

# Influence of Calcium Carbonate Filler and Mixing Type Process on Structure and Properties of Styrene–Acrylonitrile/Ethylene–Propylene–Diene Polymer Blends

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**ABSTRACT:** The properties of styrene–acrylonitrile (SAN) and ethylene–propylene–diene (EPDM) blends containing different types of calcium carbonate filler were studied. The influence of mixing type process on the blend properties was also studied. Two different mixing processes were used. The first one includes mixing of all components together. The other process is a two-step mixing procedure: masterbatch (MB; EPDM/SAN/filler blend) was prepared and then it was mixed with previously prepared polymer blend. Surface energy of samples was determined to predict the strength of interactions between polymer blend components and used fillers. The phase morphology of blends and their thermal and mechanical properties were studied. From the results, it can be con-

cluded that the type of mixing process has a strong influence on the morphological, thermal, and mechanical properties of blends. The two-step mixing process causes better dispersion of fillers in blends as well as better dispersion of EPDM in SAN matrix, and therefore, the finest morphology and improved properties are observed in blends with MB. It can be concluded that the type of mixing process and carefully chosen compatibilizer are the important factors for obtaining the improved compatibility of SAN/EPDM blends. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** blends; styrene–acrylonitrile; ethylene–propylene–diene; mixing; filler

## INTRODUCTION

The scientific and commercial progress in the area of polymer blends during the past decades has been tremendous. Polymer blends represent a new group of polymer materials with interesting and sometimes very specific properties.<sup>1</sup> The reason for the manufacture of polymer blends is the will to eliminate or to diminish the drawbacks that characterize the polymers and also desire to drop the price of the expensive polymers by mixing them with the cheaper ones, without significant deterioration of their properties. Moreover, the manufacturing process of blends is already being known as generally much faster than designing and manufacturing the new polymers. Certain properties, mainly physical properties, for example, density, hardness, impact resistance, and tensile strength, can be improved by mixing process.<sup>2</sup>

In our work, the properties of composite polymer blends prepared from styrene–acrylonitrile copolymer (SAN) and ethylene–propylene–diene rubber (EPDM)

with calcium carbonate filler have been studied. To improve the toughness, that is, to improve the impact resistance of SAN, which is an extensively used elastomer, some rubber component is needed to be added in its rigid matrix. For that purpose, EPDM or polybutadiene rubber is often used. EPDM has excellent resistance to factors such as weather, ozone, and oxidation, attributed to its nonconjugated diene component, and it could be a good alternative for substituting polybutadiene-based rubbers in polystyrene or SAN toughening.<sup>3,4</sup>

However, the immiscibility of many polymer pairs is a serious problem in the preparation of polymer blends. To overcome this problem, it is necessary to improve the compatibility and to obtain the blend with good mechanical properties. For this reason, it is needed to introduce the compatibilizer in polymer blend. It locates at the border of two phases of the both polymers and causes enhanced interactions between polymer components due to reduced interfacial tension.<sup>5</sup> As compatibilizers for immiscible polymer blends, some other type of polymers, graft copolymers, functional monomers, or nanofillers are often used.<sup>6</sup> Commonly applied fillers for modification of polymer blends are powder mineral fillers,

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**TABLE I**  
**Composition of SAN/EPDM/Filler Polymer Blends**

Sample name	wt % of filler	Preparation method
SAN/EPDM	0	Dry mixing + extrusion
SAN/EPDM/F1	13	Dry mixing + extrusion
SAN/EPDM/F2	13	Dry mixing + extrusion
SAN/EPDM/F3	13	Dry mixing + extrusion
Masterbatch (MB) SAN/EPDM/F3	23	Dry mixing + extrusion
SAN/EPDM/F1 + MB	13.4	MB + dry mixing + extrusion
SAN/EPDM/F2 + MB	13.4	MB + dry mixing + extrusion
SAN/EPDM/F3 + MB	13.4	MB + dry mixing + extrusion

for example, calcium carbonate, graphite, molybdenum disulphide, barium sulfate(VI), and titanium white. Because of the presence of the filler in polymer blend, all properties of the pure polymers are more or less changed, and in fact, a new material is created by blending a polymer with inorganics. The properties of the resulting composite material are determined by the properties of the components, namely, the type of polymer and filler, filler particle size, shape and modulus, the concentration of filler in the polymer matrix, and the type of interactions between the filler particles and polymer host.<sup>7-9</sup> Synthetic filler, so-called precipitated calcium carbonate, is one of the frequently used fillers for polymer blends. Its particles are expected to modify the viscosity of the polymer melt. Their good thermal conductivity contributes to the homogeneity of the melt and good dispersion in the polymer matrix.<sup>10,11</sup> Another aspect, which is also very important in polymer blend preparation, is the type of mixing process. The properties of the polymer blends not only depend on the type of the components but also significantly on the mixing method that includes the order of the addition of the components.<sup>2,12</sup> For this purpose, a multistep process for the preparation of polymer blends is often used. This kind of preparation especially manifests in the change of the mechanical, thermal, and processing properties of polymer blends.

In this work, the influence of the type of mixing process on the properties of SAN/EPDM polymer blends with calcium carbonate filler was studied. The first one includes mixing of all components together. The other mixing process consists of two steps. In the first step, a masterbatch (MB; composite with high ratio of EPDM and filler) was prepared. Then followed the second mixing step when such prepared MB was extruded with already prepared SAN/EPDM blends. The effect of the type of mixing process on SAN/EPDM composite polymer blends was studied by scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and by the determination of mechanical properties.

