

## Properties of Melt Processable PTFE/PEEK Blends: the Effect of Reactive Compatibilization Using Electron Beam Irradiated Melt Processable PTFE

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**ABSTRACT:** For the first time, blends of melt processable polytetrafluoroethylene (MP PTFE) with polyetheretherketone (PEEK) in the MP PTFE/PEEK ratio of 100/0, 80/20, 50/50, 20/80, and 0/100 w/w were prepared and characterized. MP PTFE/PEEK blends are attractive materials due to the combination of low coefficient of friction and universal chemical resistance of MP PTFE with good wear resistance and mechanical strength of PEEK while maintaining high thermal stability of both. Miscibility, phase morphology, and mechanical properties of the new MP PTFE/PEEK blends were investigated. To improve their end-use properties, an attempt of reactive compounding with the electron beam irradiated MP PTFE (e-beam MP PTFE) was made. The reactive compounding was done in two steps, that is, the preparation of a masterbatch (MB) consisting of e-beam MP PTFE/PEEK (50/50 w/w) and subsequent melt blending of MP PTFE/PEEK with varying concentrations of MB. The e-beam irradiation of MP PTFE carried out in air atmosphere and at room temperature with a dose of 50 kGy results in its chain scission associated with formation of —COF and —COOH functional groups. Such modified MP PTFE can be used to compatibilize MP PTFE/PEEK blends. Reactive compatibilized blends exhibit improved phase morphology and mechanical properties. Especially for MP PTFE/PEEK 50/50 blends, a great improvement of almost 250% in strain at break, 40% in stress at break, and more than 600% in toughness was achieved. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** blends; compatibilization; properties and characterization; thermoplastics; melt processable polytetrafluoroethylene; polyetheretherketone; e-beam irradiation; reactive extrusion

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### INTRODUCTION

Polymer blending is an important tool to design new materials having a full set of desired properties or an improved specific property. Further, it is more economical than development of a new polymeric material. However, due to the low entropy of blending, most of the polymer blends are immiscible and require compatibilization to improve their properties.<sup>1–3</sup>

Melt processable polytetrafluoroethylene (MP PTFE) is a copolymer of polytetrafluoroethylene (PTFE) which comprises small amounts of perfluoropropylvinylether (PPVE) and, hence, bridges a gap between PTFE homopolymer and perfluoroalkoxy (PFA) copolymer. MP PTFE exhibits all the superior properties of PTFE, such as high thermal stability, universal chemical resistance, low dielectric constant, and low coefficient of friction.<sup>4</sup> The main difference between PTFE and MP PTFE is that due to

the very high melt viscosity of PTFE its processing is limited to, for example, sintering process, whereas MP PTFE, characterized by lower melt viscosity, can be processed by the conventional melt processing methods. Consequently, only PTFE blends with less than 30 wt % (weight percent) of PTFE can be produced by a melt extrusion process otherwise only a compression moulding process is possible.<sup>5</sup> Moreover, due to the high melt viscosity of PTFE, melt blending of PTFE powder in polymer matrix results in filler-matrix morphology. The tendency of the PTFE powder to agglomerate and a lack of an adhesion between PTFE phase and the polymer matrix are responsible for the reduced mechanical properties of PTFE blends. In contrast to PTFE blends, in MP PTFE blends, the lower viscosity of MP PTFE enables its better dispersion and distribution within the polymer matrix. Thus, in comparison with PTFE blends, better mechanical performance for MP PTFE blends is expected.

Polyetheretherketone (PEEK) is a semicrystalline thermoplastic material with attractive mechanical properties such as high stiffness, strength, comparatively high fatigue resistance as well as good wear resistance and therefore, has been applied as a matrix material for high performance composites. In spite of a good wear resistance, it has some serious drawbacks, namely a high coefficient of friction and a reduced toughness under some operating conditions. In contrast to PEEK, MP PTFE is a very tough material characterized by a very low coefficient of friction but a high wear rate. Thus, blends of PEEK and MP PTFE should show favorable tribological properties, that is, good wear resistance and low coefficient of friction. Moreover, blending of MP PTFE with PEEK could provide an enhancement of mechanical properties of MP PTFE (e.g., enhanced strength and stiffness, lower creep tendency) on the one hand, and improvement in toughness of PEEK on the other hand, while maintaining their high thermal and chemical stability.

Blends of PTFE and PEEK have been a subject of several papers within the last 30 years, and the main driving force was the enhancement of the tribo-potential of PEEK.<sup>5–8</sup> However, until now less has been reported about the relationship between their morphology and mechanical properties.<sup>7</sup>

PEEK/PTFE blends were found to be immiscible over the composition range.<sup>9</sup>

Compatibilization of PTFE in a variety of polymer matrix can be achieved by its irradiation. It is well known that the irradiation of PTFE in the solid state leads to its degradation. This process is associated with the formation of carbonyl end groups and end-chain double bond structures. Recently, reactive extruded blends of electron beam irradiated PTFE with polyamide (PA) materials have been extensively studied. It was shown that during the extrusion a chemical reaction between PA and modified PTFE took place leading to improved properties of prepared blends.<sup>10–12</sup>

The objective of this article is to study the miscibility, phase morphology, and mechanical properties of blends of the new class of PTFE, namely MP PTFE and PEEK as well as the potential of electron beam irradiated MP PTFE (e-beam MP PTFE) in compatibilization of these blends.

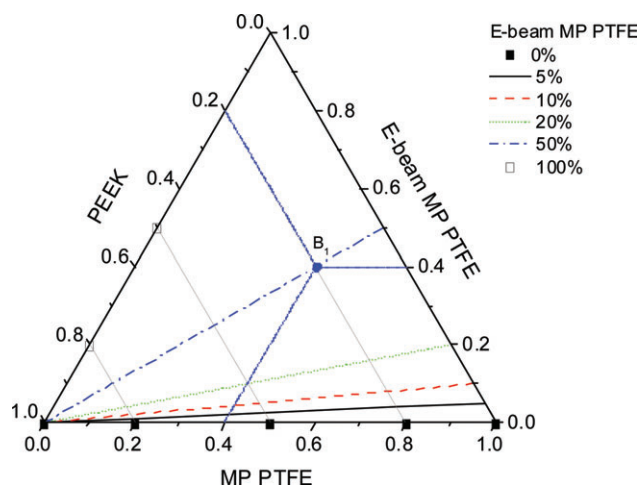
## EXPERIMENTAL

### Materials

Materials used in this study were MP PTFE (Moldflon®: ElringKlinger Kunststofftechnik GmbH, Bietigheim-Bissingen, Germany) and PEEK (VICTREX® PEEK TM 450G, Victrex Europa GmbH, Hofheim, Germany).

### Electron Beam Irradiation

An electron accelerator ELV-2 (Budker Institute of Nuclear Physics, Novosibirsk, Russia) installed in the Leibniz-Institut für Polymerforschung Dresden e. V. was used for the irradiation. The irradiation facility was described in detail in Ref. 13. The MP PTFE samples were placed in polyethylene bags filled with air and placed on the transportation tray passing under electron beam accelerator. The irradiation period was done at room temperature with an absorbed dose of 50 kGy using an electron energy of 1.0 MeV and an electron current of 4 mA. Per one pass a dose of 2.5 kGy was absorbed and thus to achieve 50



**Figure 1.** Blending strategies of MP PTFE/e-beam MP PTFE (MB)/PEEK blends, Example B<sub>1</sub>—40/40/20, see Blend code in Table III. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

kGy, 20 passes were required. The irradiation period was about 90 minutes.<sup>14</sup>

### Preparation of the Blends

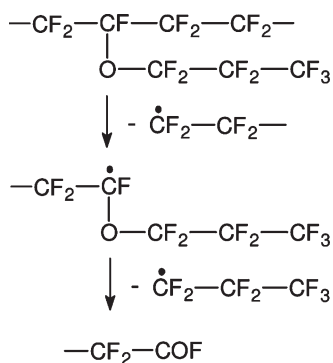
MP PTFE/PEEK blends (100/0, 80/20, 50/50, 20/80, 0/100 w/w) were prepared in a Berstorff ZE25 A-UTX (KraussMaffei Berstorff, Hannover, Germany) twin screw extruder with a length to diameter ratio of 38 at varying screw rotational speed of 50, 100, and 200 rpm. The temperature profile within the cylinder length was as follows: 78, 345, 355, 365, 365, 370, 370, 345, and 340°C.

