered by the supplier of virgin non-modified PTFE nanopowder was 17.7 μm compared to our determined agglomerate size of 5.0 μm. This might be due to the ability of PTFE nanopowder to re-agglomerate as can
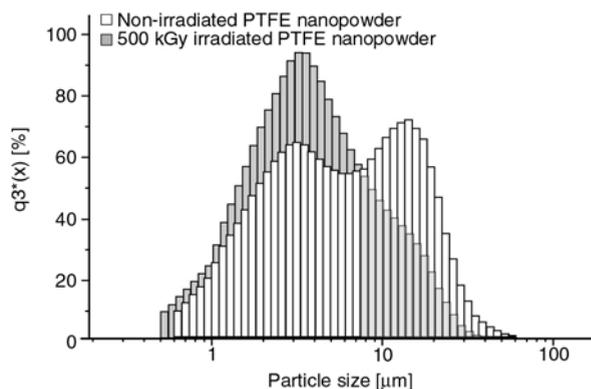
Figure 5. Particle size distribution of non-irradiated and 500 kGy irradiated PTFE nanopowder

be seen in the particle size distribution in Figure 5. The particle size distribution suggests that non-irradiated L100X PTFE nanopowder has a broad particle size distribution compared to 500 kGy irradiated PTFE nanopowder. The non-irradiated PTFE nanopowder shows a characteristic bimodal distribution compared to unimodal distribution of 500 kGy irradiated PTFE nanopowder. This specific bimodal distribution clearly signifies that non-irradiated L100X PTFE nanopowder is mainly composed of bigger agglomerates which tend to re-agglomerate. On the contrary, 500 kGy irradiated PTFE nanopowder indicates finely dispersed smaller agglomerate particles. This can also be seen in the SEM micrographs of 500 kGy irradiated PTFE nanopowder. Effect of absorbed dose on the agglomerate morphology of (a) non-irradiated L100X and (b) 500 kGy irradiated PTFE nanopowder is shown in Figure 6. It is evident that the agglomerate size and morphology of these nanopowders are apparently distinguishable from each other. Non-irradiated PTFE nanopowder are huge solid-structured agglomerates formed by the random re-agglomeration of PTFE agglomerates. In comparison, 500 kGy irradiated PTFE nanopowder shows fine homogeneous coarse particles dispersed individually over the area without the formation of huge agglomerates.

Figure 7 shows result of the contact angle measurements on PTFE nanopowders having different absorbed doses in comparison to 0 kGy (non-modified) L100X PTFE nanopowder. The horizontal line indicates contact angle value of a typical commercial PTFE. It is observed that the water contact angles of modified PTFE discs are lower than non-modified PTFE disc and is systematically decreas-
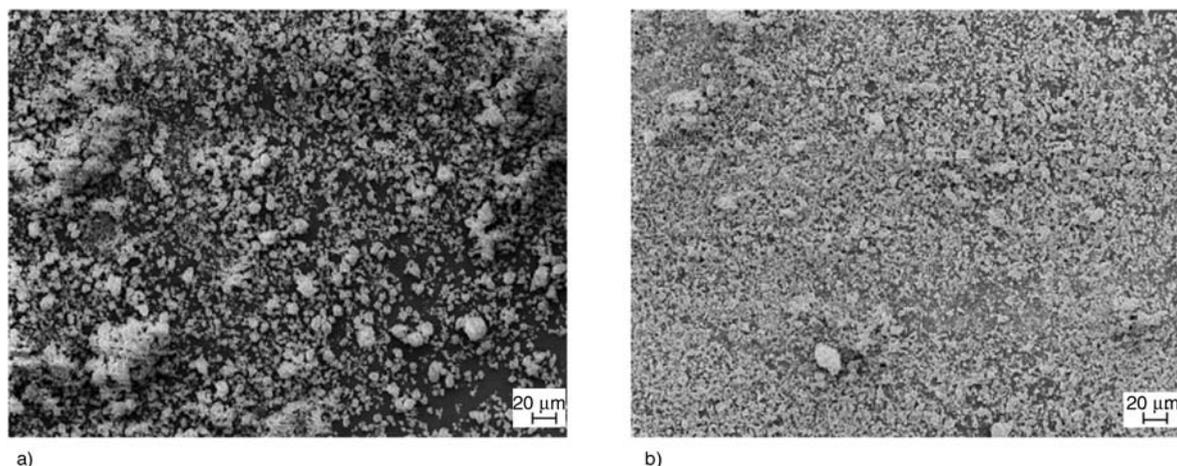
Figure 6. Scanning electron micrographs of (a) non-irradiated and (b) 500 kGy irradiated PTFE nanopowder
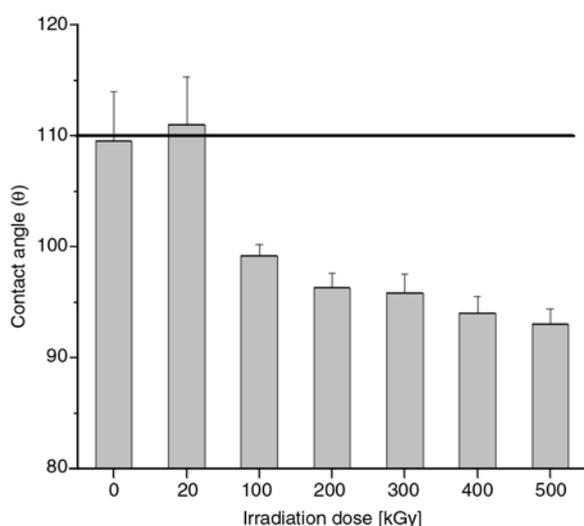
Figure 7. Effect of the absorbed dose on the contact angle of modified PTFE discs in comparison to non-modified PTFE. The horizontal line indicates contact angle value of a commercial PTFE