## EXPERIMENTAL

### Materials

Blends of SAN (containing 24 wt % of acrylonitrile, Tyril 790; The Dow Chemical Company, France) and EPDM (containing 55 wt % of ethylene and 4 wt % of ethylidene norbornene, Keltan 312; DSM, Netherlands) were prepared from three different types of calcium carbonate fillers (Solvay, Belgium). For all filler types, about 90% of filler particles were smaller than 2.6  $\mu\text{m}$ . All types of fillers were modified by the controlled surface pretreatment by sodium stearate, which becomes chemically bonded to filler.<sup>13</sup> Filler F1 contains 2 wt % of sodium stearate, whereas fillers F2 and F3 contain the same amount of sodium stearate (3 wt %); however, they are prepared as two batches and showed different values of surface energies.

### Preparation of polymer blends

For the preparation of SAN/EPDM polymer blends, Haake Rheocord system 9000 twin-screw extruder was used (corotating extruder with standard nonintensive screw characteristics; Haake, Karlsruhe, Germany). Temperature profile of the extruder, from hopper to die, was 180/190/210/210°C; the rotating speed was 65 rpm. During the sample preparation, all components were first dry mixed and then extruded. The ratio of SAN and EPDM in blends was 80 : 20.

To improve the mixing of polymers and filler, a MB was prepared (blend with high ratios of EPDM and filler). The MB was prepared by dry mixing and extrusion of SAN (7.7 wt %), EPDM (69.3 wt %), and filler (23 wt %). Then, the blend was prepared by dry mixing of MB (4 wt %) with other components (96 wt %) and then extruded. The composition of the samples is given in Table I.

### Characterization

#### Determination of surface energies

Measurements of filler surface energies were done at 23°C on pellets of used calcium carbonate fillers, through measurements of contact angles using Data

**TABLE II**  
Surface Tensions ( $\gamma_1$ ) and Their Dispersive ( $\gamma_1^d$ ) and Polar ( $\gamma_1^p$ ) Components of Test Liquids<sup>13</sup>

Liquid	Surface tension (mJ/m <sup>2</sup> )		
	$\gamma_1^d$	$\gamma_1^p$	$\gamma_1$
Water	21.8	51.0	72.8
Formamide	39.0	19.0	58.0
Diiodomethane	50.8	0.0	50.8

Physics OCA 20 Instrument. Three types of liquids were used for characterization: sessile drops (2  $\mu$ L) of water (distilled twice  $\lambda = 1.33 \mu\text{L}/\text{cm}$ ), formamide (p.a. 99.5%; Fluka), and diiodomethane (p.a. 99%; Aldrich). The contact angle was determined from 10 to 30 s after drop deposition. Average values of at least five drops on different spots of the same sample were taken, and the standard deviation was always less than 2°. Surface free energies of the fillers were calculated using harmonic mean equation (Wu model)<sup>14,15</sup>:

$$\gamma_{lv} (1 + \cos \theta) = \frac{4\gamma_s^d \gamma_l^d}{\gamma_s^d + \gamma_l^d} + \frac{4\gamma_s^p \gamma_l^p}{\gamma_s^p + \gamma_l^p} \quad (1)$$

where  $\gamma^d$  is the dispersive component and  $\gamma^p$  is the polar component of the surface free energy;  $\gamma_l$  and  $\gamma_s$  are the surface free energies of the liquid and solid, respectively; and  $\theta$  is the contact angle. Surface tensions of the test liquids used for contact angle measurements are presented in Table II.

#### Scanning electron microscopy

SEM FEI Quanta 200 was used to study the morphology of the prepared polymer. The extruded samples were cryogenically fractured in liquid nitrogen and then gold sputtered for examining.

#### Dynamic mechanical analysis

For dynamic mechanical measurements, DMA (Q800; TA) instrument was used. Measurements were carried out in nitrogen atmosphere, within the temperature range from  $-100$  to  $150^\circ\text{C}$  at heating rate of  $5^\circ\text{C}/\text{min}$ , frequency of 1 Hz, and deformation of 0.1%. Specimens for DMA measurement were molded as sheets of  $12 \text{ cm} \times 12 \text{ cm} \times 0.1 \text{ cm}$  at  $230^\circ\text{C}$  and with a pressure of 10 MPa. Samples were cut as rods of  $5.0 \text{ cm} \times 1.0 \text{ cm} \times 0.1 \text{ cm}$ .

#### Thermogravimetric analysis

Thermal stability of studied SAN/EPDM polymer blends was studied in the temperature range from 25 to  $550^\circ\text{C}$  using thermogravimetric analyzer TA Instruments Q500. The measurements were carried out in nitrogen at a flow rate of  $100 \text{ cm}^3/\text{min}$  and heating rate of  $5^\circ\text{C}/\text{min}$ .