The preparation of compatibilized MP PTFE/PEEK blends was performed in a two-step process. In the first step, the reactive extrusion of e-beam irradiated MP PTFE/PEEK 50/50 w/w masterbatch (MB) was done. In the second step, the compatibilizer/e-beam MP PTFE/PEEK (MB)/was added to MP PTFE/PEEK blends in different concentrations with respect to MP PTFE, as shown in Figure 1 (see also Table III). The preparation of masterbatch is more convenient for industrial uses compared with adding of the e-beam MP PTFE directly. The properties of masterbatch retain unchanged within the time and thus are of greater feasibility in comparison with e-beam MP PTFE which due to its reactivity is susceptible to changes in molecular structure. Moreover, the processing conditions of masterbatch can be tailored to achieve the best mixing and compatibilization between the components.

E-beam MP PTFE/PEEK (MB) and MP PTFE/e-beam MP PTFE/PEEK (MB)/PEEK blends were prepared at a screw speed of 50 rpm 1 month after the irradiation of MP PTFE.

The compounded blends were compression moulded into plates at a temperature of 380°C for 15 min at a pressure of 1.3 MPa and cooled at a temperature of about 50°C in a cold press for 10 min at 0.9 MPa. Their thickness was in the range from 1.0 to 1.2 mm. The samples for mechanical and thermomechanical analysis were punched out from the compression moulded plates. The samples were in the form of tensile bars with the dimensions (length = 38 mm, parallel length = 22 mm, parallel width = 5 mm, and shoulder width = 8 mm) according to DIN EN ISO 12086-2:2006.





**Figure 3.** Possible degradation of PPVE units (after Ref. 22).

found to be more sensitive to radiation than TFE units. Rosenberg et al.<sup>23</sup> proposed that the degradation of PFA starts in the main chain adjacent to the side chain, as demonstrated in Figure 3, while the formed radicals were believed to be stable and not to undergo crosslinking. IR spectra of irradiated PFA show the band assigned to —COF and —COOH end groups.<sup>13,22–25</sup>

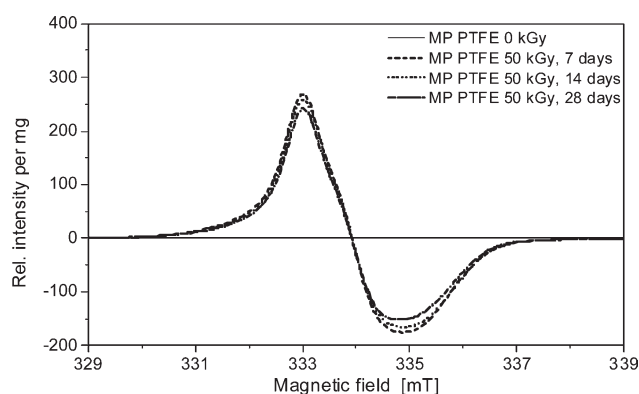
MP PTFE is expected to behave similar to PTFE and PFA when treated with electron beam.

#### EPR and FTIR Analysis

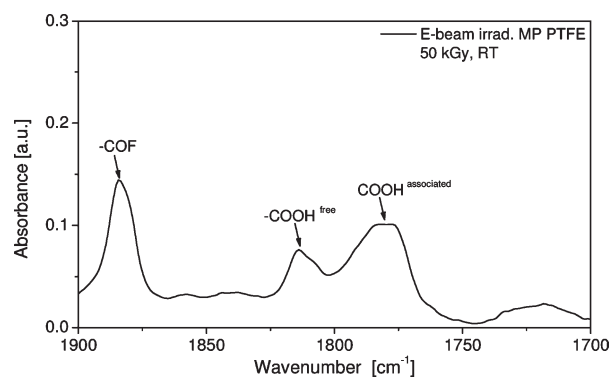
Due to the chain scission, free radicals and reactive functional groups are generated in e-beam irradiated MP PTFE as shown in EPR (Figure 4) and FTIR spectra (Figure 5), respectively.

In the case of e-beam irradiated MP PTFE, free radicals were detected. In the case of nonirradiated MP PTFE, no free radicals were observed. The EPR signal intensity, indicating the radical concentration, slightly decreases with the storage time. Therefore, it can be assumed that the life time of free radicals in e-beam irradiated MP PTFE is extended.

The FTIR-spectrum shows that due to the irradiation, functional —COF and —COOH groups are formed. E-beam irradiated MP PTFE is characterized by the —COF absorption band at 1884  $\text{cm}^{-1}$  and COOH absorption bands at 1814 and 1776  $\text{cm}^{-1}$  assigned to the free and associated —COOH groups, respectively. The presence of the functional groups is important to achieve the compatibilization of e-beam MP PTFE with PEEK.



**Figure 4.** EPR spectra of e-beam irradiated MP PTFE, influence of the storage time on the signal intensity.



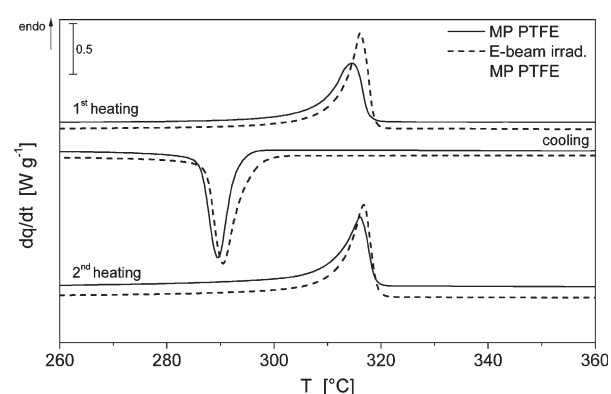
**Figure 5.** FTIR difference spectrum of MP PTFE irradiated with a dose of 50 kGy in air at room temperature.

#### Thermal Analysis

The effect of the absorbed dose of 50 kGy on the thermal properties of MP PTFE is shown in Figure 6 and Table I. The comparison of first heating curves of MP PTFE and e-beam irradiated MP PTFE shows the effect of the irradiation process on the structural changes in the e-beam irradiated MP PTFE as well as the thermal history (manufacturing conditions, e-beam irradiation process, heat treatment in a DSC instrument) of the analyzed samples. Cooling and second heating curves provide information about the effect of the irradiation on the chains' crystallization process and the final crystallinity.<sup>23</sup>

By studying the crystallization process, it is noticed that the irradiated MP PTFE starts to crystallize at higher temperature than the nonmodified MP PTFE. Moreover, the comparison of the melting behavior (second heating) shows a slight increase in the melting temperature of 0.9 K and increase in the heat of melting of about 21% for the modified material.

