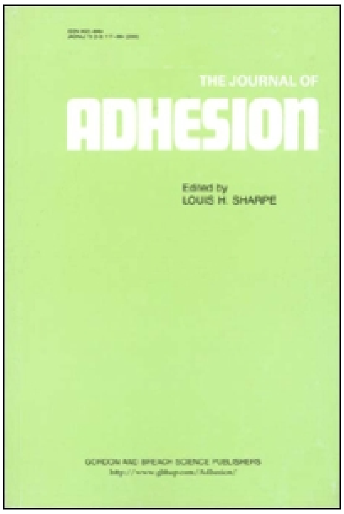

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Claes O. Hammer[a]; Frans H. J. Maurer[a]
[a] Department of Polymer Technology, Chalmers University of Technology, Gothenburg, Sweden

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Barium Sulphate-Filled Blends of Polypropylene and Poly(styrene-co-acrylonitrile): Microstructural Control*

CLAES O. HAMMER and FRANS H. J. MAURER**

Chalmers University of Technology, Department of Polymer Technology, S-412 96 Gothenburg, Sweden

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The morphology of blends of polypropylene (PP), poly(styrene-co-acrylonitrile) (SAN) and barium sulphate ($BaSO_4$) filler was studied as a function of filler particle size and amount and type of maleic anhydride-grafted polypropylene (PP-g-MAH) in the polypropylene matrix. The methods employed were scanning electron microscopy (SEM), dynamic mechanical analysis (DMA) in the solid state and a theoretical model using a core shell model structure. The study showed the possibility of controlling the phase in which the filler is occluded as a function of the chemical character of the PP matrix and the filler particle size. The morphology and dynamical mechanical properties vary in a systematic way, related to the location of the filler in the blends. Theoretical calculations supported the experimental observations.

Keywords: Filled polymer blends; morphology; dynamic mechanical properties; polypropylene; poly(styrene-co-acrylonitrile); barium sulphate

INTRODUCTION

Filled blends of immiscible polymers obtained by melt mixing have a complex microstructure that is a crucial determinant of the properties. Blends of polypropylene can combine the best properties of the ma-

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*One of a Collection of papers honoring Yuri S. Lipatov on the occasion of his 70th birthday, 10 July 1997.

**Corresponding author.

terials involved, provided that the morphology can be controlled in the desired way. This is usually necessary, as most blends are generally immiscible with low interfacial adhesion, which results in poor mechanical properties. Lipatov investigated heterogeneous systems, including filled blends, from a thermodynamic point of view, and concluded that the introduction of fillers in incompatible blends affects compatibility through the formation of a border layer or interlayer [1, 2]. Several other authors have conducted investigations relevant to this work, one of the first being Stamhuis [3, 4, 5] in a study of multiphase-filled polypropylene blends with elastomers and a talc or glass fiber filler. He found that the filled blends had a different balance of impact strength and rigidity, primarily owing to the tendency of the elastomer to cover the filler. Pukánszky *et al.* [6–13] investigated blends of polypropylene, elastomer and filler, mainly EPDM and $CaCO_3$, concluding that the surface character of the filler is a very important factor in controlling the phase structure, as it determines the tensile and impact properties. They also showed that the phase structure changes according to processing, depending on the adhesion and shear force balance in the filled blends. Scott *et al.* [14–17] explored the properties of polyethylene/EPDM/filler multicomponent composites and concluded that the surface properties of the filler and the chemical character of the rubber phase greatly affect the dynamic mechanical and impact properties of the filled blends. Other work of relevance to this study has been done by Mülhaupt [18] on PP/SAN blends, demonstrating the efficiency of polypropene-block-polystyrene and polypropylene-block-poly(styrene-co-acrylonitrile) block copolymers as blend compatibilizers. Kosfeld *et al.* [19, 20] and Theisen *et al.* [21] studied multicomponent blends of polypropylene, EPDM and different inorganic fillers, including $BaSO_4$, where this filler was shown to have poor interactive capabilities with the polymers. The above mentioned investigations have demonstrated the importance of controlling the surface properties of the filler and the chemical character of the polymers in multicomponent blends. The influence of volume shares and melt viscosity on the resulting morphology when melt mixing is used is described by Paul and Barlow [22], and is of importance because of its effect on polymer particle size [23]. This was taken into consideration here when choosing polymers and volume relations in the blend.

The goal of this study was to investigate the microstructural modifications of a filled immiscible blend consisting of a PP matrix and a

SAN-dispersed phase with a barium sulphate filler, as a function of filler particle size and amount and type of maleic anhydride-grafted polypropylene in the polypropylene matrix. The PP-g-MAH affects the chemical character of the polypropylene matrix and, thereby, the potential for interaction with the filler. The filled blends were characterized and analyzed with regard to dynamic mechanical properties in the solid state and compared with the interlayer model [24]. This was done by successive application of the model when the filler was present in both phases.

EXPERIMENTAL

Characteristics of the polymers used are listed in Table I and the $BaSO_4$ fillers used are presented in Table II. The molecular masses of the polymers were determined by size exclusion chromatography (SEC), calibrated with broad polyethylene standards in the case of PP-type polymers and with narrow polystyrene standards for the SAN polymer. The PP and PP-g-MAH (MA1, MA4 and MA7) samples were dissolved prior to SEC analysis in TCB at 135 and 150°C, respectively. The SAN samples were dissolved in THF at

TABLE I Characteristics of the polymers used in this study

Material id.	*Producer*	*Code used in this study*	*MFI*[1]	*M_n(kg/mole)*	*M_w (kg/mole)*	*Melt Delta H (J/G)*	*Acid No.*[1] *(mg KOH/g)*	*Total MA Content*[1] *(%)*
Stamylan P16M10	DSM	PP	5.5 dg/min at 230°C and 21.2 N	31	216	98		
Hostaprime HC5	Hoechst	MA4		8.4	25	69	65	>4[2]
Hostamont TP AR 500	Hoechst	MA1		4.5	27	23	5	1
Hostamont TP AR 504	Hoechst	MA7		3.2	45	32	40	7
Luran 368R	BASF	SAN	10 ml/10 min at 220°C and 10 N	98	205			

[1] According to the manufacturer. [2] Bound maleic anhydride.

TABLE II Characteristics of the fillers used in this study

Material id.	*Producer*	*Average part. Diam. (μm)*	*BET area (m^2/g)*	*ρ (kg/m^3) 10^{-3}*
Sachtoperse HU	Sachtleben Chemie, Germany	0.1	31.4	4.4
Blanc Fixe F	Sachtleben Chemie, Germany	1	3.4	4.4
Blanc Fixe N	Sachtleben Chemie, Germany	3.5	1.4	4.4

120°C. To compare the crystallinity of the polypropylene and the maleic anhydride-grafted polypropylenes, differential scanning calorimetry (DSC) was performed on a Perkin-Elmer 7 DSC to obtain the heat of fusion, ΔH [J/g]. The DSC heating rate was 10°C/min and the second heating run is used in Table I. All $BaSO_4$ grades are commerical products and are of precipitated qualities. The BET specific filler surface areas in Table II were determined by nitrogen adsorption with a Digisorb 2600 instrument (Micromeritics). The BET surface area determinations were based on five experiments at relative pressures of nitrogen in the range of 0.05–0.21, and the cross section area of the nitrogen adsorbate was 0.162 nm^2.