#### Determination of mechanical properties

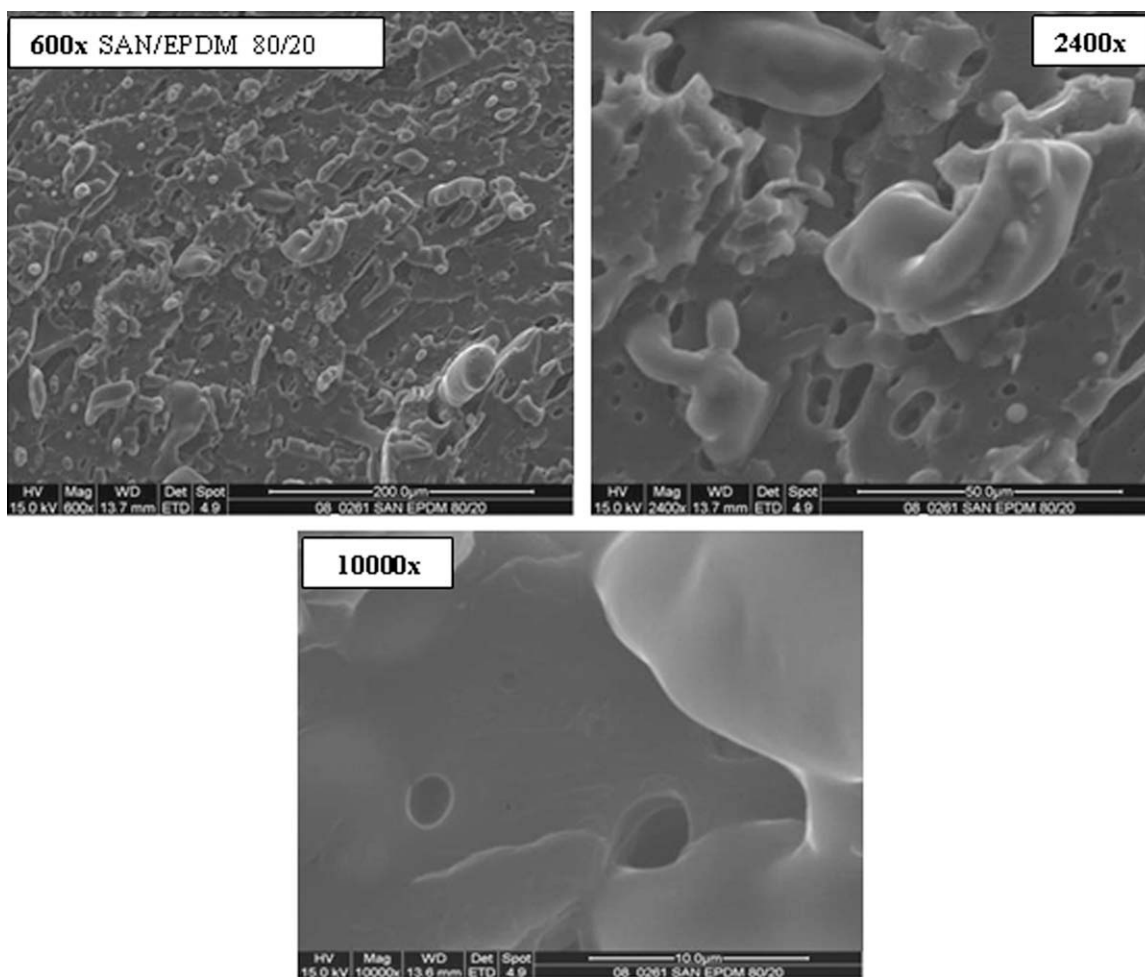
Testing of mechanical properties was done using Universal Testing Machine (model 1185; Zwick) at a constant temperature ( $23^\circ\text{C}$ ) and humidity (50% RH). A gauge length of 25 mm and crosshead speed of 50 mm/min were used to determine the tensile strength and the elongation at break (ISO 527-1:1993, ISO 527-2:1993). For each data point, five measurements have been made. Impact strength and Izod notch were determined according to ISO 180:1993 and ASTM 4508, respectively.

## RESULTS AND DISCUSSION

#### Scanning electron microscopy

SEM was used for morphology characterization of the prepared blends. One of the goals of this work was to study the influence of the filler on morphology and properties of SAN/EPDM blends. Another very important aspect was the impact of mixing type process on the blend properties. The morphology of blends and the influence of studied fillers could be seen in micrographs (Figs. 1 and 2).

The two-phase morphology of SAN/EPDM blend is shown in Figure 1, in which the dispersed EPDM phase in SAN matrix is observed. SAN and EPDM are incompatible materials, which lead to poor interfacial adhesion. The morphology of SAN/EPDM blend is not homogeneous because the EPDM phase is not uniformly dispersed in SAN phase due to the immiscibility of the polymers. The lack of adhesion between SAN and EPDM is observed due to high interfacial tension between them. In these conditions, the holes in SAN matrix instead of EPDM nodules are shown. After the addition of the stearate-pretreated fillers (F1, F2, and F3), the morphology of SAN/EPDM blends [presented in Fig. 2(a–c)] becomes more homogeneous in comparison to blend without filler. From the micrographs, it can be seen that the size of dispersed EPDM phase in blends with filler is smaller in comparison to pure SAN/EPDM blends (Fig. 1). This is especially shown after the addition of the stearate-pretreated filler F3. The morphology of that blend [presented in Fig. 2(c)] became more homogeneous with smaller size of dispersed EPDM phase. It is known that the addition of fillers to polymer blends leads to the increase of miscibility of blend constituents. The amount of filler in blends also has a significant role in blend properties.<sup>11,16,17</sup> The certain amount of filler is necessary to produce the improvements in properties due to the interactions with blend components.<sup>11,16,17</sup> On the other hand, the higher amount of filler might produce the agglomerates that lower the quality of blend, that is, the homogeneity and the properties of



**Figure 1** SEM micrographs of SAN/EPDM 80/20 blends.

blends are poor. For this reason, it is necessary to optimize the amount of fillers in blends. In this study, the amount of filler in all prepared blends is kept in constant level (about 13 mass %; Table I). Furthermore, the interactions between the components of polymer blend depend on the values of surface free energies.<sup>18–20</sup> The values of the polar and the dispersive components as well as the values of total surface energy of polymers and used fillers are given in Table III. The filler F3 has the optimal surface energy (between the values for SAN and EPDM), and it is supposed to be situated at the interface. Therefore, its role is to enhance the interactions between SAN and EPDM, resulting in improved properties of blend.