ing with increasing absorbed dose. The water contact angle of 111° of non-modified L100X PTFE nanopowder indicates its inherently hydrophobic behavior. Post-modification to different absorbed doses result in the decrease in contact angle from 114.8 to 92° for 500 kGy PTFE nanopowder. That is, compared with non-modified PTFE, the wettability of 500 kGy is significantly increased. The increase in wettability is due to the strong interaction between water and the hydrophilic groups (COF/COOH) generated on the surface of PTFE nanopowder after electron treatment in the presence of air. As can be seen, increasing absorbed dose results in lower contact angles due to the generation of oxygen containing groups on the PTFE surface. Lower contact angles correspond to higher

surface energy and thus higher adhesion and higher interfacial compatibility. As shown in Figure 3 an increasing absorbed dose results in higher concentration of C=O groups (1777 cm^{-1}). This shows that the chemical structure of PTFE nanopowder was changed due to electron treatment.

3.2. Effect of structural changes on the compatibility with EPDM

Figure 8a–8c show TEM micrographs of PTFE$^{0\,kGy}$-EPDM, PTFE$^{300\,kGy}$-EPDM and PTFE$^{500\,kGy}$-EPDM blends. The enhanced interfacial compatibility in case of PTFE$^{300\,kGy}$-EPDM and PTFE$^{500\,kGy}$-EPDM can be seen in Figures 8b and 8c. The modified agglomerate particles are embedded and enwrapped by EPDM. No clear and visible interphase can be seen between the two incompatible polymers. Slightly light and dark regions around modified PTFE powder are an indication of a reinforced compatible interphase due to radical coupling with EPDM. It is also observed that modified PTFE agglomerate acts as a PTFE core sorrounded by EPDM shell. On the other hand, PTFE$^{0\,kGy}$-EPDM shows non-modified PTFE nanopowder as solid embedded bodies lacking interfacial compatibility with EPDM. The interface is distinctively separated from each