Comparing crystallization and melting behavior of virgin and irradiated MP PTFE, it can be assumed that MP PTFE undergoes mainly chain scission when irradiated in air atmosphere and at room temperature with the dose of 50 kGy. A decrease in molecular weight results in better polymer chains packing leading to a formation of more ordered and thus thermally more stable crystals which melts at higher temperature. The increase in the heat of melting is consistent with the degradation as well.<sup>23</sup>



**Figure 6.** DSC measurements; comparison of melting and crystallization behavior of MP PTFE and e-beam irradiated MP PTFE.

**Table I.** Influence of the E-Beam Irradiation on the Thermal Transitions of MP PTFE: Results are Average Values of 3 Measurements

Sample	$T_{m1}$ (°C)	$\Delta H_{f1}$ (J/g)	$T_c$ (°C)	$T_{m2}$ (°C)	$\Delta H_{f2}$ (J/g)
MP PTFE	315.2 ± 0.6	29.3 ± 0.8	289.3 ± 0.1	316.2 ± 0.1	33.7 ± 1.4
E-beam MP PTFE	316.8 ± 0.9	38.4 ± 1.6	290.4 ± 0.4	317.1 ± 0.2	40.9 ± 1.4

$T_{m1}$ ,  $T_{m2}$ , melting temperature;  $\Delta H_{f1}$ ,  $\Delta H_{f2}$ , heat of fusion: 1st and 2nd heating;  $T_c$ , crystallization temperature.

### Rheological Characterization

The complex viscosity curves of MP PTFE and e-beam irradiated MP PTFE are presented in Figure 7. The examined materials exhibit different pseudoplastic behavior. At a low angular frequency, e-beam irradiated MP PTFE is characterized by higher value of complex viscosity in comparison with nonirradiated material. Moreover, irradiated MP PTFE shows more pronounced shear thinning behavior (at higher angular frequency) indicating its broader molar mass distribution.<sup>24</sup>

Because the zero viscosity of polymers is proportional to the average molecular weight ( $M_w$ ) by well known relationship ( $\eta_0 = K \cdot M_w^{3.4}$ ), it could be assumed that a polymer build-up (e.g., crosslinking, grafting, branching) took place.

The branched structure of irradiated MP PTFE would be consistent with Lunkwitz et al.<sup>22</sup> who reported that in contrast to PTFE, some branching reactions can occur in PFA when irradiated at room temperature. In our opinion, the observed rheological behavior of irradiated MP PTFE might be explained by branching and/or cross-linking reactions which can take place during the measurement under the action of a shear and temperature of 380°C. The sufficient chain mobility in polymer melt allows the free radicals to undergo recombination processes. Therefore, based on the rheological characterization of e-beam irradiated MP PTFE it is not possible to conclude unambiguously whether branching reactions take place during e-beam irradiation. However, based on DSC results and the fact that irradiated MP PTFE does not possess any mechanical strength, it is certain that MP PTFE undergoes chain scission when irradiated in air at room temperature with a dose of 50 kGy.

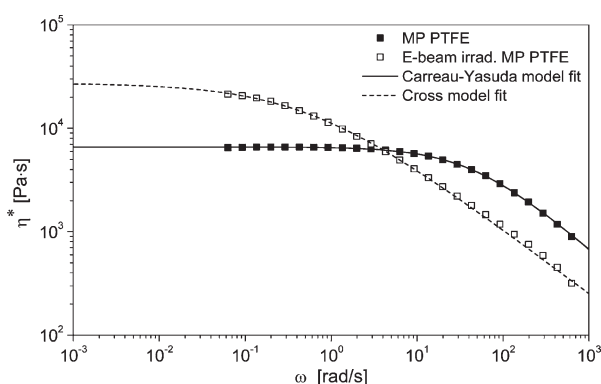
### MP PTFE/PEEK Blends

**Miscibility of MP PTFE/PEEK Blends.** The great majority of polymer blends are immiscible and show multiphase, matrix-dis-

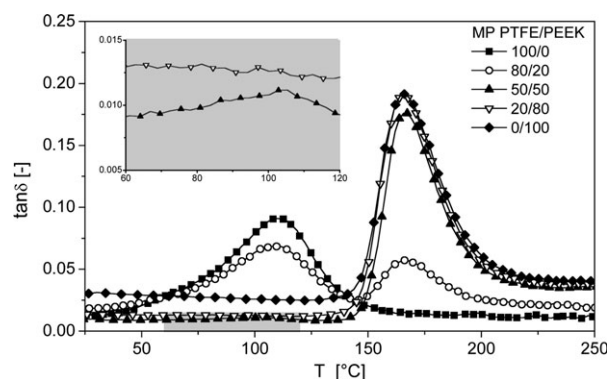
persed type of morphology. Due to the negligible small change in the entropy for polymer blends, only polymer pairs with specific interactions such as, for example, hydrogen bonding or dipole-dipole interaction are thermodynamically miscible.<sup>26,27</sup>

A common method to study the miscibility of polymer blends is the determination of the glass transition temperature ( $T_g$ ) while for a miscible blend a single, composition-dependent  $T_g$  is expected. In general,  $T_g$  of miscible blends increases as a function of composition with a more or less pronounced deviation from a simple weighted average of the two  $T_g$ s of the polymer components. Several equations predicting the  $T_g$  composition dependence for miscible polymer blends have been proposed in the literature.<sup>26,27</sup>

The  $T_g$ s of MP PTFE/PEEK blends were determined from DMA measurements based on the peak maximum of the  $\tan \delta$  curves. MP PTFE/PEEK blends, except for 20/80, exhibit two distinguishable glass transition temperatures as reported in Figure 8 and Table II, whereas for 50/50 blends the  $T_g$  of MP PTFE component is less expressed. The observed  $T_g$ s do not change significantly over the considered composition range and the lower  $T_g$  corresponds to the  $T_g$  of MP PTFE and the higher  $T_g$  to that of PEEK. This indicates that in MP PTFE/PEEK blends two distinct phases, consisting of almost pure polymer components, are present and thus MP PTFE and PEEK are immiscible in the amorphous phase. The fact that for MP PTFE/PEEK 20/80 blends only one peak maximum corresponding to the  $T_g$  of PEEK component is resolved can be attributed to the limited resolution of DMA. As mentioned before, already for 50/50 blends the  $T_g$  of MP PTFE component is very less expressed. The  $T_g$  measured for MP PTFE/PEEK 20/80 blends is not composition dependent and comparable with the  $T_g$  of PEEK what confirms the immiscibility of MP PTFE/PEEK blends over the composition range.



**Figure 7.** Rheological characterization of MP PTFE and e-beam irradiated MP PTFE.



**Figure 8.** DMA measurements; loss factor ( $\tan \delta$ ) plots of MP PTFE/PEEK blends.

**Table II.** Results From DSC and DMA for MP PTFE/PEEK Blends

MP PTFE/PEEK	$T^g$ (MP PTFE) [°C]	$T^g$ (PEEK) [°C]	$T^{m2}$ (MP PTFE) [°C]	$\Delta H^{f2}$ (MP PTFE) [J/g]	$T^{m2}$ (PEEK) [°C]	$\Delta H^{f2}$ (PEEK) [J/g]	$T^c$ [°C]	$\Delta H^c$ [J/g]
100/0	109.8	-	316.2	34.8	-	-	289.4	-34.7
80/20	109.6	166.1	316.8	30.2	341.4	5.5	296.6	-41.5
50/50	105.3	167.3	316.9	23.3	342.7	14.9	296.8	-46.5
20/80	-	165.7	318.7	17.5	342.3	25.6	297.8	-50.8
0/100	-	166.0	-	-	343.0	43.9	297.7	-51.6

$T_{m2}$ , melting temperature,  $\Delta H_{f2}$ , heat of fusion 2nd heating;  $T_c$ , crystallization temperature;  $\Delta H_c$ , heat of crystallization.