The surface energy of the different polymers gives a quantitative image of the interfacial tension. Interfacial tension between two phases is primarily expressed by the difference in polarity. If the constituents of the blend have different polarities, there is a significant interfacial tension between them.<sup>21,22</sup> This explains the poor contact of EPDM particles with the SAN matrix for pure SAN/EPDM blend obtained by SEM (Fig. 1). The values of surface ener-

gies for modified fillers presented in Table III vary from 32 to 40 mJ/m<sup>2</sup>. The modification of filler surface was done to bring them close to the values of SAN and EPDM. As it can be seen, the value of the surface energy for untreated filler was 72 mJ/m<sup>2</sup>, and it was successfully decreased by the surface modification with sodium stearate. It is expected that the surface energy of the filler, whose value is between the values of blend constituents, will result in the effective adhesion at the interface and consequently in the improved morphology.<sup>18–20,23</sup> When the stearate-pretreated filler is added to SAN/EPDM blends, it is expected that the morphology of blends will become finer in comparison to the blends without filler.<sup>24,25</sup> This behavior is in accordance with SEM results (Fig. 2). The more homogeneous morphology is obtained in blend with filler F3 in comparison to blends prepared with fillers F1 and F2. The agglomeration of EPDM phase in blends with fillers F1 and F2 is higher.

Furthermore, the property enhancements in these systems depend largely on the dispersion of filler in the polymer matrix. The most crucial factor in controlling the morphology and achieving different

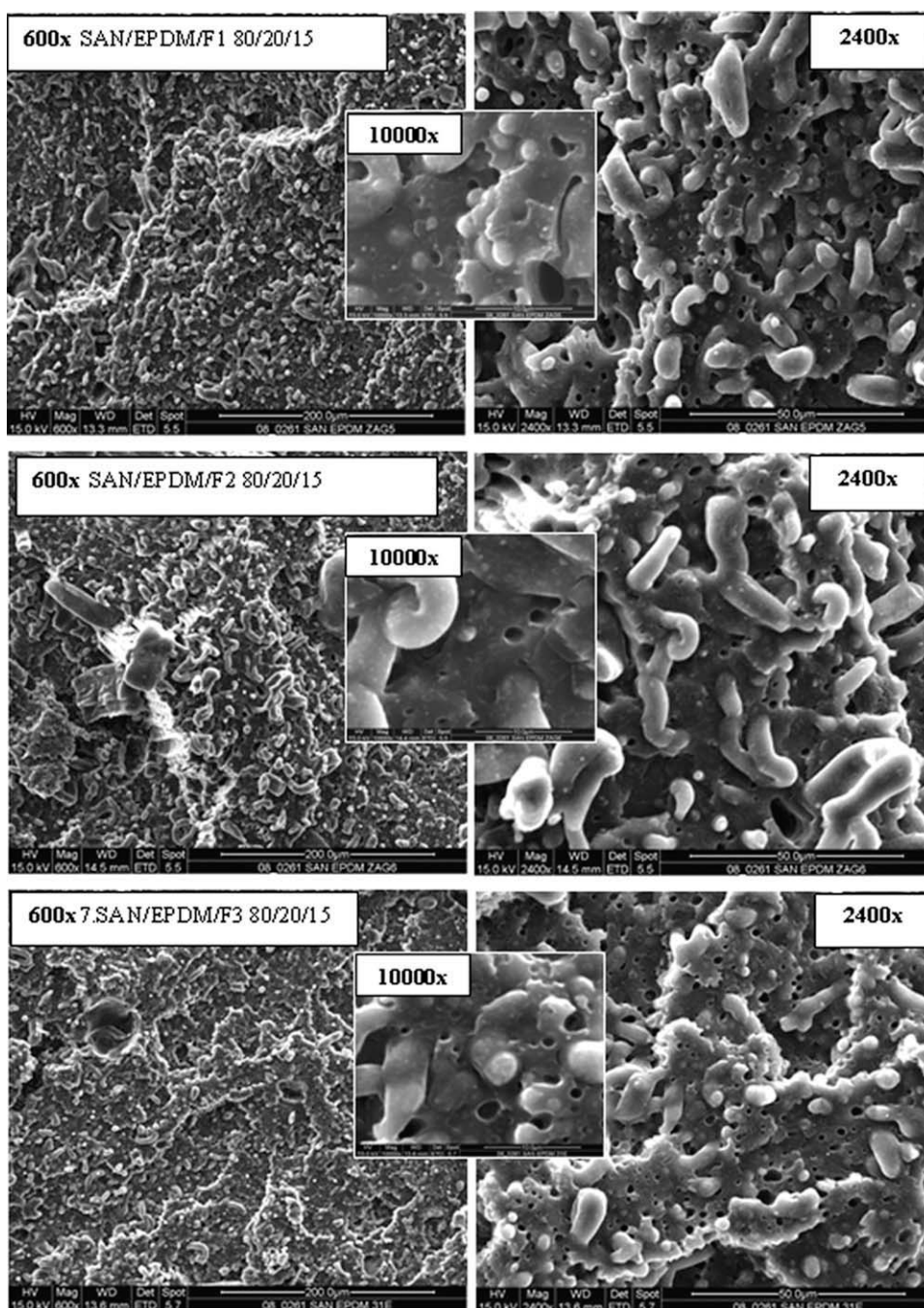


Figure 2 SEM micrographs of SAN/EPDM/filler blends.

levels of dispersion is the extent of interaction between filler and the polymer matrix.<sup>26</sup> Many studies have also dealt with the control of the phase dispersion in polymer blends. The bulk morphology created by melt mixing is shown to depend on parameters such as polymer components ratio, filler amount, shear rate, viscosity, viscosity ratio, elasticity, elasticity ratio, interfacial tension reactivity of functional groups, mixing time, and especially the type of mixing process.<sup>27</sup> The order of the addition of the components in mixing type process has significant influence on blend properties.<sup>2</sup> The simplest