other. No mutual compatible interphase exists as observed in both PTFE$^{300\,kGy}$-EPDM and PTFE$^{500\,kGy}$-EPDM blends. Modified agglomerates in case of PTFE$^{500\,kGy}$-EPDM are elongated and outstretched in a specific direction. The modified PTFE particles due to enhanced compatibility and dispersion are oriented under high-shearing during reactive blending. However, non-modified PTFE
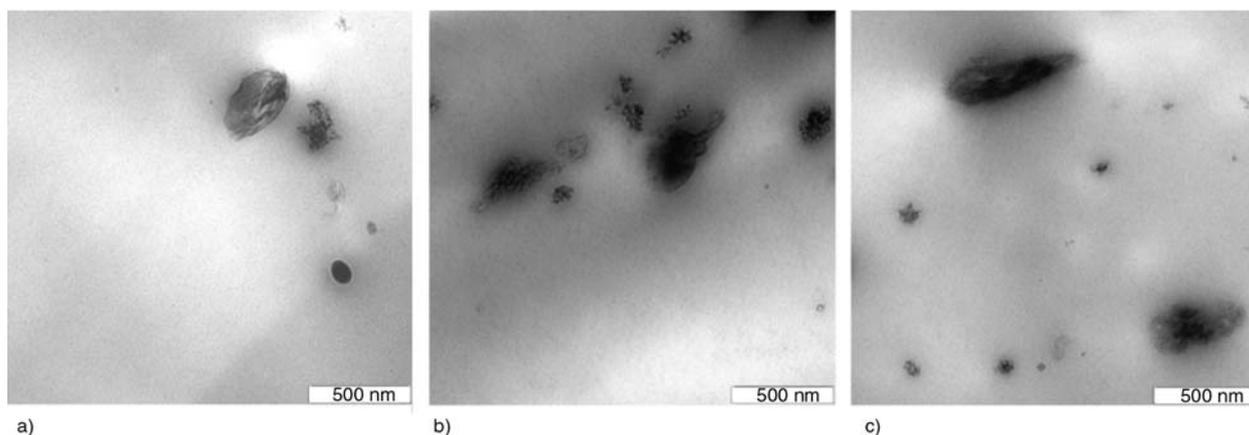
Figure 8. TEM morphologies of a) PTFE[0 kGy]-EPDM; b) PTFE[300 kGy]-EPDM and c) PTFE[500 kGy]-EPDM blends
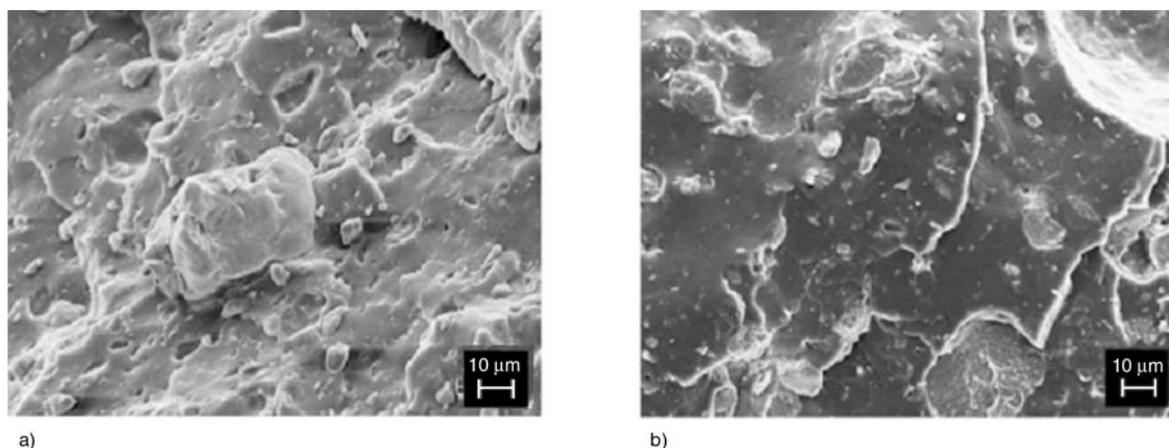
Figure 9. SEM micrographs of the tensile fractured surfaces of a) PTFE[0 kGy]-EPDM and b) PTFE[500 kGy]-EPDM blends

nanopowder being inert remained as huge rounded agglomerates even under high shearing. This behavior can also be seen in microdispersion in EPDM matrix. Figures 9a and 9b shows SEM micrographs of the tensile fractured surfaces of PTFE[0 kGy]-EPDM and PTFE[500 kGy]-EPDM. It is evident that the surface features are apparently distinguishable from each other. The PTFE[500 kGy]-EPDM vulcanizate surface is smooth, with agglomerates embedded and homogenously dispersed in the EPDM matrix while PTFE[0 kGy]-EPDM shows an uneven, inhomogeneous surface with large vacuoles on the fractured surface. This indicates that the PTFE particles are being pulled out of the matrix on application of stress due to the absence of interfacial interaction or coupling with the matrix. It can be observed that the non-modified PTFE particles are bigger in size and tend to form huge irregular agglomerates in the EPDM matrix even under high shearing during blending operation. Non-modified L100X PTFE particles lack both the compatibility and the dispersion efficiency. Figure 10 shows the
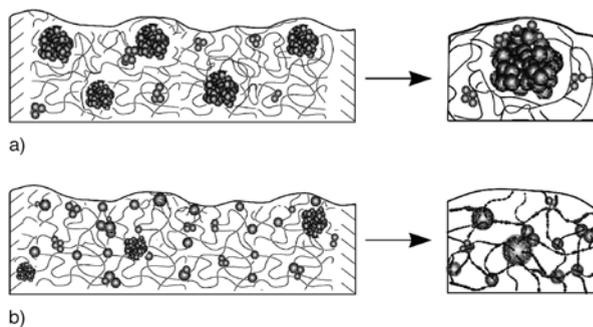
Figure 10. Schematics of the (a) non-modified and (b) modified PTFE nanopowder in EPDM

schematics of the (a) non-modified and (b) modified PTFE nanopowder in EPDM.