Before mixing in a Brabender AEV 330, with a batch volume of 50 ml, all materials except the polypropylene were dried overnight, under vacuum, at 60°C. The polymers were preblended for 5 minutes with an additional 10 minutes' blending with filler at a melt temperature of 190°C at 40 rpm. The filled polymer composites were then pressed at 190°C into samples for dynamic mechanical tests. These were carried out on a Rheometrics Dynamic Analyzer RDAII in the solid state with a rectangular torsion fixture at 1 rad/s. The time between pressing and testing was kept constant at approximately 24 hours. Scanning electron microscope (SEM) analysis was performed with a Zeiss DSM 940A apparatus on samples fractured at liquid nitrogen temperature, followed, if nothing else is indicated, by 2 hours' selective extraction of SAN in THF at room temperature. The densities used to estimate the volume fractions were 910 kg/m^3 for the PP and PP-g-MAH, 1080 kg/m^3 for the SAN polymer and 4400 kg/m^3 for the $BaSO_4$. The compositions studied with regard to filler size and concentration of the dicarboxylic acid-grafted low molecular weight polypropylenes are listed in Table III. The volume share of polypropylene plus PP-g-MAH was kept constant at 60%. The concentration of PP-g-MAH is given as volume percentage of the PP matrix. The SAN and filler volume shares were kept equal and constant at 20% each.

THEORETICAL APPROACH

The interlayer model [24, 25] is used to simulate the dynamic mechanical properties of the filled blends. The model is derived from the van der Poel model [26, 27] corrected by Schwarzl [28] and Smith [29]. The representative volume element in the interlayer model includes the geometry of an elastic sphere covered by a shell of interlayer, which, in turn, is surrounded by a shell of matrix material. Finally, there is a homogeneous phase with properties equivalent to those of the heterogeneous dispersion surrounding the spheres. The model assumes perfect dispersion of spherical particles in the matrix without taking into account any interactions, particle size or particle size distribution. The method accounts only for the pure mechanical-geometrical effect of the presence of the particle and layers. The most important condition is that the representative volume element reacts to external stresses as a cube of homogeneous composite material and that displacements and radial and tangential stresses are continuous at the boundaries of the phases. With these limitations, a set of linear equations is obtained as a result of the continuity conditions in a rotationally-symmetrical shear stress field. The determinants of the coefficients of the linear equation system should be zero to obtain a solution that is not trivial with which to calculate the shear modulus. This leads to a quadratic equation with the following form:

$$40\left(\frac{G_c}{G_m}\right)^2 |X| + \left(\frac{G_c}{G_m}\right)^2 (2|Y| + 8|Z|) - 5|T| = 0 \tag{1}$$

where G_c and G_m are the shear moduli for the composite and matrix, respectively, and $|X|, |Y|, |Z|$ and $|T|$ are tenth-order determinants of the 10×10 matrixes, X, Y, Z and T, respectively. The determinants depend on the shear modulus, Poisson's ratios and the volume fractions of the substrates. The extension of the elastic solution for Eq. (1) to a viscoelas-

TABLE III Prepared filled blends (x) of PP/SAN/$BaSO_4$ with volume relations: 60/20/20. Different concentrations of PP-g-MAH and average filler sizes are used in the filled blends

Conc. of PP-g-MAH in vol.% PP matrix	*PP-g-MAH: MA4 Filler: 0.1 μm*	*PP-g-MAH: MA4 Filler: 1 μm*	*PP-g-MAH: MA4 Filler: 3.5 μm*	*PP-g-MAH: MA1 Filler: 1 μm*	*PP-g-MAH: MA7 Filler: 1 μm*
10	x	x	x	x	x
7.5	x	x	x	x	x
5.0	x	x	x	x	x
2.5	x	x	x	x	x
0	x	x	x	x	x

tic solution is made on the basis of the correspondence principle [25, 30]. The mechanical properties of the constitutive polymeric materials used are shown in Figures 6a–b. The data used by the model in the calculations are the complex shear modulus, volume shares and Poisson's ratio of the constituents. Calculations of the mechanical properties of the mineral-filled PP/SAN/$BaSO_4$ blends of constant volume relations 60/20/20(%) are made with a filler sphere, a SAN interlayer and a PP matrix/outer layer. With the addition of PP-g-MAH, the properties are calculated by successive application of the model. The calculations of the mechanical properties were found to be insensitive towards an PP-g-MAH (MA4) interlayer, which was disregarded in the calculations presented in this paper. Five different filler volume percentage were used in the calculations: 0, 33, 50, 67 and 100% of the filler occluded in the SAN phase.

A Poisson's ratio of 0.4 was chosen in the calculations for SAN, PP and PP-g-MAH. The calculations in the solid state proved to be insensitive to the Poisson's ratio. For the $BaSO_4$ filler, the Poisson's ratio was set to 0.3 [31], and the dynamic shear modulus, G_d, for this filler was set to a value [31] of 1.15×10^{10} Pa. The filler is considered to be elastic, *i.e.* the dynamic shear loss modulus, $G''_{\text{filler}} = 0$.

MORPHOLOGY STUDY BY SEM

The PP/SAN system with a volume ratio of 70:30 is an immiscible blend with a domain size of approximately 10–20 μm, having PP as the continuous phase. SEM micrographs not included in this paper show no signs of interaction between PP and SAN in the pure PP/SAN system or in the filled PP/SAN/$BaSO_4$ (60:20:20) systems. Compared with the unfilled system, the PP/SAN/$BaSO_4$ blend morphology is much more irregular in shape, with approximately the same domain sizes. The interface between the PP and SAN/$BaSO_4$ phases is quite distinct and clearly observable. A tendency of the SAN droplets to elongate in the unfilled blends can be seen; this was also observed earlier by Maiti *et al.* [32].

The effect of the MA4 concentration on the blends with a 1-μm average filler size is shown by the SEM micrographs in Figures 1a–d. The residues of the PP + MA4/SAN/$BaSO_4$ system are visible after selective extraction of the SAN phase by THF. The polypropylene matrix is unaffected by the THF solvent. In the PP/SAN/$BaSO_4$ blend in Figure 1a, the filler is occluded in the SAN phase but the percentage of filler in the PP phase increases as the concentration of PP-g-MAH is increased from 0 to 7.5% volume percent of the PP matrix in Figures 1a–d. An increased concentration up to 10% MA4 does not give a visible effect compared with 7.5%, indicating a saturation level.

The dependence on filler size can be seen in Figures 1–3, where the average particle sizes are 1, 3.5 and 0.1 μm, respectively. For the larger sized particles in Figures 2a–b, it is sufficient to add 2.5% MA4 to occlude the barium sulphate filler in the PP phase. The corresponding filled blends, with an average particle size of 0.1 μm, are represented in Figures 3a–b. It is not possible to see the individual mineral particles in the filled blend without PP-g-MAH in Figure 3a, but the microstructure is similar to the two other corresponding blends in Figures 1a and 2a, with a domain size of 10–20 μm. The surface relation depicted in Figure 3a indicates a 60/40 system by volume shares. This represents a filler-extended SAN phase. The appearance of Figure 3b indicates an 80/20 system, suggesting that all the mineral filler particles with an average particle size of 0.1 μm are present in the PP phase. This situation seems to be reached at 7.5% MA4, compared with 5% for the case with a 1 μm average filler size and 2.5% MA4 for the case with a 3.5 μm average filler size.