TABLE III  
Results of Surface Free Energy (Wu Model)

Sample	Surface energy (mJ/m <sup>2</sup> )		
	$\gamma^d$	$\gamma^p$	$\gamma$
SAN (film from solution)	44.66	0.92	45.59
EPDM	28.59	0	28.59
Untreated filler	38.41	33.61	72.02
F1	40.26	0	40.26
F2	32.19	0	32.19
F3	36.15	0	36.15

procedure and the most reported in the literature is the addition of the components all together in the mixer. They are blended at a temperature high enough to ensure that the polymers will transform into viscous fluids; however, a stage where the materials are solid and then progressively melted precedes the actual melt blending. The process is complex, and it involves mixtures of solids and viscous fluids and there occurs the dispersion and migration of the particles inside the molten material as well as the simultaneous evolution of the morphology of the polymer blend.<sup>2</sup> With this mixing procedure, if one polymer melts at a temperature significantly lower than the other, the solid particles may be incorporated into it preferentially even though the mentioned polymer does not have the better affinity. As the obtained initial distribution will not be that corresponding to the thermodynamic equilibrium, the filler sometimes will not migrate to the preferred phase or to the interface. A second alternative consists in melting the two polymers and afterward adding the filler so that the filler particles do not see any solid medium. Third possibility is to mix and then extrude the filler with one or the both types of polymers (preparing of MB) and then to add such prepared MB to polymers and filler in the second step of extrusion. An efficient strategy consists of first dispersing part of phase A within phase B all together with filler and then adding it in larger amount of phase A (the final matrix) and phase B. For this reason, in our experiment, another group of SAN/EPDM polymer blends was prepared with addition of MB. The idea of MB preparation is based on the fact that filler with controlled surface energy will be first dispersed in MB with higher amount of EPDM phase and then will be more equally dispersed after the addition of such prepared MB in SAN/EPDM blends. The morphology of the blends with MB is illustrated in Figure 3. The more or less homogeneous morphology, observed in Figure 2, for the same blend composition (80/20/filler) is improved with the addition of MB. As can be seen in Figure 3, the rubber particles are spherical and randomly distributed in the matrix. Such distribution of the rubber particles was attended to achieve with the above discussed type of mixing, which includes MB preparation. SEM results show a remarkable decrease of rubber particle size and more uniform dispersion, especially in the case of blend SAN/EPDM/F2 + MB. The best effect on the morphology improvement in blend SAN/EPDM/F2 + MB might be the result of the good dispersion of filler F2 in MB. The value of the surface energy of filler F2 ( $\gamma_{F2} = 32.19$ ; Table III) is close to that of EPDM ( $\gamma_{EPDM} = 28.59$ ), which finally results in good dispersion of filler. The chemical modification of the filler surface enhances affinity of the filler particles toward polymers in blend and they will be thermodynamically stabilized at the

interface.<sup>2</sup> Despite the optimal surface energy of filler F3 ( $\gamma_{F3} = 36.15$  mJ/m<sup>2</sup>; Table III), the blend with MB and filler F2 shows the better morphology in comparison to the blend with MB and F3. In general, it can be concluded that the two-step blending results in better dispersion of EPDM and filler in SAN matrix.

### Dynamic mechanical analysis

DMA provided a clear idea about the viscoelastic properties and phase structure of the blends. The DMA results for studied SAN/EPDM samples prepared with different fillers and for SAN/EPDM blends prepared with MB are given in Table IV and in Figures 4–6. DMA method has been used to analyze the phase behavior of SAN/EPDM polymer blends. As it is known, this technique is a more sensitive technique than DSC for detecting the transitions in polymers. As it could be seen from the results (Table IV), the two main glass transitions in SAN/EPDM blends are obtained by DMA measurements. The lower transition ( $T_{g1}$ ) characterizes soft EPDM phase in the area around  $-50^\circ\text{C}$ , whereas the higher transition ( $T_{g2}$ ) represents hard SAN phase and it is found in the region around  $109^\circ\text{C}$ . It is known that the results of dynamic mechanical measurements are used to predict the miscibility of the system.<sup>25,28</sup> The effect of compatibilizer on the position of  $T_{g}$ s is a reflection of compatibilization extent in polymer blends. In general, for an incompatible blend, the storage modulus inflection point ( $E'$ ), the loss modulus maximum ( $E''$ ), and the loss tangent maximum ( $\tan \delta$ ) versus temperature show the presence of two main transitions corresponding to the glass transition temperatures of individual polymers in blend. For the miscible blend, the DMA curve would show only one main phase transition, that is, the single peak in between the transition temperatures of the components. In the case of the compatible and/or partly compatible blends, there are two main phase transitions, which might be shifted to higher or lower temperatures as a function of the composition and compatibility. These results show that the addition of filler has the influence only on the glass transition temperature of the soft EPDM phase ( $T_{g1} = -50^\circ\text{C}$ ), which is more or less shifted to the higher temperature. In other words, the glass transition temperatures of SAN and EPDM are moved toward each other. On the other hand, the added filler showed only slight influence on SAN phase ( $T_{g2}$  at  $109^\circ\text{C}$  remains almost the same).