3.3. DSC investigations

Figure 11 shows the thermal traces of (a) non-modified and 500 kGy irradiated PTFE nanopowder and (b) corresponding blends PTFE[0 kGy]-EPDM and PTFE[500 kGy]-EPDM. The crystallization peak of 500 kGy irradiated PTFE nanopowder shifts to a lower temperature of about 303.5°C. Also, the crys-
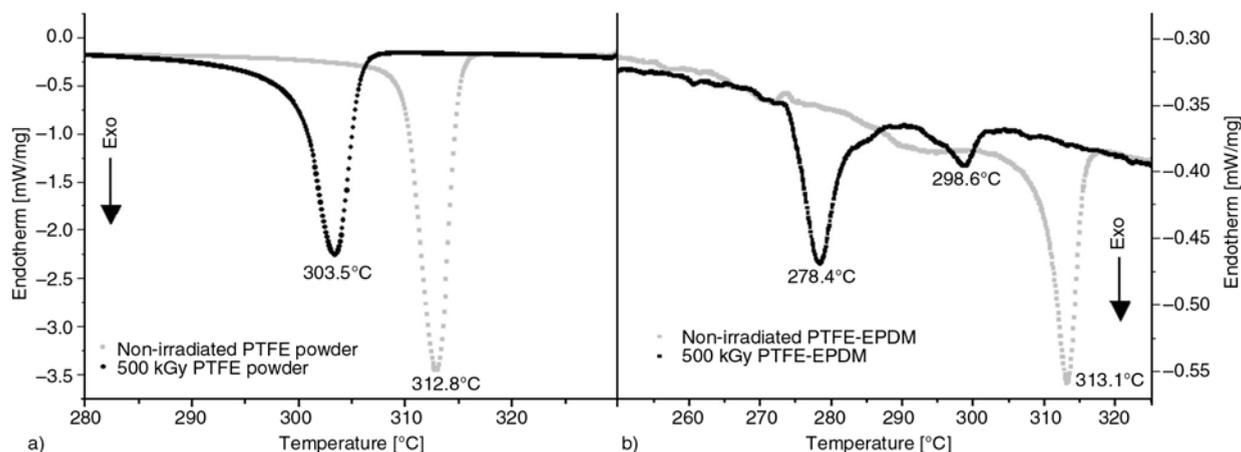
Figure 11. DSC cooling scans of the non-irradiated and 500 kGy irradiated PTFE nanopowder (a), and their corresponding EPDM blends (b)

tallization onset occurred at lower temperature and continued down to approx. 290°C. These distinct variations in 500 kGy compared to non-modified PTFE nanopowder is due to the electron beam treatment process which caused degradation of 500 kGy PTFE nanopowder. The molecular weight decreases due to chain scission and leads to PTFE macromolecules of different chain lengths. As a result, the crystallization peak occurs at lower temperatures and the crystallization process continues till much lower temperatures in comparison to the non-modified PTFE nanopowder.

In case of blends, PTFE[500 kGy]-EPDM shows two crystallization peaks located at distinct temperatures. The second crystallization step at lower temperature also called fractionated crystallization occurred at 278°C along with the bulk crystallization peak at 298°C [34–35]. The area of the first bulk crystallization peak is smaller as compared to the area of the second peak. However, the crystallization temperature (298.6°C) of the first peak is close to 500 kGy irradiated PTFE nanopowder (303.5°C). The first crystallization peak is attributed to the content of PTFE nanopowder in EPDM having comparatively bigger and incompatible agglomerates. The PTFE agglomerates could be compatibilized only on the surface and the core consists of pure agglomerated PTFE nanopowder. These agglomerates show crystallization temperatures similar to pure PTFE bulk crystallization. However, for PTFE[0 kGy]-EPDM, no fractionated crystallization except bulk crystallization similar to non-irradiated PTFE powder is observed at 313°C. This stems from the fact that non-irradiated PTFE

nanopowder is difficult to de-agglomerate and disperse homogeneously. The variations in the position of the transition-melting peaks observed in PTFE[500 kGy]-EPDM is due to the specific chemical compatibility of the electron beam modified PTFE with EPDM. This unique fractionated crystallization behaviour is mainly due to the fine dispersion of 500 kGy irradiated PTFE nanopowder in EPDM. The outstanding dispersion of 500 kGy irradiated PTFE nanopowder is also attributed to its smaller particle size and enhanced compatibility as is evident in Figure 8. PTFE[0 kGy]-EPDM on the other hand has significantly poor dispersion and compatibility with EPDM.