Changes in the amount of grafted maleic anhydride in the PP-g-MAH graft copolymer are shown in Figures 1,4 and 5. Hardly any of

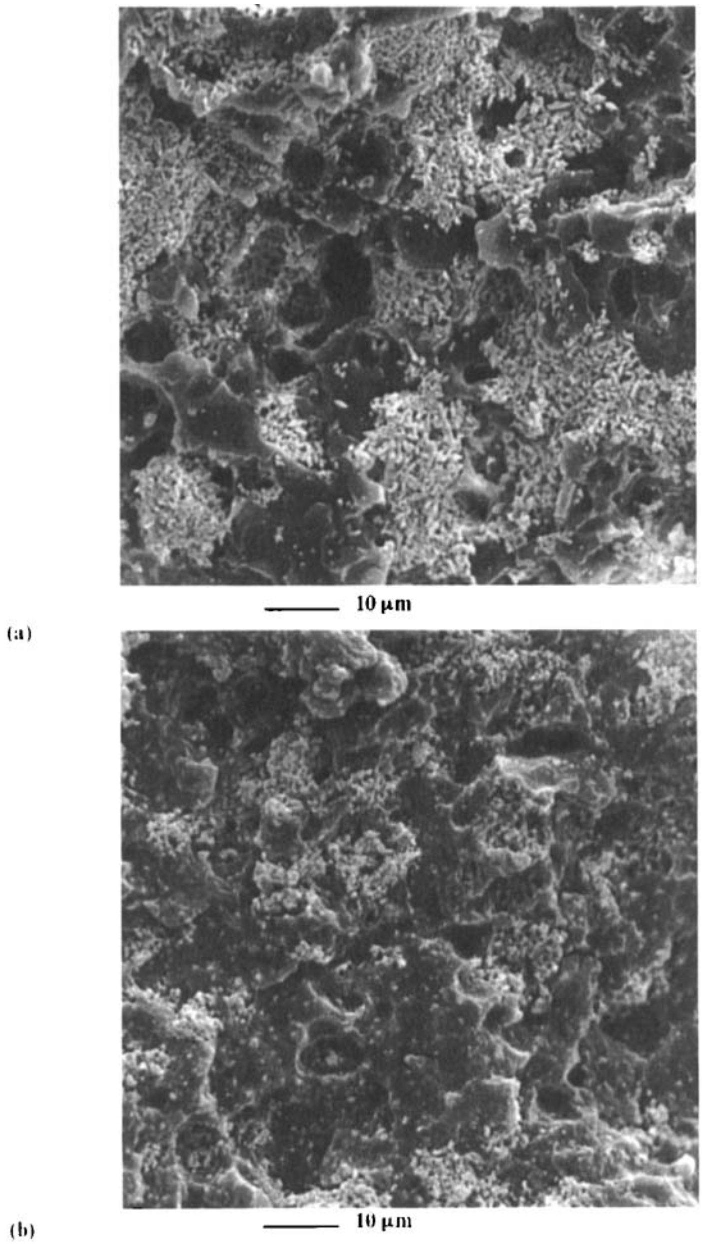


FIGURE 1 Morphology of a PP/SAN/$BaSO_4$ blend (60/20/20) with an average filler size of 1 μm after extraction of SAN. (a) without PP-g-MAH, (b) 2.5% of the PP is substituted by MA4, (c) and (d) 5 and 7.5% MA4 are added, respectively.

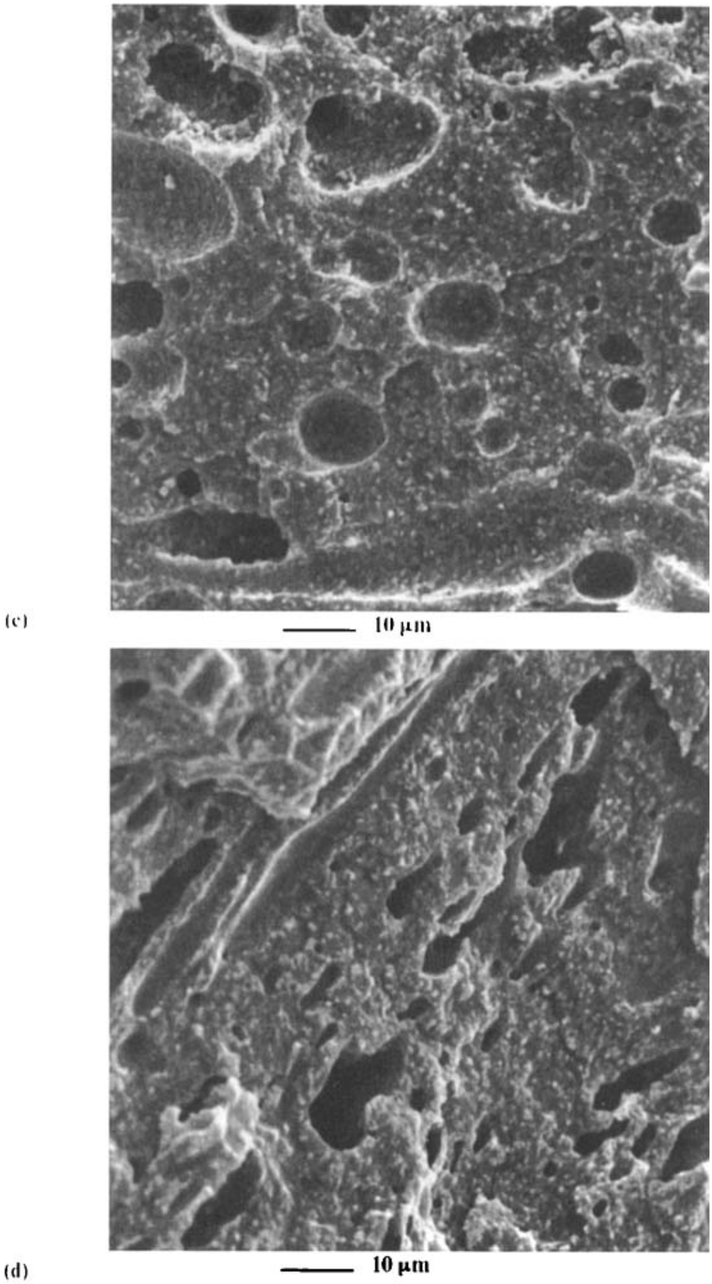


FIGURE 1 (Continued).