Immiscibility of MP PTFE/PEEK blends is also manifested in the separated melting temperatures of its components as determined by DSC measurements. Two melting peaks (Figure 9, and Table II) indicate that MP PTFE/PEEK blends form segregated crystals over the considered composition range and are not miscible in the crystalline region.

Because of the similar crystallization temperatures of MP PTFE and PEEK, MP PTFE/PEEK blends show one exothermic peak in the DSC cooling curves. Nevertheless, this fact is not considered as a cocrystallization process but rather as a separate crystallization of MP PTFE and PEEK phase taking place at the same temperature range. In immiscible polymer blends, due to the altered nucleation and growth conditions, changes in crystallization process leading to coincident crystallization as well as accelerated or retarded crystallization process can occur.<sup>28</sup>

PEEK which is the high- $T_m$  component governs the crystallization process of the blends and therefore the crystallization temperatures of PEEK and MP PTFE/PEEK blends are comparable and show only a slight tendency to shift toward lower temperatures with increasing MP PTFE content. In consequence, the crystallization temperature of MP PTFE of 289.4°C increases significantly up to 296.6°C for 80/20 MP PTFE/PEEK blends.

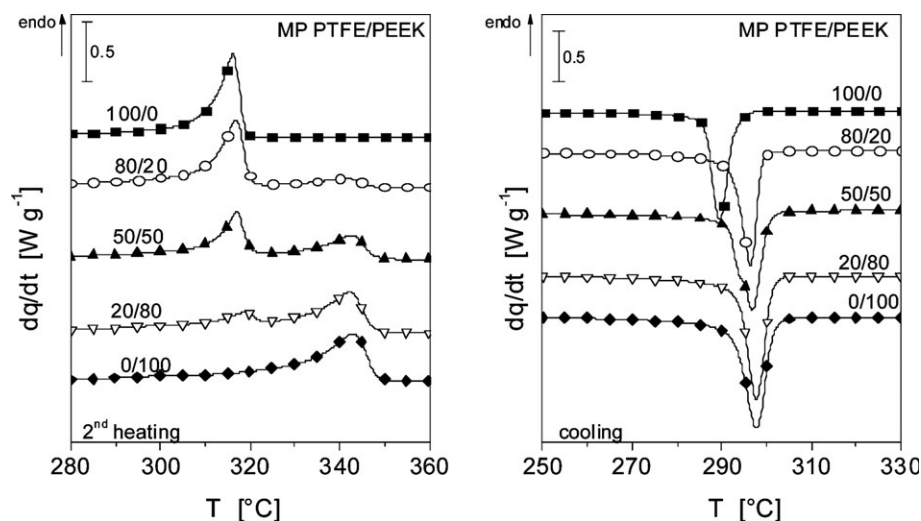
The phase behavior of MP PTFE/PEEK blends (Figure 10) shows that these blends are not miscible over the composition

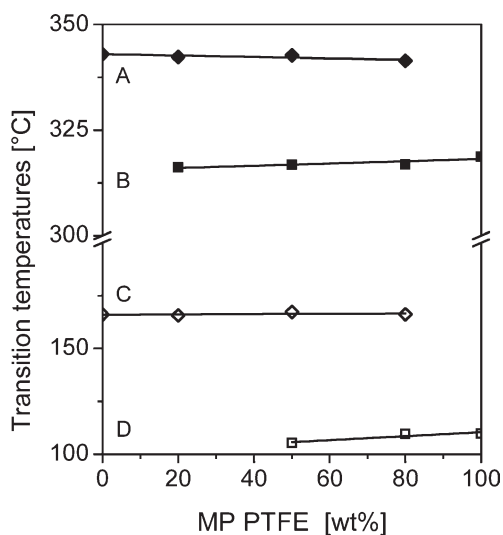
range and at room temperature exhibit four-phase morphology in which two different crystalline phases and two different amorphous phases exist, as proved by DSC and DMA.

**Morphology and Mechanical Properties of MP PTFE/PEEK Blends.** The mechanical properties of immiscible polymer blends are strongly affected by their phase morphologies. The phase morphology depends on the mixing conditions (shear stress) as well as rheological characteristics of the polymers to be mixed, blend composition, and interfacial tension.

During mixing of the blend components, the minor phase is progressively dispersed in a continuous phase of the major component. On acting of a shear flow, the minor phase deforms into long fibrils or thin films. When interfacial tension forces can no longer balance the viscous forces (tending to elongate the droplets), the deformation becomes unstable and the dispersed fibrils break into small droplets. At the same time, the dispersed particle can colloid and merge together leading to a coarsening of blend morphology (coalescence process). The final phase morphology is determined by the balance between breakdown and coalescence.<sup>29</sup>

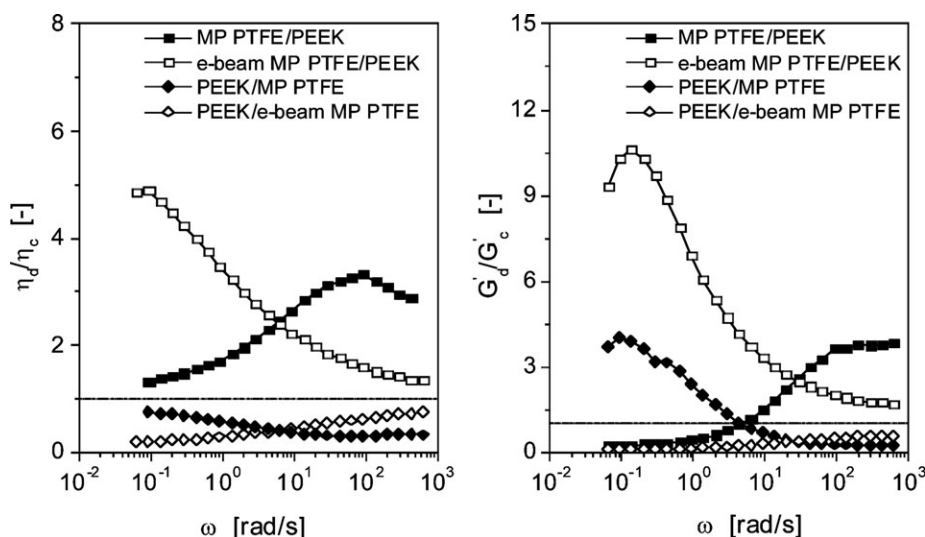
The decisive factor in a dispersion of polymer blends is the viscosity ratio of dispersed phase to matrix phase. In Newtonian liquid systems subjected to a simple shear field, drop breakup is the easiest when the viscosity ratio of a dispersed

**Figure 9.** DSC measurements; thermal properties of MP PTFE/PEEK blends.



**Figure 10.** Phase diagram of MP PTFE/PEEK blends showing the melting temperatures of PEEK (A) and MP PTFE (B) and the glass transition of PEEK (C) and MP PTFE (D).

to a continuous phase is within the range 0.3–1.5, whereas above 3.8 the deformed droplets will not break down.<sup>1,30</sup> Molten polymers are viscoelastic liquids in which the deformation of the droplets is determined not only by the viscous forces but also by the deformation resisting forces arising from the elasticity. In general, it was found that viscoelastic droplets are more stable than the Newtonian ones and require more shear stress for breaking. Moreover, it was reported that matrix elasticity assists with the deformation of the droplet, whereas higher droplet elasticity stabilize the deformed droplets, making the dispersing process more difficult.<sup>1,31</sup> For the viscoelastic systems, Wu<sup>32</sup> found that the viscosity ratio values of 0.1–1 were the best for promoting drop breakup and the smallest droplets were obtained when the viscosity ratio was close to 1; nevertheless, in the cited study the aforementioned elastic effect was not explicitly treated.