3.4. Physical properties

Figures 12a and 12b show tensile strength and elongation at break of PTFE-EPDM blends as a function of absorbed irradiation dose. The horizontal line represents EPDM gum. In case of PTFE[0 kGy]-EPDM, tensile strength and elongation at break are lower than modified PTFE filled EPDM. With increasing absorbed dose, tensile strength and elongation at break of modified PTFE coupled EPDM compounds increase systematically. Tensile strength and elongation at break of EPDM gum and PTFE[0 kGy]-EPDM are almost the same because of poor compatibility and dispersion. On the other hand, PTFE[500 kGy]-EPDM shows the highest tensile strength and elongation at break. Modified PTFE particles having smaller agglomerate sizes and compatible surfaces enhance its degree of dispersion and compatibility. The improvement of physi-
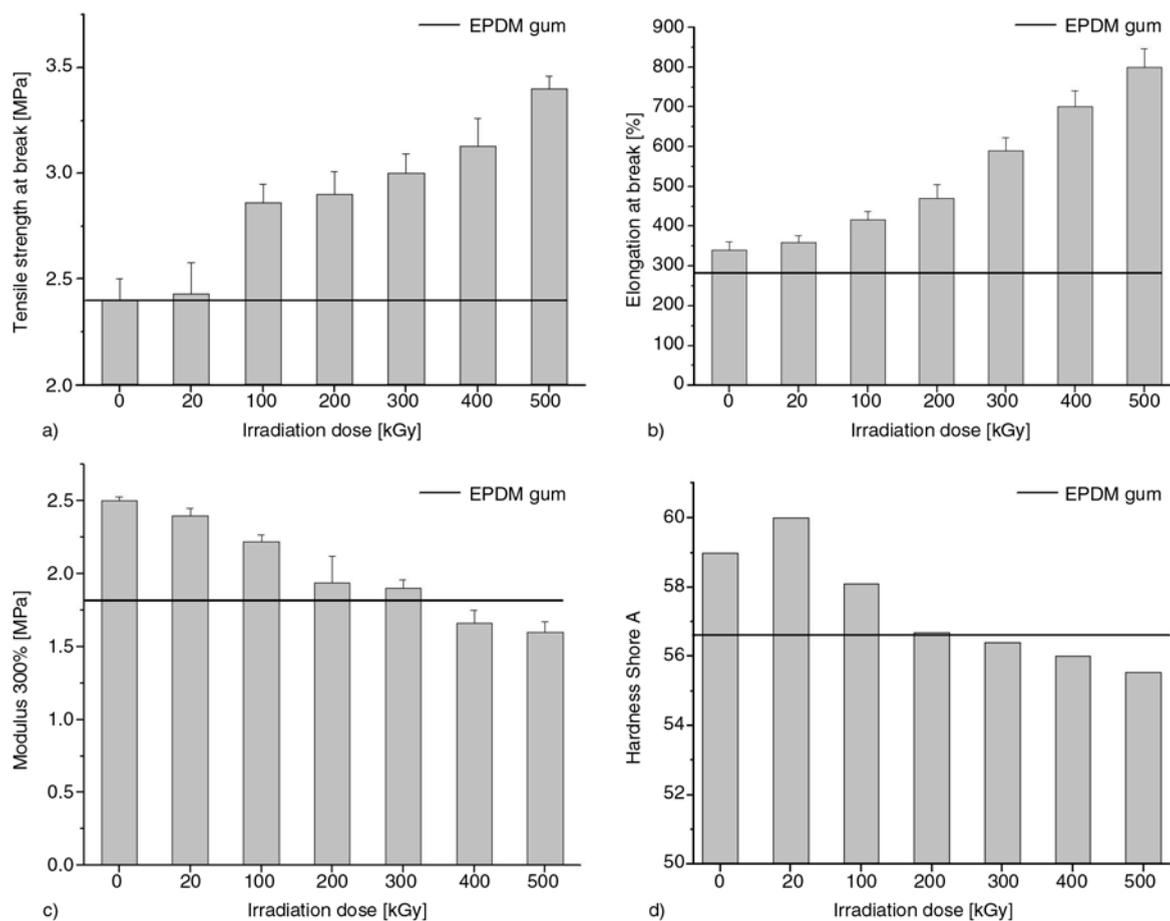
Figure 12. Tensile strength at break (a), elongation at break (b), modulus 300% (c) and hardness (d) as a function of absorbed dose of PTFE nanopowder in EPDM