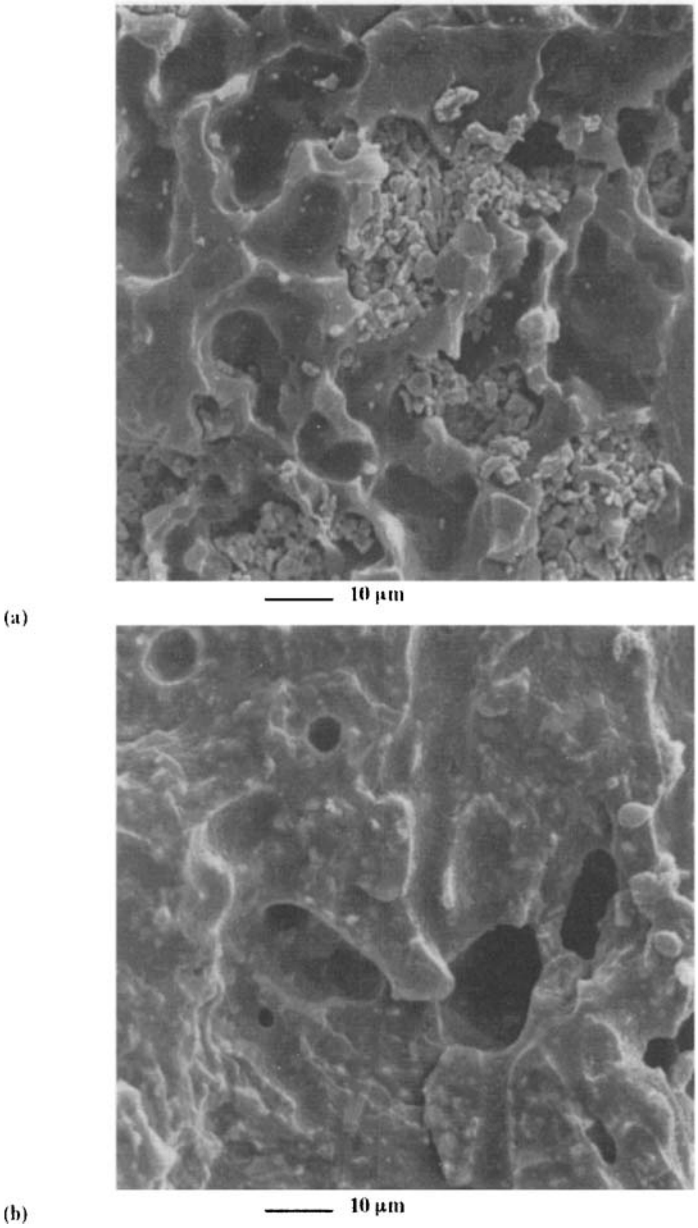


FIGURE 2 Morphology of a PP/SAN/$BaSO_4$ blend (60/20/20) with an average filler size of 3.5 μm after extraction of SAN. (a) without PP-g-MAH and (b) 2.5% of the PP is substituted by MA4.

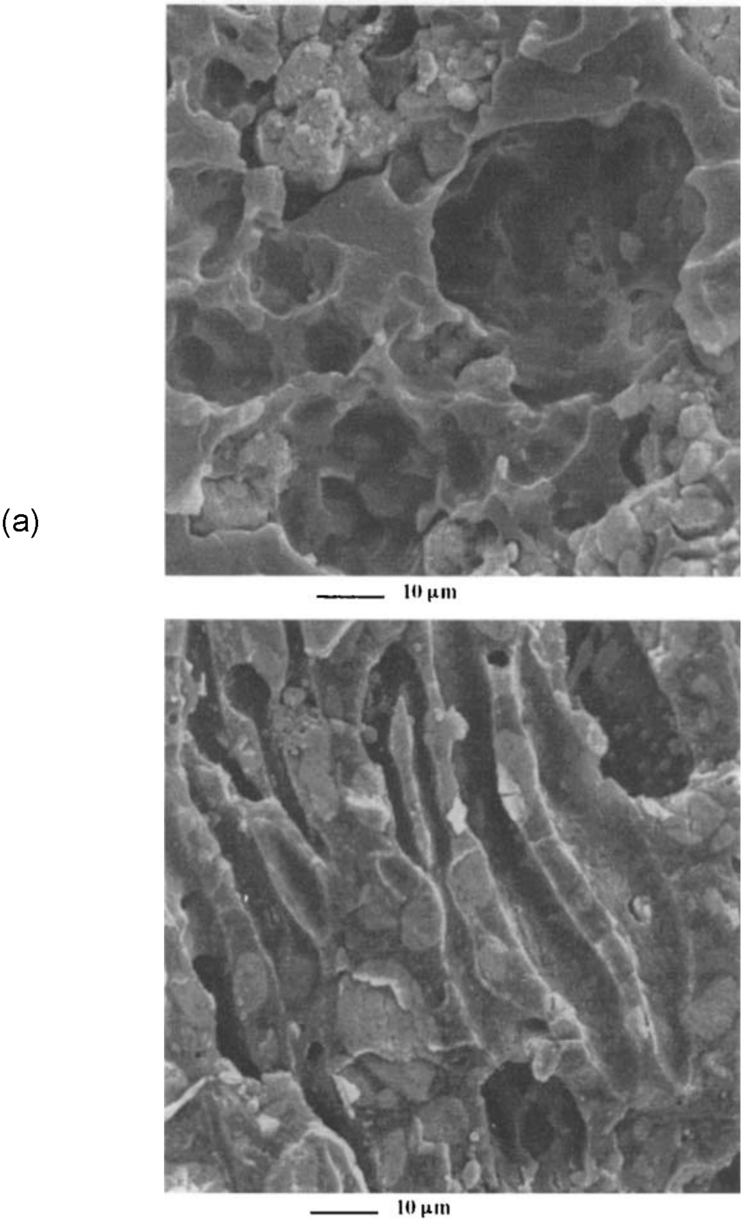


FIGURE 3 Morphology of a PP/SAN/$BaSO_4$ blend (60/20/20) with an average filler size of 0.1 μm after extraction of SAN. (a) without PP-g-MAH and (b) 7.5% of the PP is substituted by MA4.

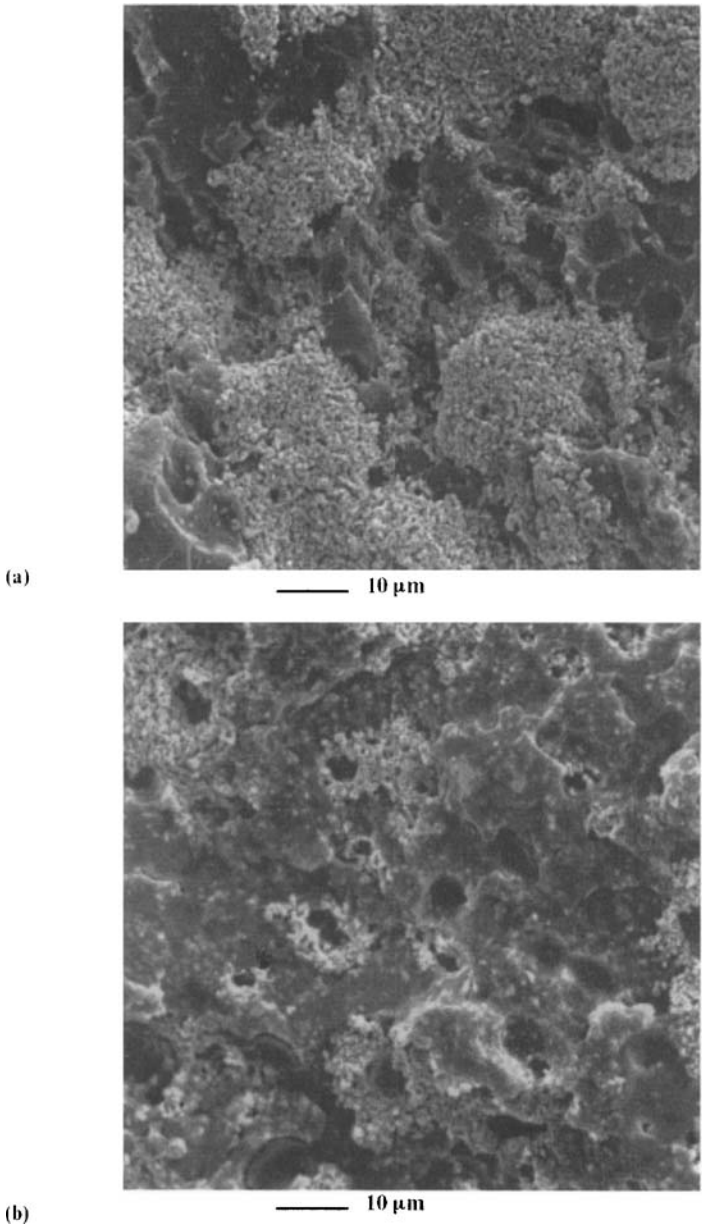


FIGURE 4 Morphology of a PP/SAN/$BaSO_4$ blend (60/20/20) with an average filler size of 1 μm after extraction of SAN. (a) 2.5% of the PP is substituted by MA1 and (b) 10% MA1 is added.