From the results, it can be seen that  $T_{g1}$  of most studied samples is only slightly shifted to the higher values. The highest shift of EPDM glass transition temperature is observed for blend SAN/EPDM/F2 + MB (from  $-50$  to  $-44^\circ\text{C}$ ). This change is in good correspondence to the explained morphology of this blend (Fig. 3). On contrary, the transition  $T_{g2}$ , which describes SAN phase, did not change its position

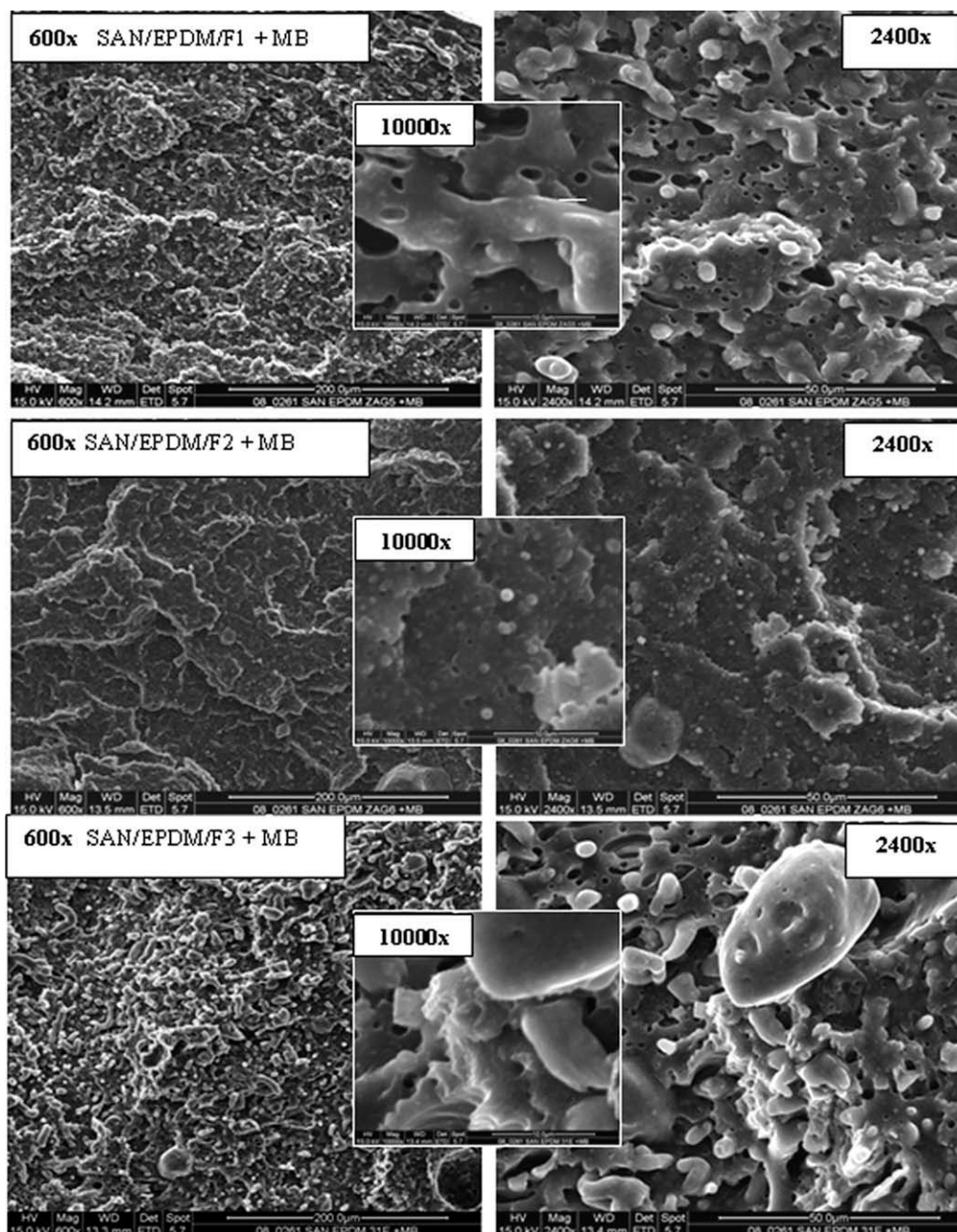


Figure 3 SEM micrographs of SAN/EPDM/filler blends prepared with masterbatch.

TABLE IV  
Glass Transition Temperatures of EPDM ( $T_{g1}$ ) and SAN ( $T_{g2}$ ) and Storage Modulus ( $E'$ ) for SAN/EPDM Blends

Samples	$T_{g1}$ (°C) (from $E''$ )	$T_{g2}$ (°C) (from $E''$ )	$E'$ (MPa) ( $T = -10^\circ\text{C}$ )	$E'$ (MPa) ( $T = 25^\circ\text{C}$ )	$E'$ (MPa) ( $T = 100^\circ\text{C}$ )	$E'$ (MPa) ( $T = 140^\circ\text{C}$ )
SAN	–	109	–	–	–	–
EPDM	–50	–	–	–	–	–
SAN/EPDM	–46	108	2271	2025	1304	4.80
SAN/EPDM/F1	–46	107	2223	1989	1247	24.26
SAN/EPDM/F2	–47	107	2208	1977	1273	22.28
SAN/EPDM/F3	–46	107	2017	1783	1140	28.33
SAN/EPDM/F1 + MB	–47	107	1674	1502	943	5.61
SAN/EPDM/F2 + MB	–44	106	2325	2076	1262	9.98
SAN/EPDM/F3 + MB	–48	108	2106	1889	1221	5.44

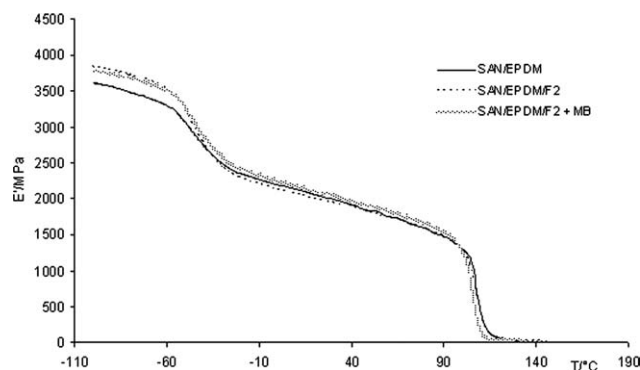


Figure 4 Storage modulus ( $E'$ ) of SAN/EPDM blends.