cal properties of EPDM filled with electron treated PTFE is essentially due to the synergistic effect of their homogeneous dispersion and desirable compatibility. Figure 12c displays the stress at 300% elongation (so-called modulus 300%, M300) as a function of absorbed dose. The M300 decreases for modified PTFE filled EPDM with increasing irradiation dose. PTFE$^{0 \text{ kGy}}$-EPDM shows the highest M300. However, the corresponding values of PTFE$^{400 \text{ kGy}}$-EPDM and PTFE$^{500 \text{ kGy}}$-EPDM are lower even than EPDM gum. Figure 12d shows the corresponding Shore A hardness values of PTFE-EPDM blends. The effect of absorbed dose of PTFE nanopowder on vulcanizate hardness can be seen in their decreasing values of hardness. EPDM filled with PTFE having absorbed irradiation doses higher than 20 kGy results in decreasing hardness values of PTFE-EPDM blends. PTFE$^{20 \text{ kGy}}$-EPDM has the highest hardness while PTFE$^{500 \text{ kGy}}$-EPDM showed the lowest. It is interesting to note that hardness of the blends above PTFE$^{200 \text{ kGy}}$-EPDM is

even lower than that of EPDM gum. Non-modified PTFE nanopowder as shown in Figure 8 and 9 are huge uncovered agglomerates dispersed as solid rigid bodies in a matrix. Being incompatible they are not covered by EPDM molecules and hence tend to segregate in EPDM matrix. The presence of these huge inert bodies provides strength and hardness to the host matrix.

3.5. Reaction mechanism

The lack of reinforcement or compatibility of PTFE with other polymers is due to its inherent inert molecular structure. However, surface modification by high-energy electrons provides compatibility between PTFE and an unsaturated rubber matrix by a radical coupling reaction. The radicals of the irradiated PTFE react with olefinic unsaturated groups of EPDM as shown in Figure 13. Since several EPDM molecules are coupled to the surface of PTFE particles, these inter-chain bonds between
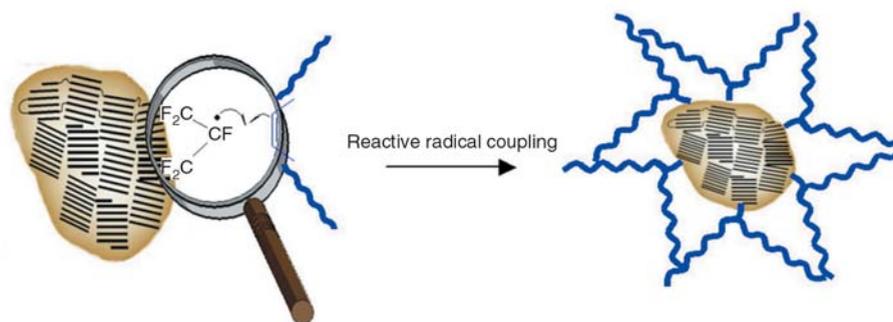
Figure 13. Radical coupling mechanism of modified PTFE radicals and the unsaturated diene EPDM

PTFE and EPDM provide compatibility by strong intermolecular network formation, the result of which is obvious in the improved physical properties of modified PTFE-EPDM blends.

4. Conclusions

We have described a method to develop PTFE coupled EPDM compounds with desired physical properties by simple, easy and effective controlled-modification of PTFE nanopowder. The existence of compatibility between modified PTFE nanopowder and EPDM was revealed by TEM, DSC and SEM. The resultant modified PTFE-EPDM blends demonstrate exceptionally enhanced physical properties by enwrapping of modified PTFE nanopowder by EPDM. Water contact angles indicate that the wettability of the modified PTFE nanopowder was increased by functional groups compared with non-modified PTFE nanopowder. The synergistic effect of enhanced compatibility by chemical coupling and micro-dispersion of PTFE agglomerates results in a significant improvement of physical properties of PTFE coupled EPDM compounds. In conclusion, PTFE coupled EPDM compounds prepared by the described approach offer the potential use of PTFE nanopowder in wide range of polymers for special purpose applications. Accordingly, they are promising in various fields.

Acknowledgements

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