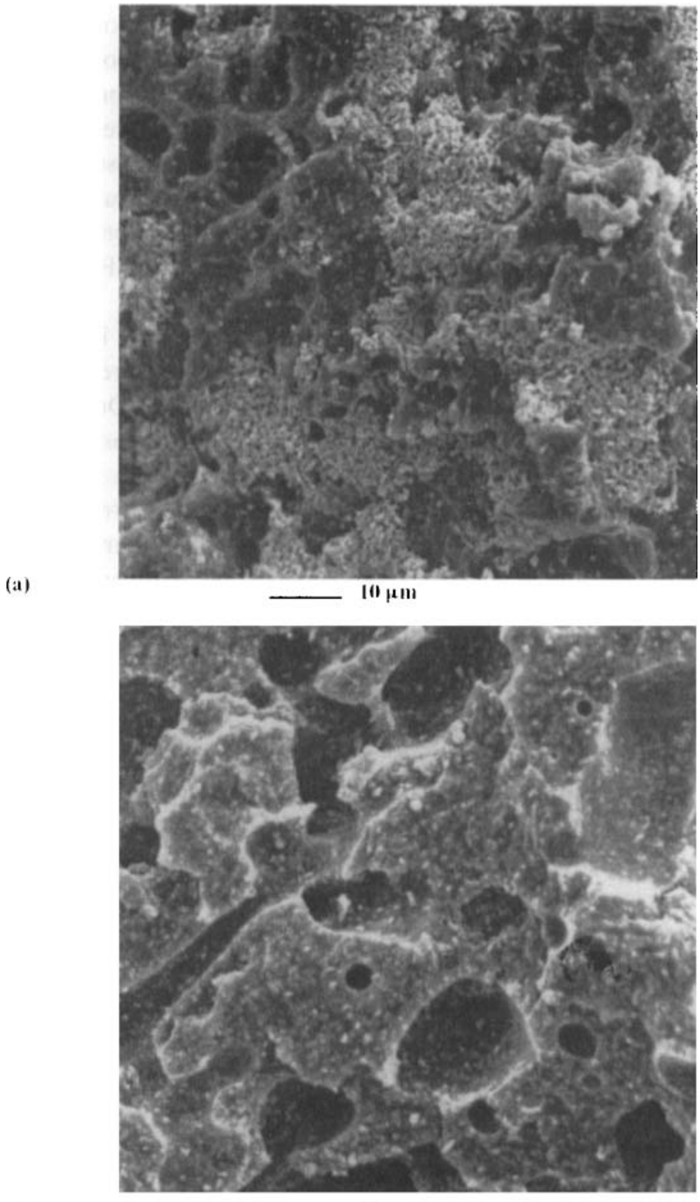


FIGURE 5 Morphology of a PP/SAN/$BaSO_4$ blend (60/20/20) with an average filler size of 1 µm after extraction of SAN. (a) 2.5% of the PP is substituted by MA7 and (b) 5% MA7 is added.

the filler particles are occluded by the PP phase with 2.5% of the PP matrix replaced by MA1 with a low maleic anhydride content in Figure 4a. With 10% MA1 in Figure 4b, the filler is still present in both phases. The effect of the MA7, which has a high maleic anhydride content, is similar to the effect of the MA4. This is illustrated in Figure 5a, where the 2.5% concentration of the MA7 is sufficiently high to occlude part of the mineral filler in the polypropylene phase, and, finally, in Figure 5b, with almost all of the filler in the PP phase with 5% MA7.

The occlusion of the filler in the SAN phase in the case in which there is no addition of PP-g-MAH must be a result of preferential interaction between SAN and the barium sulphate filler. Due to its chemical structure, PP-g-MAH gives the PP phase a functionality for interaction with the filler and competes successfully with the SAN for the $BaSO_4$ filler, whose character seems to depend on the surrounding media. The dependence of the charge of barium sulphate particles on the surrounding media of $BaSO_4$ is also reported by Winkler [33].

DYNAMIC MECHANICAL MEASUREMENTS IN THE SOLID STATE

Dynamic mechanical analysis was used as an analytical tool to investigate the microstructure of the filled blends and to investigate whether the properties could be correlated with the SEM micrographs. The measurements were carried out in the solid state, from -50 to 160°C at 1 rad/s and 0.03% strain. Special attention was paid to the SAN glass transition region with a tan δ maximum at about 116°C ($T_{G''\max}=$ 110°C). In the PP/SAN/$BaSO_4$ blends without PP-g-MAH, the filler is located in the SAN phase, meaning that the SAN/$BaSO_4$ part of the blend is highly filled (50/50 vol.%) and sensitive to the strain amplitude of the measurements, especially over the glass temperature of SAN. The known reason for this sensitivity is a structure formed by the filler particles [34, 35]. A strain amplitude of 0.03% and a temperature ramp rate of 2°C/minute at a frequency of 1 rad/s was chosen to ensure that the measurements were performed in the linear viscoelastic region.

Figure 6a illustrates the shear storage modulus, G', and the shear loss modulus, G'', as a function of temperature for the pure PP, SAN

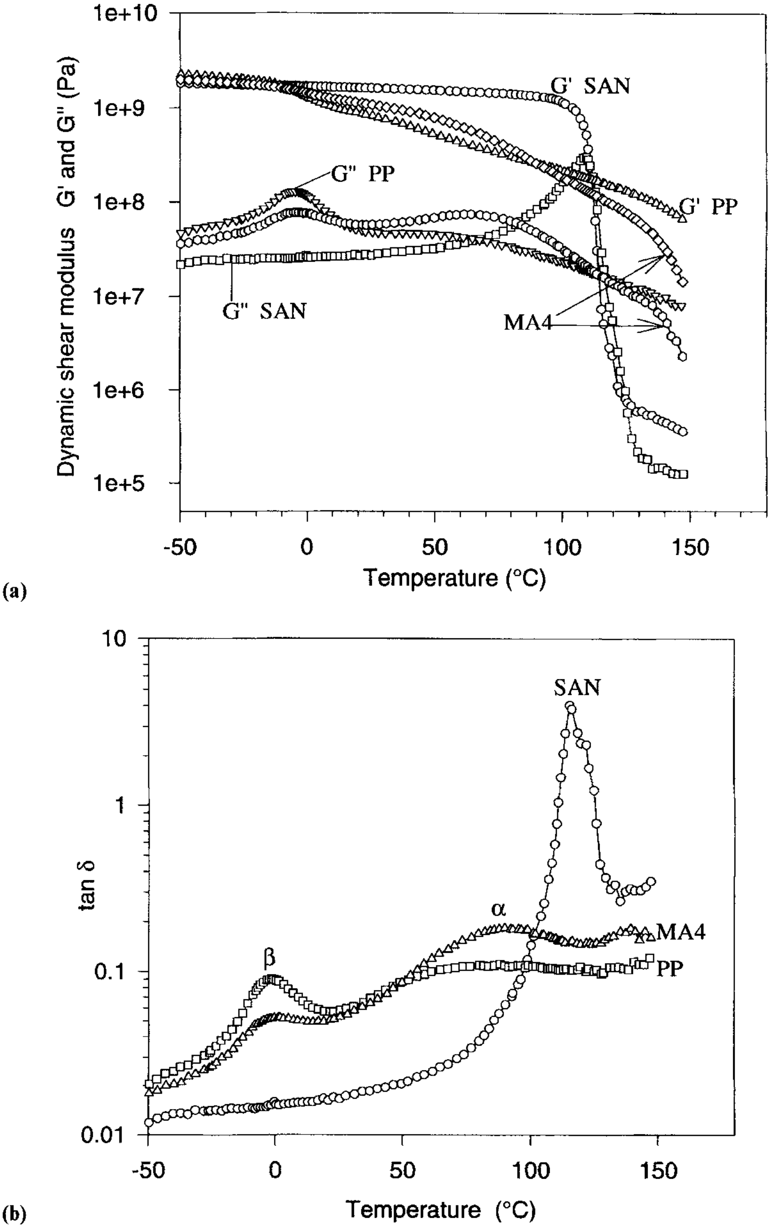
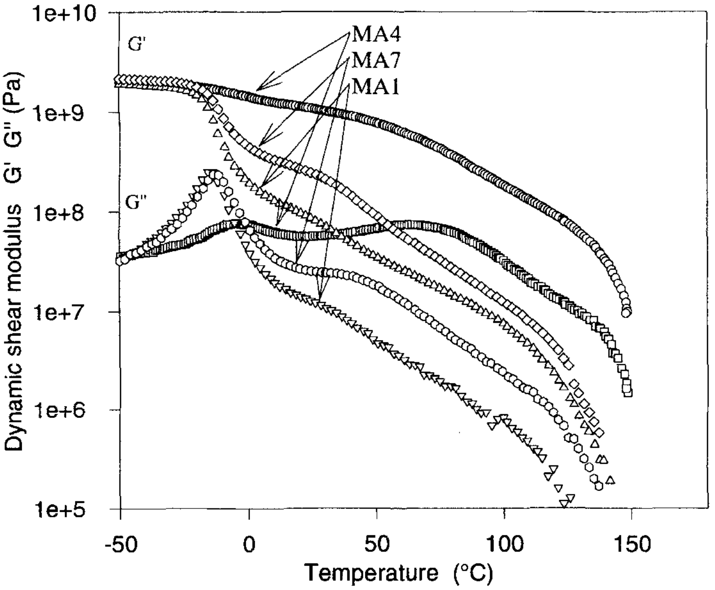