with filler addition, which is in correlation with the conclusion that fillers added in the blend mostly affect the soft EPDM phase. The variation of the storage modulus  $E'$  with the temperature is also shown in Table IV. In general, it is known that the addition of filler induces increase of storage modulus as well as the increase of  $T_g$  temperatures due to the increase in stiffness.<sup>29</sup> The highest value of the storage modulus is observed for blend SAN/EPDM/F2 + MB due to its fine morphology (Table IV and Fig. 4). It is known that the higher storage modulus ( $E'$ ) indicates the higher rigidity and stiffness of blends.<sup>30</sup>

Figure 5 illustrates the values of  $\tan \delta$  for studied samples. The lowest intensity of  $\tan \delta$  for soft EPDM phase is observed for the unfilled blend SAN/EPDM, whereas with filler addition, the intensity increases. The maximal increase in  $\tan \delta$  at approximately  $-50^\circ\text{C}$  is observed for the blend SAN/EPDM/F2 + MB, and it illustrates the greatest effect of the added filler F2 on the dispersed EPDM phase. The increased value of  $E''$  at maximum in Figure 6 and the high value of  $\tan \delta$  in Figure 5 indicate the higher possibilities of motions in soft EPDM phase in SAN/EPDM/F2 and SAN/EPDM/F2 + MB. SAN/EPDM blend without filler shows the opposite properties. It has the lowest value of  $E''$  and  $\tan \delta$ . The DMA results are in accordance to the SEM results, in which the finer morphology is found in

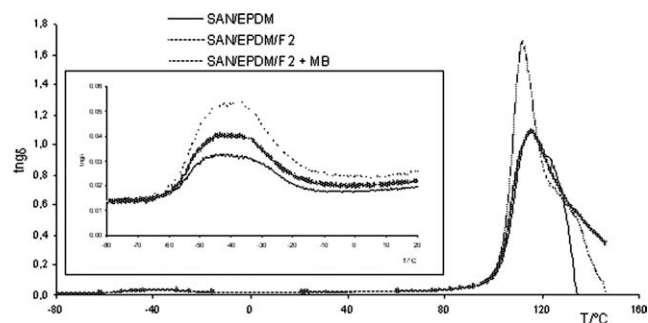


Figure 5  $\tan \delta$  of studied SAN/EPDM blends.

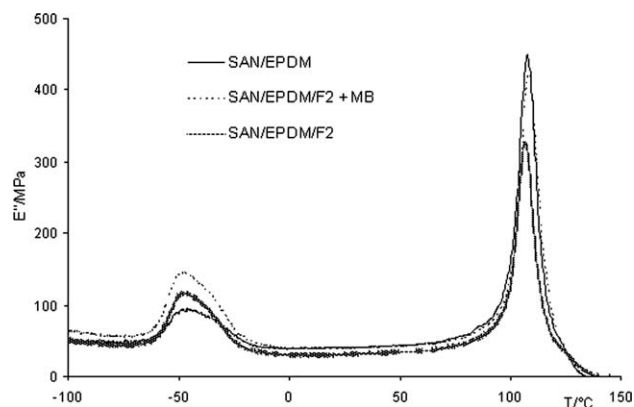


Figure 6 Loss modulus ( $E''$ ) of SAN/EPDM blends.

the blend prepared with filler F2 and MB (SAN/EPDM/F2 + MB).

### Thermogravimetric analysis

Thermal stability of prepared SAN/EPDM polymer blends was studied by TGA. This method determines the mass loss rate of material, which occurs due to sample decomposition at high temperatures. The results of TGA measurements are shown in Table V and Figure 7. The temperature  $T_{90}$  represents the beginning of the thermal degradation of sample, that is, the temperature at which the 10 mass % of the sample was decomposed. Temperature  $T_{50}$  represents mass loss of 50%, which is the first significant indicator for the determination of thermal stability of sample.

TGA was used to reveal the influence of composition of the polymer blends on their properties. For the sample SAN/EPDM 80/20, it can be seen that the temperature  $T_{90}$  is almost equal to the value of  $T_{90}$  for neat SAN ( $\sim 359^\circ\text{C}$ ), because SAN is the major component of the studied polymer blend. For polymer blends prepared with filler, the value of  $T_{90}$  is almost unchanged for the blends SAN/EPDM/F1 and SAN/EPDM/F2, whereas for the blend SAN/

TABLE V  
Thermogravimetric Analysis of Studied SAN/EPDM Blends

Sample	$T_{90}$ ( $^\circ\text{C}$ )	$T_{50}$ ( $^\circ\text{C}$ )	Carbonized residue (wt %)
SAN	359.29	383.19	0.31
EPDM	418.87	436.61	0.59
SAN/EPDM	359.12	388.20	3.35
SAN/EPDM/F1	359.19	391.13	13.05
SAN/EPDM/F2	360.59	393.19	12.58
SAN/EPDM/F3	367.56	402.10	12.68
SAN/EPDM/F1 + MB	358.13	390.71	13.96
SAN/EPDM/F2 + MB	365.70	399.69	14.01
SAN/EPDM/F3 + MB	359.98	395.31	14.53



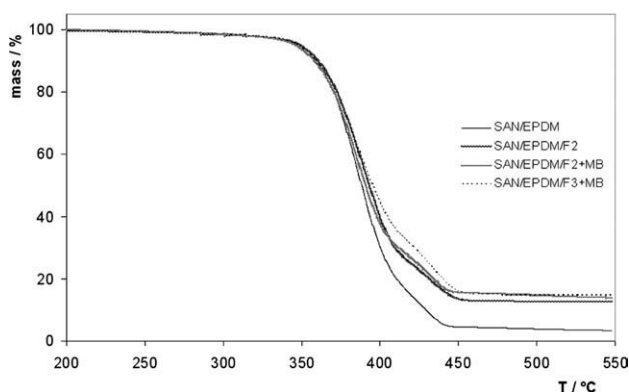


Figure 7 TGA curves of studied SAN/EPDM blends.