**Figure 11.** Viscosity and elasticity ratios of the blend components versus the angular frequency.

The viscosity and the elasticity ratios of blend components, as obtained from rheological analysis, are presented in Figure 11. By applying the Cox-Merz rule<sup>33</sup>  $\eta^*(\omega) = \eta(\dot{\gamma})$  at  $\dot{\gamma} = \omega$  the complex viscosity can be treated as a steady shear flow viscosity and the angular frequency can be directly converted to the shear rate.

For MP PTFE/PEEK blends with MP PTFE phase in a minority, that is, as a dispersed phase in PEEK matrix, the viscosity ratio at 100 rad/s is around 3.3 and decreases with increasing angular frequency. On the other hand, the elastic ratio shows a slight tendency to increase with the angular frequency. The viscosity ratio for blends with PEEK as a dispersed phase shows a small variation with increasing angular frequency. Based on the rheological characterization, it is expected that in contrast to blends with MP PTFE as a dispersed phase, the morphology development of MP PTFE/PEEK blends with PEEK as a dispersed phase should be less sensitive to varying shear rate.

MP PTFE/PEEK blends were blended at three different screw rotational speeds: 50, 100, and 200 rpm. The morphological investigations (Figure 12) indicate that at the lowest compounding speed the finest dispersion of minor phase in the matrix for the considered blend compositions is obtained. The explanation is, that the same factor which favors drop break up (increasing screw speed—increasing shear rates), can also increase the probability of coalescence, leading to increasing dispersed particle size. Moreover, for the blends with a dispersed MP PTFE phase, with increasing shear rate (frequency), the melt elasticity ratio increases resulting in a higher resistance of dispersed phase to deformation and thus more difficult dispersing process.

The phase morphology of immiscible polymer blends has a significant influence on their mechanical performance. The ultimate tensile properties of MP PTFE/PEEK blends are found to be consistent with the results of morphological investigation and the blends prepared at a screw speed of 50 rpm, which are characterized by the best state of dispersion show the best mechanical behavior.

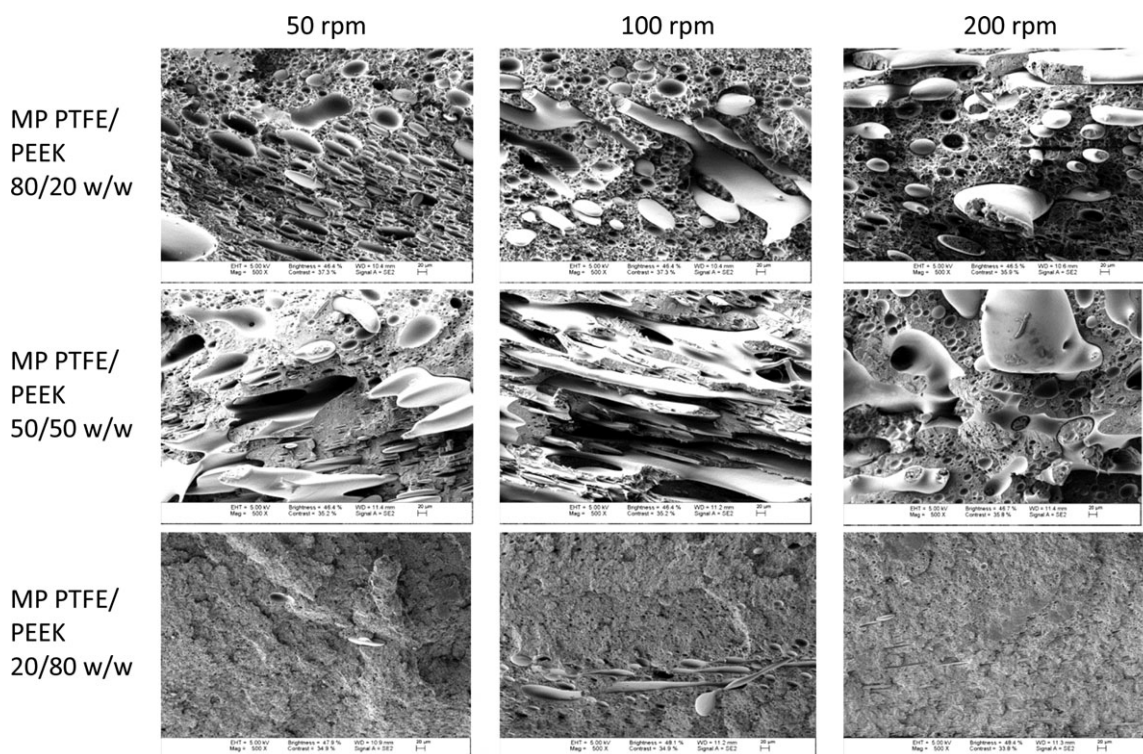


Figure 12. SEM cryo fracture micrographs of MP PTFE/PEEK blends prepared at different screw speeds (magnification: 500 $\times$ ).

The ultimate tensile properties (strain and stress at break) of tested blends are shown in Figure 13. Apart from MP PTFE/PEEK 20/80, the mechanical properties of MP PTFE/PEEK are characteristic for immiscible polymer blends. Due to the poor interfacial adhesion, mechanical behavior of MP PTFE/PEEK blends follows a negative deviation from the mixing rules. On the other hand, in PEEK-rich blends (MP PTFE/PEEK 20/80) by applying appropriate blending conditions a fine dispersion of MP PTFE phase can be achieved with the mechanical behavior close to the mixing rule.

#### MP PTFE/e-Beam MP PTFE/PEEK (MB)/PEEK Blends Reactive Extrusion.

The reactive extrusion was done in a two-step process. In the first step, a MB consisting of e-beam irradiated MP PTFE and PEEK 50/50 w/w was prepared and then blended in various concentrations with MP PTFE and PEEK materials. The compounding process was performed with a screw speed of 50 rpm.

It was expected that during melt blending a chemical coupling of the e-beam modified MP PTFE and PEEK by a reaction of