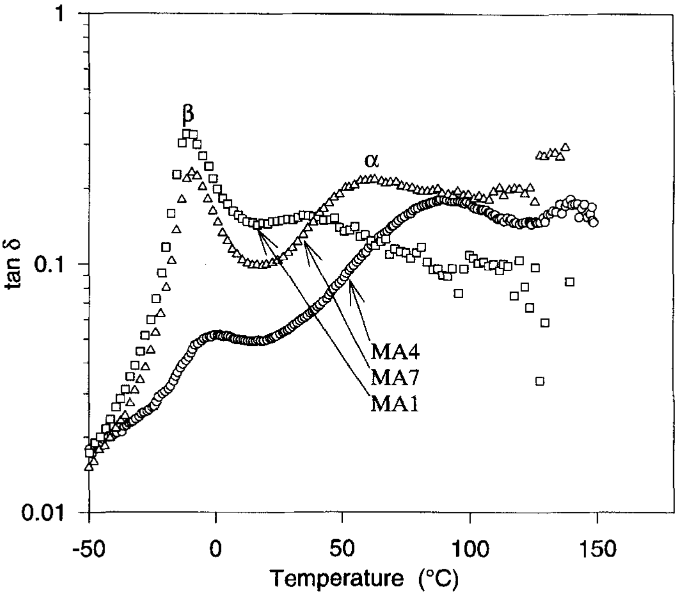
FIGURE 6 The dynamic mechanical properties of the pure PP, SAN and MA4 measured as a function of temperature at 1 rad/s. (a) shows the shear storage and loss modulus and (b) the tan δ.

and MA4. The dynamic mechanical properties of the SAN material at temperatures just over T_g up to 150°C were measured in the melt with a parallel plate fixture. Figure 6b shows the tan δ values from the same measurements. The MA4 is a dicarboxylic acid-grafted low molecular weight polypropylene and, as can be seen from Figure 6a, the properties measured are similar to those of the polypropylene. The graft copolymer MA4 has a relatively high crystallinity according to the DSC measurements. The crystalline structure is further explained in Figure 6b, where the tan δ values for the α-transition show that the amorphous phase in connection with the crystalline phase is larger for the MA4 than for the pure PP and that there is a more dominant amorphous tan δ peak in the β-transition for the polypropylene. This would agree with a more disturbed crystallinity for the MA4 than the PP [36]. The dynamic mechanical properties of the three different PP-g-MAHs are shown in Figures 7a–b. In Figure 7a, the shear storage modulus drop at 5°C (T_g of PP) is greatest for MA1 and smallest



(a)

FIGURE 7 The dynamic mechanical properties of MA4, MA1 and MA7 measured as a function of temperature at 1 rad/s. In (b) the ordinate is tan $\delta = G''/G'$. (a) shows the shear storage and loss modulus and (b) the tan δ.



(b)

FIGURE 7 (Continued).

for MA4. The shift of the α-transition to higher temperatures in Figure 7b for the MA4 as compared with MA7 is a sign of the higher crystallinity as a result of increased crystal lamella thickness [36].

The temperature dependence of the dynamic mechanical properties in the PP/SAN/$BaSO_4$ blends shows an interesting behavior around 116°C in Figures 8a–c. This temperature characterizes the glass transition of SAN, measured as the location of the tan δ peak. The size of the tan δ peak is either a function of added PP-g-MAH or a function of the apparent volume share of the SAN phase, which can be extended with the $BaSO_4$ filler. If the $BaSO_4$ filler is not occluded in the SAN phase, but rather in the polypropylene phase owing to preferential interaction caused by the PP-g-MAH additive and thereby extending the PP phase, the result will be a smaller G' modulus drop at the SAN glass transition temperature. Similar observations for other filled immiscible blends are described and used in studies by Kolarik [7] and Scott *et al.* [16]. In Figures 8a–c the tan δ of the filled blend is depicted as a function of temperature at 1 rad/s. For the 3.5 and 1 μm filler size, in Figures 8a and 8b, respectively, the results are easily correlated with