EPDM/F3, its value is increased ( $367.56^{\circ}\text{C}$ ). This indicates the better thermal stability of this blend, which is caused by its better homogeneity due to filler addition. It is known<sup>31</sup> that the present filler causes the better dispersion of particles, which further increases the thermal stability of polymers. This is also shown by previously discussed results of SEM and DMA. For blends prepared with MB, the highest value of  $T_{90}$  shows blend SAN/EPDM/F2 + MB. If we note the values for  $T_{50}$ , the same trend could be observed. The blend SAN/EPDM has almost the same value as neat SAN. The highest increase (for  $19^{\circ}\text{C}$ ) in thermal stability could be observed for the blend SAN/EPDM/F3 and blend with MB SAN/EPDM/F2 + MB (increase for  $16^{\circ}\text{C}$ ). The obtained values of carbonized residue also indicate the thermal stability of studied polymer blends. The increased value of carbonized residue in blends prepared with MB indicates that the filler acts as an isolator during the exposure of the sample to high temperatures. Filler creates the isolation layer at the surface of the polymer matrix and prevents the heat transfer to the bulk. These blends showed the better dispersion of EPDM resulting in homogeneous structure due to improved mixing process.

From the results, it can be seen that the samples prepared with filler show the increased thermal stability. The midpoint of degradation ( $T_{50}$ ) is moved to higher values and the higher carbonized residue is obtained. The highest value of the carbonized residue (14.53%) is observed for the samples SAN/EPDM/F2 + MB and SAN/EPDM/F3 + MB, which is the result of the formed "isolating layer" of the filler on the surface of blends. On the other side, the sample SAN/EPDM/F3, which has the highest value of  $T_{50}$ , shows the lower carbonized residue and the higher degradation rate. This can be explained by the different mechanism of the sample decomposition. In Figure 7, it can be observed that the samples with higher content of carbonized residue have the lower degradation rate and that their decomposition occurs in two steps. The different mechanism of the decomposition

indicates the formation of the different morphology of polymer blends influenced by the type of mixing process. The two-step preparation of blends results in different dispersion of filler and EPDM in SAN matrix, which further influences the thermal stability and the mechanism of blend decomposition.

### Mechanical properties

The results of mechanical testing of studied blends are given in Table VI. The impact strength, tensile strength, and elongation at break were determined for all the samples. The obtained results could be divided into two groups: the results for blends with and without MB. The results show higher values of tensile and impact strength for blends prepared without MB. The highest value for impact strength is seen in the blend SAN/EPDM/F3. This result could be explained by optimal surface energy of filler F3. Because of this value of surface energy, this filler has the greatest chance for migration to the interface and positioning between SAN and EPDM phases in blend. For the samples prepared with MB, the decrease of the impact and tensile strength is observed due to the change in morphology caused by different types of mixing processes. The only exception is the blend SAN/EPDM/F2 + MB, which has the improved tensile and impact strength as well as the elongation at break. The result for elongation at break is in good correlation with that of  $\tan \delta$  peak, increase of which indicates flexibility and toughness. In general, the higher values of elongation at break are expected for the samples prepared with MB due to their low tensile strength and previously discussed results for storage modulus. For this sample, all results are in very good agreement: it has the finest morphology, that is, the most uniform dispersion of the filler and EPDM in SAN matrix. Furthermore, this blend has the best thermal properties and, generally, it shows increased compatibility of SAN and EPDM due to improved mixing process.

TABLE VI  
Impact Strength, Tensile Strength, and Elongation at Break of Studied SAN/EPDM Blends

Sample	Impact strength (kJ/m <sup>2</sup> )	Tensile strength (MPa)	Elongation at break (%)
SAN/EPDM	1.76	36	17.8
SAN/EPDM/F1	1.99	39	13.7
SAN/EPDM/F2	1.89	38	13.0
SAN/EPDM/F3	2.02	38	12.0
SAN/EPDM/F1 + MB	1.81	32	12.2
SAN/EPDM/F2 + MB	1.92	47	16.8
SAN/EPDM/F3 + MB	1.92	32	11.2

## CONCLUSIONS

The results show that surface modification of the fillers is a significant factor for establishing the interactions between the filler and polymers in blends. The extent of these interactions influences the blend morphology and different levels of filler and EPDM dispersion in SAN matrix.

Two different mixing processes are used in this work. The first one includes the addition of all components together in the mixer. The other is a two-step mixing procedure and deals with MB preparation, which is mixed with previously prepared polymer blend in the second step. From the results, it can be concluded that the type of mixing process has strong influence on the morphological, thermal, and mechanical properties of blends. The two-step mixing process caused better dispersion of fillers in polymer matrix as well as better dispersion of EPDM in SAN matrix. The blends prepared with MB and filler F2 show the finest morphology and improvements in thermal and mechanical properties. In general, it can be concluded that the type of mixing process and carefully chosen filler, which acts as a compatibilizer, are the crucial factors for obtaining the improved properties of SAN/EPDM blends.

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