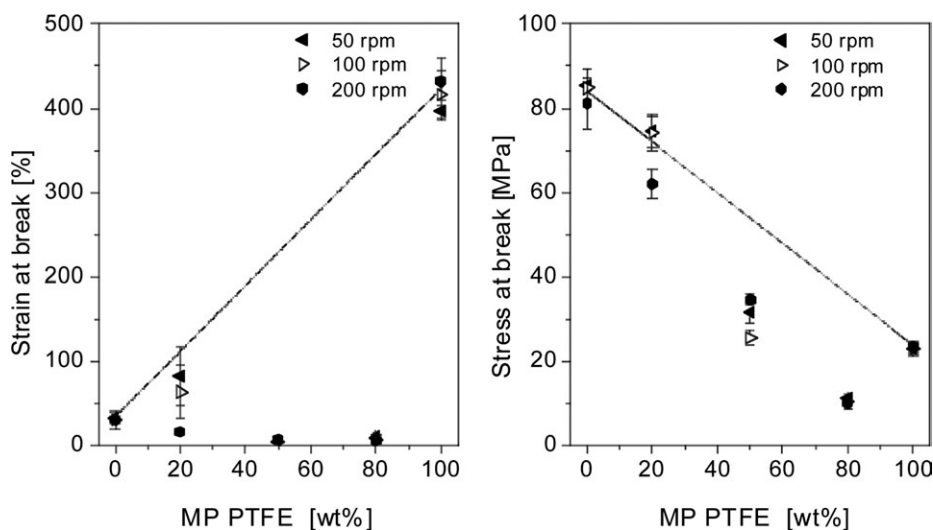
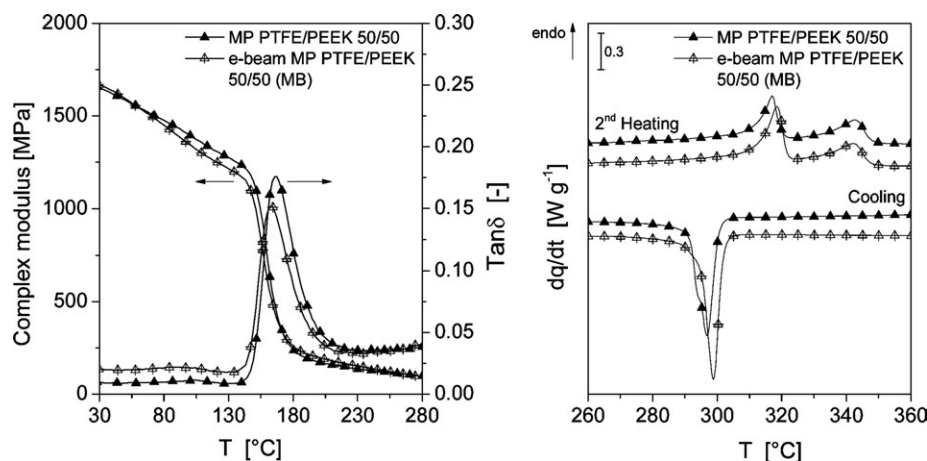


Figure 13. Dependence of ultimate tensile properties on MP PTFE concentration for three screw speeds, dashed line—mixing rule.





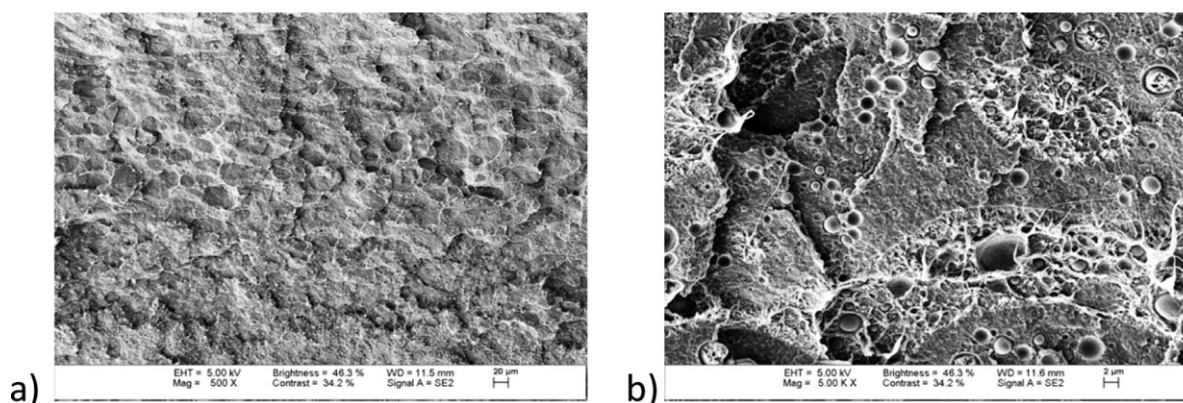
**Figure 14.** DMA (left) and DSC (right) characterization of e-beam MP PTFE/PEEK (MB) in comparison with MP PTFE/PEEK 50/50.

the functional —COF and —COOH groups of the former one with functional groups of the latter one may take place.<sup>34</sup> Subsequently, the chemically coupled e-beam irradiated MP PTFE/PEEK (MB) could be used as a compatibilizer in MP PTFE/PEEK blends.

The e-beam MP PTFE/PEEK (MB) was characterized by DMA, DSC, rheological, and morphological investigations. The comparison of DMA and DSC data of e-beam MP PTFE/PEEK (MB) and MP PTFE/PEEK 50/50 is presented in Figure 14. In case of the reactive extruded e-beam MP PTFE/PEEK (MB), a noticeable shift in the glass transition of the PEEK phase, indicating enhanced interactions (compatibilization) between the blend components, is observed. The  $T_g$  of PEEK component for MP PTFE/PEEK 50/50 occurs at a temperature of about 167°C, whereas for e-beam MP PTFE/PEEK (MB) at a temperature of 163°C. The increase in the crystallization temperature for e-beam MP PTFE/PEEK (MB) is due to the structural changes of e-beam MP PTFE (see Figures 6 and 7) and thus its different crystallization behavior in comparison with MP PTFE. Moreover, due to the modification of MP PTFE, in the second heating curves of e-beam MP PTFE/PEEK, a shift of the melting temperature of MP PTFE phase toward higher temperatures is observed.

The rheological behavior of e-beam MP PTFE differs considerably from that of MP PTFE (Figure 7). E-beam MP PTFE exhibits a strong pseudoplastic behavior and at high shear rates is characterized by lower viscosity than the nonirradiated MP PTFE. As a consequence, e-beam MP PTFE/PEEK shows better viscosity match in comparison with MP PTFE/PEEK, as depicted in the plot of viscosity ratio of blend components versus frequency in Figure 11. The better viscosity match should lead to an improved mixing process, that is, better dispersion and distribution of the dispersed e-beam MP PTFE phase in PEEK matrix. Since, the efficiency of mixing process is crucial for a successful coupling or compatibilization between e-beam MP PTFE and PEEK,<sup>35</sup> the preparation of masterbatch and its subsequent addition to MP PTFE/PEEK blends seems to be more advantageous in comparison with direct mixing of e-beam MP PTFE with the other blend components.

The chemical coupling of e-beam MP PTFE and PEEK and the better viscosity match between these two materials should lead to improved phase morphology and mechanical properties of e-beam MP PTFE/PEEK 50/50. However, it must be taken into consideration that e-beam MP PTFE does not show any mechanical strength and thus can cause a decrease in ultimate tensile properties of e-beam MP PTFE/PEEK blends.



**Figure 15.** Morphology of e-beam irradiated MP PTFE/PEEK (MB) 50/50 prepared at 50 rpm; magnification: (a) 500×, (b) 5000×.

The morphological investigations of e-beam MP PTFE/PEEK 50/50 (MB) (Figure 15) show a tremendous improvement in the dispersion of MP PTFE phase in PEEK matrix in comparison with the blends nonmodified MP PTFE/PEEK 50/50 (see Figure 12). The size of the dispersed particles in the reactive extruded blend is in the range of about 2  $\mu\text{m}$ , whereas the size of the dispersed droplets in the nonmodified blend exceeds 100  $\mu\text{m}$ .

On the basis of these results, it was assumed that such a tremendous improvement in the morphology could not be possible only due to the better viscosity match of the blend components and with a high probability a compatibilization between e-beam irradiated MP PTFE and PEEK took place. The DMA results also support this assumption. Therefore, the e-beam MP PTFE/PEEK MB was expected to be a suitable compatibilizer for MP PTFE/PEEK blends.

**Morphology and Mechanical Properties of MP PTFE/E-Beam MP PTFE/PEEK (MB)/PEEK Blends.** To study the influence of e-beam MP PTFE/PEEK (MB) on the morphology development and mechanical properties of MP PTFE/PEEK blends, a series of blends with different e-beam MP PTFE/PEEK (MB) content was prepared and characterized. The list of investigated blends is given in Table III.