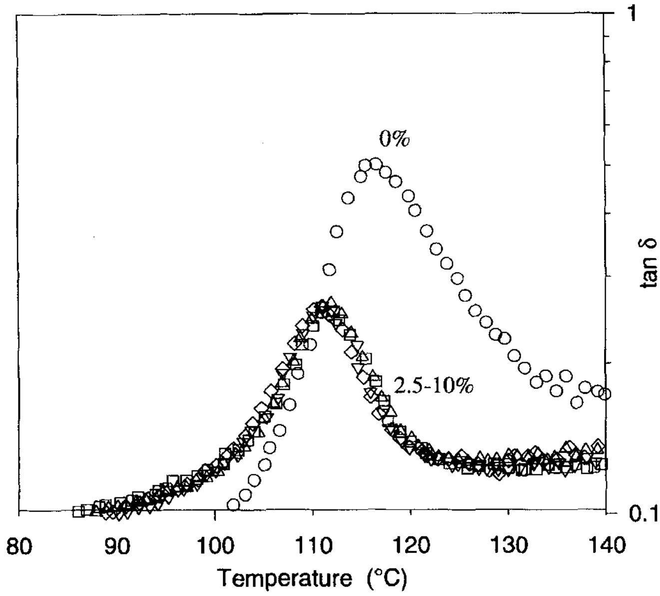
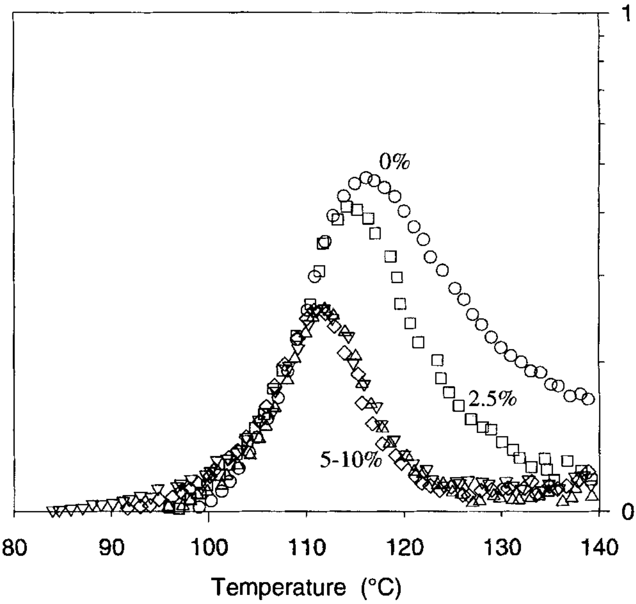
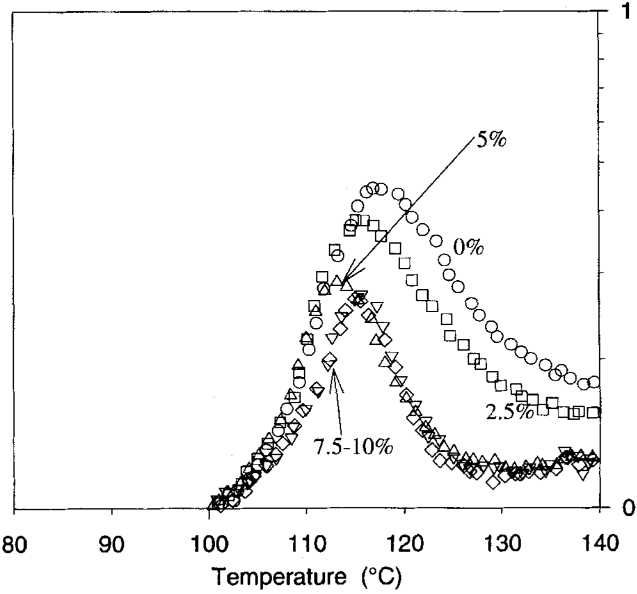


FIGURE 8 The effect of filler size and concentration of MA4 on the dynamic mechanical tan δ values of PP/SAN/$BaSO_4$ blends (60/20/20) measured in shear at 1 rad/s. The percentages refer to the amount of MA4 calculated as volume share of the PP. The average filler sizes are (a) 3.5 μm, (b) 1 μm and (c) 0.1 μm.

the SEM micrographs. The larger-sized filler will be occluded in the PP matrix when 2.5% of the PP is replaced with MA4; when the 1 μm filler is used, 5% MA4 is needed for almost total occlusion of the $BaSO_4$ filler in the PP phase. The graph (Fig. 8c) for the smallest particle size, 0.1 μm, is not as clear. At 7.5 and 10% MA4, all the filler should be dispersed in the PP phase in accordance with the tan δ peaks, but the peaks are also shifted for morphological reasons to higher temperatures as compared with the former cases. Blends with the MA7 graft copolymer show a similar pattern compared with the MA4, but with the mentioned shift of the peaks. The lower anhydride-grafted MA1 does not show a decrease of the area under the tan δ peak as a function of increased MA1 concentration. The graphs from the measurements with MA7 and MA1 are not included here. This difference in behavior, when the three different graft copolymers are



(b)



(c)

FIGURE 8 (Continued).

included in the filled blends, can also be seen in the SEM micrographs. The graphs in Figures 8a–c shows that the area under the tan δ peak is dependent on the filler size and on the modified polypropylene, *i.e.* on the chemical character of the PP matrix. The broadening of the tan δ peaks towards higher temperatures in Figures 8a–c is present only when some or all of the filler is occluded in the SAN phase. When comparing the tan δ peaks of PP/SAN blends of 80/20 and 60/40 volume relations and SAN with barium sulphate-filled SAN (50/50 vol.%) in Figure 9, it can be concluded that the broadening of the peak towards higher temperatures comes from the SAN/$BaSO_4$ phase. A high degree of filling and a tendency towards agglomeration owing to filler incompatibility with the SAN polymer [37] result in high particle-particle friction at temperatures above the glass transition of SAN. On the other hand, when the filler is occluded in the PP phase, there is no sign of this type of peak broadening. This must be dependent on the facts that there is a lower degree of filling and that

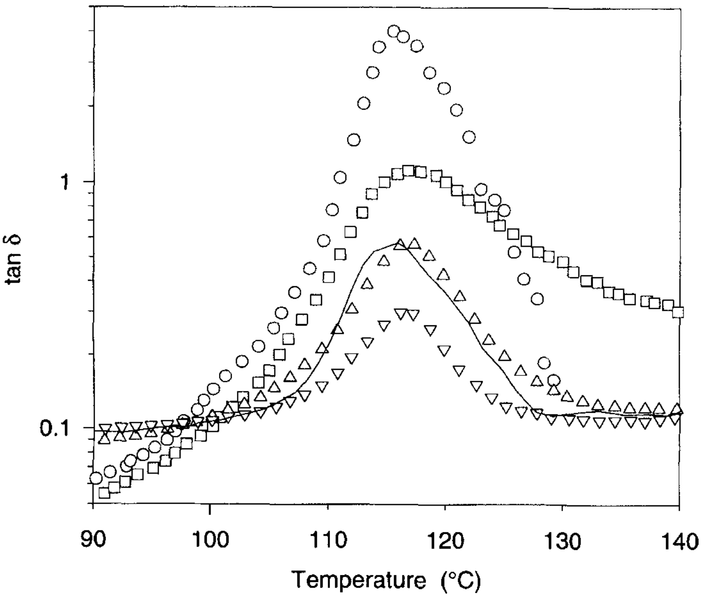


FIGURE 9 tan δ as a function of temperature at 1 rad/s for SAN (○), SAN/$BaSO_4$ 50/50 (□) and PP/SAN 60/40 (△) and 80/20 (▽). Simulation of PP/SAN/$BaSO_4$ 60/20/20 vol.% (—).

the MA4 and MA7 have a dispersive effect on the filler, compatibilizing it with the polypropylene. Scott *et al.* [16] also studied similar effects of compatibilizing fillers with the aid of coupling agents and, furthermore, also described the broadening of tan δ peaks as a result of particle-particle or particle-matrix friction.

