

Distribution of oil in olefinic thermoplastic elastomer blends

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Abstract

The distribution of processing oil in two olefinic thermoplastic elastomer (OTPE) blends was determined using dielectric spectroscopy. The OTPE blends are blends of dynamically vulcanised EPDM with polypropylene (PP), TPVs, and blends of PP with SEBS. Both blend types contain paraffinic oil, which is present in both the PP and in the elastomer phase. The determination of the actual oil concentration by measuring the reduction in the glass transition temperatures (T_g) is inaccurate using DSC or DMA, because the glass transition dynamics of the two phases overlap. The blends were made sensible for dielectric spectroscopy by the addition of a probe molecule. The oil distribution was determined by modelling of the dielectric loss of the OTPE blends in the T_g regime from the ones of the binary mixtures. The mean value for the oil distribution coefficient was found to be 0.6 for PP/SEBS blends and 0.63 for TPVs.

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1. Introduction

Thermoplastic elastomers (TPEs) combine the elastic properties of rubbers with the processability of thermoplastic polymers [1]. An important class in these materials are the olefinic thermoplastic elastomers (OTPEs). The most widely used OTPEs are blends of isotactic polypropylene (PP) with cured ethylene–propylene–diene–terpolymer (EPDM) rubber, also called thermoplastic vulcanisates (TPV) [2]. They are prepared by simultaneously curing and mixing of the EPDM with the PP. The resulting blend consists of 0.5–5 μm elastomer particles dispersed in a PP matrix. An alternative material is a blend of polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene triblock copolymer (SEBS) with PP [3,4]. The triblock copolymer is by itself a thermoplastic elastomer: the PS end-blocks cluster together and form separate domains that

act as physical cross-links for the elastomeric middle segment. The SEBS is blended with PP to make stiffer compounds and to improve the processability.

Commercial OTPEs often contain various additives in order to tailor the properties. Processing oil is a well-known additive that lowers the hardness and improves the processability. PP/EPDM TPVs and PP/SEBS blends can be largely extended with paraffinic oils. Due to the small polarity differences between the three components, the oil can be present in both the PP and in the elastomer phases. In order to understand the mechanical and rheological properties of OTPEs, the concentration of oil in each phase must be known.

Being a low molecular weight additive, the oil plasticizes both the PP and the elastomer phases [3–5]. Its concentration in the two phases can be estimated from the reduction of the glass transition temperature (T_g). Ohlsson et al. [3] defined the distribution coefficient K as the ratio of the oil concentration in the PP phase over the concentration of oil in the elastomer phase. Values of K between 0.33 and 0.47 were found in that article using the depression of the T_g in the PP phase, measured with dynamic mechanical analysis. This indicates that the oil prefers the elastomer phase. Other methods used to estimate the oil distribution were the integration of surface area of TEM images [6] and quantitative NMR analysis [7]. In the latter method,

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however, about 30 wt% of the oil could not be traced either in the PP or in the elastomer phase.

Sengers et al. determined the value of K of two OTPE blends in the melt state by micromechanical modelling of the frequency dependent dynamic shear moduli [8]. The frequency dependent moduli of the two phases were interpolated from a series of binary PP-oil and elastomer–oil mixtures. The distribution coefficient K was introduced as an additional parameter in the mechanical models to estimate the oil concentrations in the PP and the elastomer phases. The obtained values for K varied between 0.04 and 1.1 and depended on the composition. In both the OTPE blend types, K decreased with increasing PP content. In the PP/SEBS blends, the total oil content did not have a significant effect on K , while K increased with increasing oil content in TPVs.

All the above methods have some shortcomings for the present blends, especially in their utility to determine the oil distribution in the solid state. The glass transition dynamics of the PP and elastomer phases overlap in the present cases. Therefore, it is inaccurate to make use of the shift in glass transition temperatures determined by dynamic mechanical analysis or differential scanning calorimetry. In addition, the dynamic moduli may depend on the morphology of the blends. Finally, the integration of the surface area in TEM images can be misleading in some cases. At high elastomer content, the overlapping elastomer particles can give an impression that the content of the elastomer phase is higher.

Broadband dielectric relaxation spectroscopy (DRS) is used in the present article for the determination of the oil distribution in OTPE blends. This method also uses the frequency or temperature shifts of specific relaxations in each phase to determine the effect of oil. Due to its broad dynamic range, DRS enables the accurate detection of peak shifts in both the frequency domain (isothermal spectra) or in isochronal data (temperature shift), which gives more accurate results than the ones mentioned above. Peaks that may overlap in the temperature domain may be separated in the frequency domain and vice versa. Further, the measurement of the relaxation strength and relaxation time has led to a well established method to separate overlapping peaks by the use of the Havriliak–Negami equation [9].

Since the polymer blends consist of (almost) apolar components, showing no substantial dielectric relaxation processes, we have applied a recently developed technique based on a dielectric probe molecules [10]. Addition of small quantities of probe molecules was shown to specifically enhance the dielectric relaxations related to the dynamic glass transition. The applicability of this method for heterogeneous non-polar materials has also been demonstrated by detecting and separating the dynamics of polyolefin phases in immiscible blends [11]. The phases were shown to retain their intrinsic (bulk) behaviour in dielectric spectroscopy. That is, the relaxation time of the two phases corresponds to those of the pure polymers.

Furthermore, in cases of overlapping relaxations, the relaxation strength of the two components in the blend were found to be additive according to their volume fractions. In the present article, these features will enable the reconstruction of the dielectric spectra of the ternary blends from the ones of the PP and the elastomer phases. The latter are interpolated from their corresponding binary oil mixtures. In this way the oil distribution coefficient is obtained.