It was expected that the addition of chemically modified MP PTFE/PEEK (MB) to MP PTFE/PEEK blends would lead to an improvement in their phase morphology and mechanical properties, that is, e-beam MP PTFE/PEEK (MB) would act as a compatibilizer for MP PTFE/PEEK blends.

Morphological investigations on compatibilized MP PTFE/PEEK 80/20 and 50/50 blends (Figure 16) confirm that e-beam MP PTFE/PEEK (MB) promotes smaller size and uniform dispersion of the dispersed phase in the matrix. On the other hand, the phase morphology of MP PTFE/PEEK 20/80 blend (Figure 17), with dispersed MP PTFE particles with the size of around 2  $\mu\text{m}$ , is not improved by adding MP PTFE/PEEK (MB). The results of tensile testing of the binary and compatibilized MP PTFE/PEEK are consistent with the morphological investigations.

The strain at break and the stress at break of 80/20, 50/50, and 20/80 blends are presented as a function of compatibilizer concentration in Figure 18. For the MP PTFE/PEEK 80/20 blends, a considerable increase in the stress at break with increasing compatibilizer concentration is observed. However, when its concentration exceeds 2 wt %, the strain at break drops significantly.

MP PTFE/PEEK 20/80 blends which do not show any improvement in the phase morphology for the compatibilized blends, do not exhibit a significant improvement in the ultimate tensile properties as well. Only for the high concentration of e-beam MP PTFE of 50%, an increase in the strain at break and stress at break of 33 and 10%, respectively, is noticed.

The most favorable effect of e-beam MP PTFE/PEEK on the mechanical properties as well as morphology of MP PTFE/PEEK blends is pronounced for the 50/50 blends (Figures 16 and 18). The ultimate tensile properties show a local maximum for the blends with 5 wt % of e-beam MP PTFE. In comparison with the uncompatibilized blends, an improvement of about 250% in strain at break and 40% in stress at break is found.

**Table III.** Blend Compositions—(Figure 1)

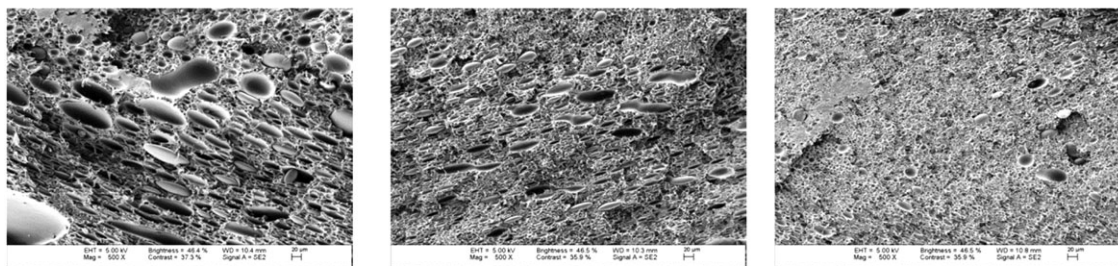
Blend code MP PTFE/e-beam MP PTFE/PEEK	E-beam MP PTFE <sup>a</sup> (wt %)	Component ratios (w/w)		
		MP PTFE	E-beam MP PTFE/ PEEK (MB)	PEEK
100/0/0	0	100	0	0
80/0/20	0	80	0	20
79.2/0.8/20	1	79.2	1.6	19.2
78.4/1.6/20	2	78.4	3.2	18.4
76/4/20	5	76	8	16
72/8/20	10	72	16	12
64/16/20	20	64	32	4
40/40/20	50 <sup>b</sup>	40	40 <sup>b</sup>	20
50/0/50	0	50	0	50
49.5/0.5/50	1	49.5	1	49.5
49/1/50	2	49	2	49
47.5/2.5/50	5	47.5	5	47.5
45/5/50	10	45	10	45
40/10/50	20	40	20	40
25/25/50	50	25	50	25
0/50/50	100 <sup>b</sup>	0	50 <sup>b</sup>	50
20/0/80	0	20	0	80
19/1/80	5	19	2	79
18/2/80	10	18	4	78
16/4/80	20	16	8	76
10/10/80	50	10	20	70
0/20/80	100 <sup>b</sup>	0	20 <sup>b</sup>	80
0/0/100	0	0	0	100

<sup>a</sup>With respect to MP PTFE component, two step blending; e-beam MP PTFE was initially reactive extruded as a masterbatch with PEEK [e-beam MP PTFE/PEEK 50/50 w/w (MB)].

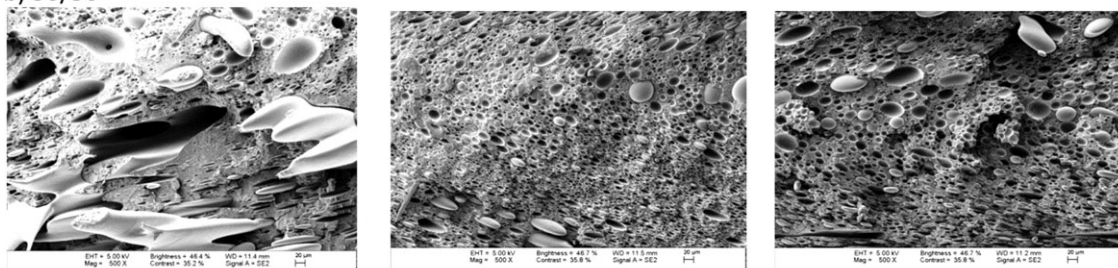
<sup>b</sup>With respect to MP PTFE component, one step blending; pure e-beam MP PTFE.

Summarizing the experimental results with regard to the potential of e-beam MP PTFE/PEEK (MB) in compatibilization of MP PTFE/PEEK blends, the biggest potential for improvement is verified for 50/50 blends. In this case, e-beam MP PTFE/PEEK (MB) provides better morphology development during blending process (better state of dispersion of MP PTFE phase in PEEK matrix) and better interfacial adhesion between the blend components [increasing of stress at break with increasing e-beam MP PTFE/PEEK (MB) content]. For 80/20 blends though the improved phase morphology for the compatibilization concentrations higher than 2 wt %, their strain at break decreases. This behavior is attributed to the fact that e-beam MP PTFE does not show any mechanical strength and by increasing its concentration the compatibilized blends become brittle and especially the blends in which MP PTFE constitutes the matrix phase. On the other hand, 20/80 blends, with MP PTFE as a disperse phase, do not show any improvement in the phase morphology when adding e-beam MP PTFE/PEEK. The mechanical properties of uncompatibilized MP PTFE/PEEK 20/

a) 80/20



b) 50/50



0 wt% e-beam MP PTFE

5 wt% e-beam MP PTFE

10 wt% e-beam MP PTFE

Figure 16. Phase morphology of MP PTFE/PEEK 80/20 and 50/50 blends with different concentration of compatibilizer.

80 blends are close to the mixing rule and the addition of compatibilizer does not lead to their significant improvement.

## CONCLUSIONS

DSC and DMA investigations show that MP PTFE/PEEK blends are immiscible over the composition range. The phase morphology and mechanical properties of the studied blends depend on the processing conditions and for the three investigated screw rotational speeds of 50, 100, and 200 rpm the lowest speed leads to the finest dispersion of minor phase (dispersed phase) in the matrix and in consequence better mechanical properties.