COMPARISON BETWEEN SIMULATIONS AND MEASUREMENTS

A comparison of the measured and calculated dynamic mechanical properties of the PP/SAN/$BaSO_4$ blend without PP-g-MAH can be seen in Figure 10a. The calculated properties of the filled blend represent the system with all the filler in the SAN phase. The average filler size is 1 μm in the measured case. In Figure 10a, the slope and value of

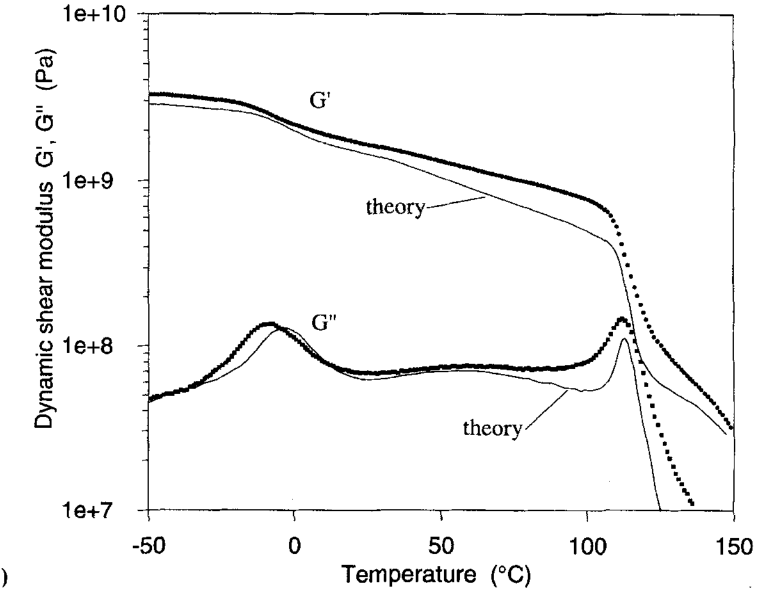


FIGURE 10 (a) Dynamic shear modulus, $G'(T)$ and $G''(T)$, at 1 rad/s for the PP/SAN/$BaSO_4$ blend and (b) $G'(T)$ for: SAN(○), SAN/$BaSO_4$ 50/50 (□), PP/SAN 60/40 (Δ) and 80/20 (∇), and PP/SAN/$BaSO_4$ 60/20/20 (◇). Simulation of the SAN/$BaSO_4$ 50/50 (__) *and* PP/SAN/$BaSO_4$ 60/20/20 (---) systems.

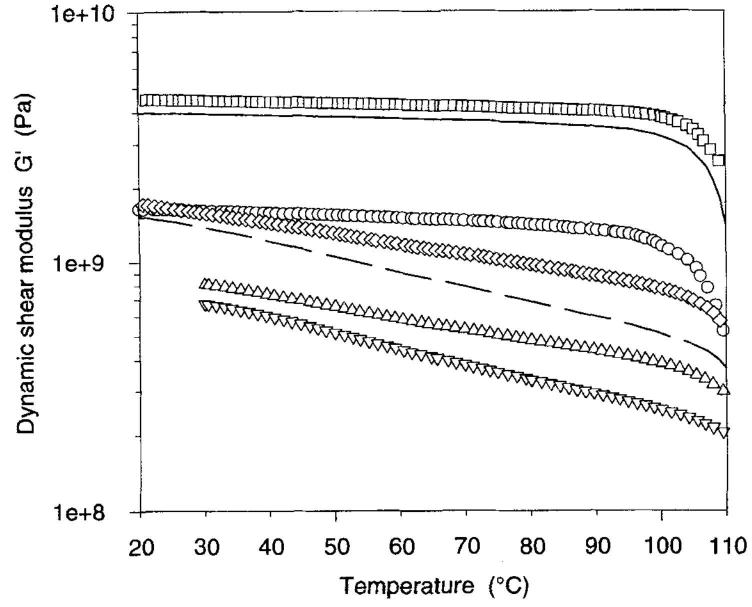


FIGURE 10 (Continued).

G' in the 20–80°C temperature interval are flatter and higher, respectively, than expected from the simulation. The loss modulus, G'', is also higher than expected. For comparison, a SAN/$BaSO_4$ composite in Figure 10b with a 50/50 volume ratio was measured and treated in the model; this represents the SAN-plus-filler phase in the PP/SAN/$BaSO_4$ blend. The slope and shape of the storage modulus, G', in the temperature interval up to 100°C were found to be quite similar for the calculated and measured SAN/$BaSO_4$ composites, but the measured value was higher than expected from the simulation, assuming perfect dispersion. Figure 10b also shows measured and calculated G' values for the PP/SAN/$BaSO_4$ blend and the measured modulus for PP/SAN blends of 80/20 and 60/40 volume relations. The difference in the slope of G' for the measured and calculated values of the PP/SAN/$BaSO_4$ blend should, in the light of this comparison, originate mainly from the PP/SAN interface or the fact that the microstructure deviates from a matrix/dispersed phase system towards a morphology with two continuous phases, the PP phase and the $BaSO_4$-filled SAN in a 60/40 volume ratio. A comparison between the simulated tan δ peak for the PP/SAN/BaSO$_4$ blend and the measured peak for PP/SAN 60/40 blend in Figure 9 shows good agreement regarding the tan δ peak area and supports the conclusion that the PP/SAN/BaSO$_4$ blend is a 60/40 system. Another indicator of the non-ideal dispersion of the filler is the height of the tan δ peak. The SAN glass transition in the calculated case for a SAN/BaSO$_4$ composite with a 50/50 volume ratio is stronger, with a peak tan δ value of 3.83 compared with 1.12 for the measured and filled SAN. The peak tan δ value for unfilled SAN is 4.01. The simulated tan δ peaks at the glass transition temperature of SAN for PP/SAN/BaSO$_4$ blends with different percentages of the filler occluded in the SAN phase are compared in Figure 11. The tendency is a small peak, with a maximum value of 0.28, when no filler is present in the SAN phase and a larger peak, with a maximum of 0.58, when all the filler particles are occluded in the SAN phase. The intermediate blends in which the mineral

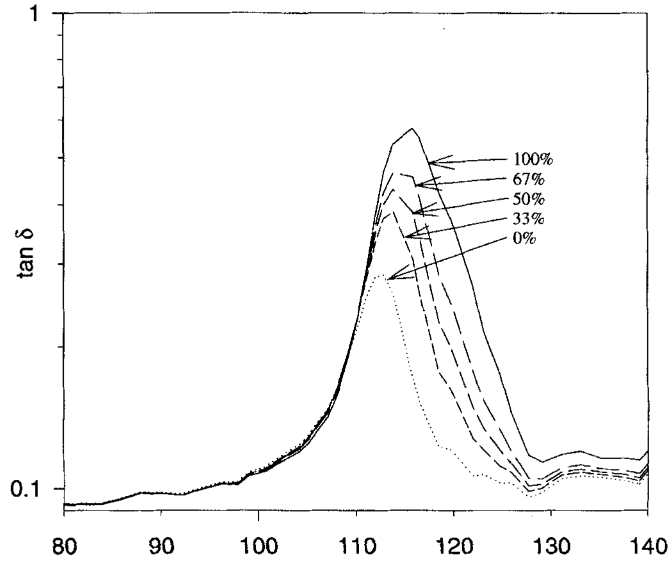


FIGURE 11 The calculated tan δ values for PP/SAN/BaSO$_4$ blends (60/20/20) as a function temperature at the T_g of SAN. The percentages refer to the share of the filler occluded in the SAN phase, *i.e.* the distribution of the filler between the phases.

filler is occluded in both polymer phases have peak values between both extremes. The simulated curves in Figure 11 describe a linear relation, *i.e.* the theoretical tan δ peak height is a measure of the volume share of the (filled) SAN phase. This supports our observation from the SEM micrographs combined with the dynamic mechanical measurements that the filler particles are gradully occluded in the PP polymer as a function of MA4 concentration.

CONCLUSIONS

This investigation has shown the possibility for systematically influencing the structure of PP/SAN/$BaSO_4$ blends in the sense that it has been viable to control the percentage of filler occluded in the SAN phase. This was done with different polypropylene-graft-maleic anhydride concentrations and qualities and average filler particle sizes. The interlayer model was found at least to be a good qualitative tool for predicting the mechanical properties of the filled blends. The deviations from the simulated mechanical properties result from the fact that the morphology of the filled blends is complex and deviates from a condition in the model, assuming a perfect core shell microstructure. Another important reason is filler particle-particle interlocking and friction.

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