It is demonstrated that the immiscible blends of MP PTFE and PEEK can be compatibilized with e-beam MP PTFE/PEEK 50/50 (MB). The electron beam irradiation of MP PTFE in air atmosphere and at room temperature with an absorbed dose of 50 kGy results in a chain scission associated with the formation of  $-COOH$  and  $-COF$  functional groups. Such a modification of MP PTFE leads to a tremendous improvement in the state of dispersion of e-beam MP PTFE/PEEK (MB). Moreover, for the

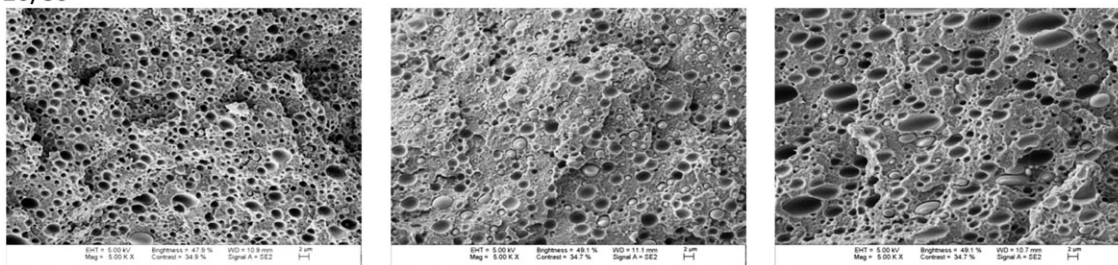
reactive extruded e-beam MP PTFE/PEEK, the glass transition temperature of PEEK phase is shifted toward lower temperatures indicating enhanced interactions between e-beam MP PTFE and PEEK. Therefore, the compatibilization between e-beam irradiated MP PTFE and PEEK is proven.

Consequently, e-beam MP PTFE/PEEK (MB) act as a compatibilizer of MP PTFE/PEEK blends and its addition results in an improved phase morphology (fine and uniform dispersion of the dispersed phase in the matrix) of 80/20 and 50/50 blends. However, for 20/80 blends no improvement is observed.

For the particular MP PTFE/PEEK blends, an optimum concentration of the compatibilizer for obtaining improved phase morphology and mechanical properties is found. The most significant influence of compatibilizer is found for MP PTFE/PEEK 50/50 blends.

For 80/20 blends, though the improvement in the state of the dispersion above the compatibilizer concentration of 2 wt % (e-beam MP PTFE with respect to MP PTFE component), the blends get brittle and no considerable improvement in their

20/80

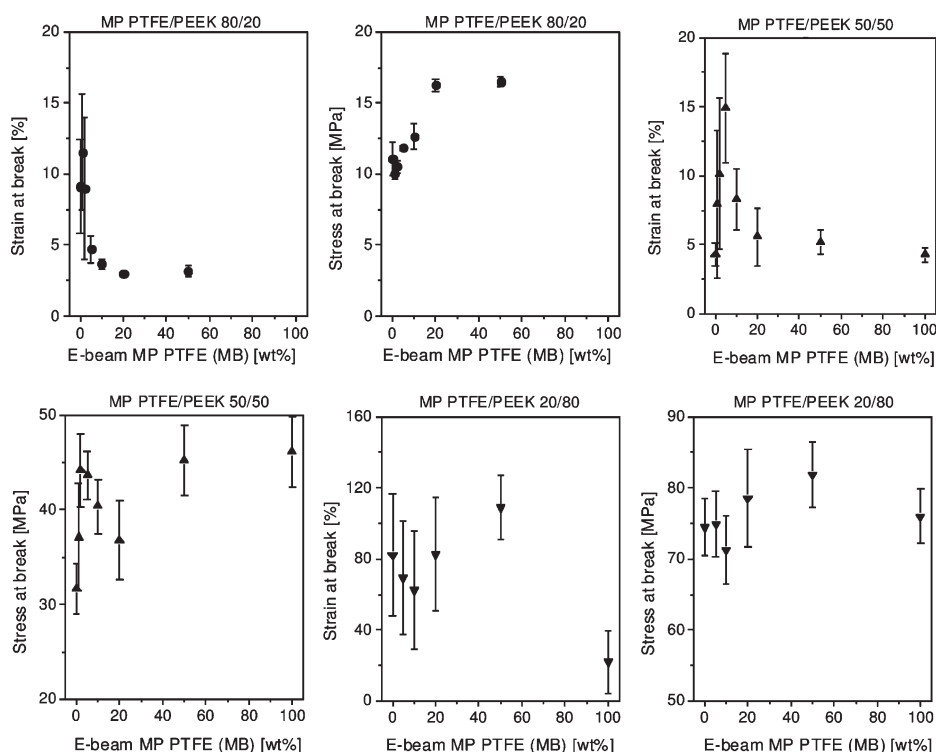


0 wt% e-beam MP PTFE

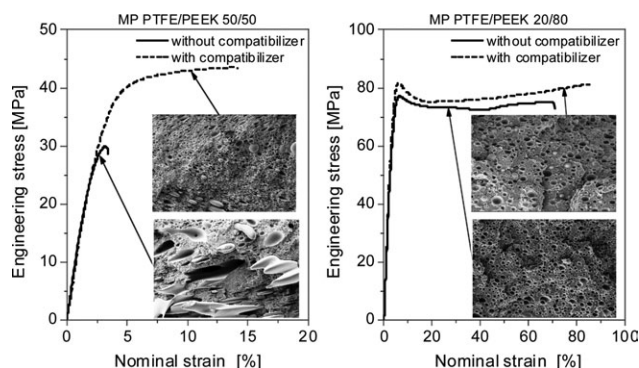
5 wt% e-beam MP PTFE

10 wt% e-beam MP PTFE

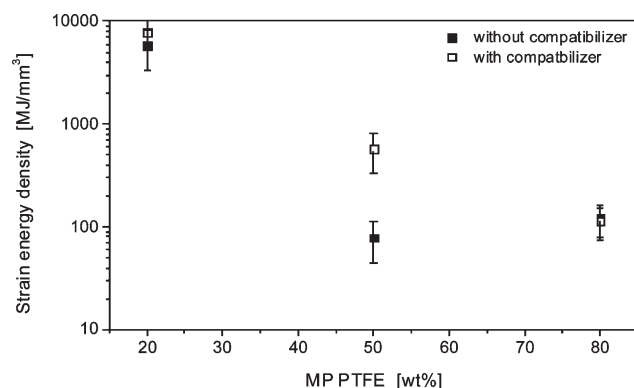
Figure 17. Phase morphology of MP PTFE/PEEK 20/80 with different concentration of compatibilizer.



**Figure 18.** Strain at break and stress at break of compatibilized MP PTFE/PEEK blends, (compatibilizer concentration is given with respect to MP PTFE component – see Table III).



**Figure 19.** Improvement in the tensile properties of compatibilized MP PTFE/PEEK blends; 50/50 – 5 wt% and 20/80 – 50 wt% of e-beam MP PTFE (MB).



**Figure 20.** Strain energy density of uncompatibilized and compatibilized MP PTFE/PEEK blends evaluated from the tensile test.

mechanical properties is found (Figures 16 and 18). For 50/50 and 20/80 blends, the compatibilizer concentration of 5 and 50 wt %, respectively, provides the most improved ultimate tensile properties (Figure 19). In consequence, an improvement in the toughness of the compatibilized blends is noticed as well, as presented in Figure 20. MP PTFE/PEEK 20/80 shows an improvement in the toughness of 35%, whereas for 50/50 a great improvement of more than 600% is noticed.

The obtained results definitely show that e-beam MP PTFE/PEEK (MB) has a potential and is suitable in compatibilization of MP PTFE/PEEK blends, because it provides an improvement in their phase morphology, interfacial adhesion, and mechanical properties.

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