2. Experimental

2.1. Materials

In this study, two types of OTPE blends are used. To make a direct comparison, the blends contain the same PP matrix (PP homopolymer with a MFI of 0.3 dg/min at 230 °C and 2.16 kg, DSM Polypropylenes) and paraffinic oil (Sunpar® 150, Sun Oil Company). The elastomer in the TPVs was EPDM (63 wt% C2, 4.5 wt% ENB, extended with 50 wt% of paraffinic oil, DSM elastomers). The PP/SEBS blends contained SEBS (KRATON® G 1651, KRATON polymers) as the elastomer. The EPDM in the TPVs was dynamically vulcanised using 5 phr phenolic curing agent (SP® 1045, Schenectady) in combination with 1 phr Stannous Chloride and Zinc Oxide (Merck). All materials contained antioxidants (0.5 wt% Irganox® 1076 and 0.5 wt% Irgafos® 168, Ciba Specialty Chemicals). For the dielectric measurements we doped the materials with the dielectric probe molecule, 4,4'-(*N,N*)-(dibutylamino)-(*E*)-nitrostilbene or DBANS (Fig. 1). The preparation of the probe is described in [10].

2.2. Sample preparation

The OTPE blends were prepared in an internal batch mixer (Brabender Plasticorder with Banbury rotors, 390 cc) at 180 °C and 80 rpm. The blend composition was varied in order to study the influence of the contents of PP and oil. Similar compositions were used for the PP/SEBS and TPV blends (Table 1). The symbol 'S' in the coding in Table 1 designates the PP/SEBS blends and E the TPV blends. The numbers x/y stand for the PP-elastomer and the oil-elastomer ratio respectively. For the DSC and DMA measurements, samples were compression moulded into sheets of 0.3 mm at 200 °C directly after the blending process.

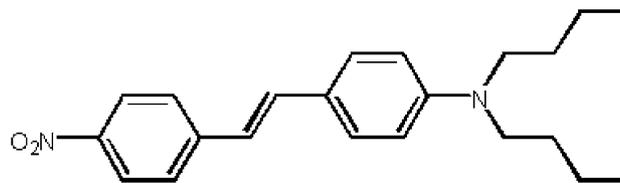


Fig. 1. Chemical structure of 4,4'-(*N,N*)-(dibutylamino)-(*E*)-nitrostilbene, (DBANS).

Table 1
Composition and crystallinity of TPE blends

Code	PP (wt%)	EPDM (wt%)	SEBS (wt%)	Oil (wt%)	PP/elastomer	Oil/elastomer	X_{PP} (-)
S0.4/1.4	14.3		35.7	50.0	0.4	1.4	0.49
S0.8/1.0	28.6		35.7	35.7	0.8	1.0	0.48
S0.8/1.4	25.0		31.3	43.8	0.8	1.4	0.47
S0.8/1.8	22.2		27.8	50.0	0.8	1.8	0.49
S1.2/1.4	33.3		27.8	38.9	1.2	1.4	0.47
E0.4/1.4	14.3	35.7		50.0	0.4	1.4	0.46
E0.8/1.0	28.6	35.7		35.7	0.8	1.0	0.44
E0.8/1.4	25.0	31.3		43.8	0.8	1.4	0.46
E0.8/1.8	22.2	27.8		50.0	0.8	1.8	0.46
E1.2/1.4	33.3	27.8		38.9	1.2	1.4	0.45

Binary PP–oil mixtures were made in another internal batch mixer (Brabender Plasticorder with Banbury rotors, 20 cc) at 180 °C and 100 rpm. The total mixing time was 8 min. After the mixing step, sheets (0.3 mm) were made by compression moulding at 200 °C. The SEBS–oil mixtures were prepared by dry blending the SEBS pellets with oil at room temperature followed by compression moulding at 150 °C to make sheets of 0.3 mm. The EPDM–oil vulcanisates with different oil concentration were prepared by preblending the EPDM with curatives (same amount as in the TPVs) on a two-roll mill, followed by curing in compression moulding at 200 °C. An additional sample containing 60 wt% vulcanised EPDM was prepared by extracting first the oil from the EPDM–oil batch using n-hexane, precipitating the EPDM in acetone and adding the appropriate amount of oil and curatives for the vulcanisation. The extracted pure EPDM was also used in DSC and DRS measurements. The sample coding of the binary mixtures consists of the component and its weight fraction, e.g. PP80/Oil20.

2.3. Dynamic mechanical analysis

The glass transition temperatures of the binary mixtures and the OTPE blends were determined by dynamic mechanical analysis (DMA). Experiments were performed in a Perkin–Elmer DMA 7, in tensile mode, at a frequency of 1 Hz. Samples were heated from –80 to 0 °C at a rate of 2 K/min. The peak temperatures in the loss modulus were taken to define operational ‘mechanical’ glass transition temperatures.

2.4. Differential scanning calorimetry

DSC heat flow curves were recorded with a Perkin–Elmer DSC 7. Indium was used for the temperature calibration. All samples were annealed for 10 min at 200 °C to erase their thermal history, and subsequently cooled at a rate of 10 K/min. to –100 °C. The glass transition temperatures were determined at the half ΔC_p values. The degree of crystallinity of the PP, X_{PP} , was calculated from the heat of crystallisation of the blend,

ΔH_{TPE} , the heat of crystallisation of PP, ΔH_{PP} (=209 J/g [12]) and its mass fraction, m_{PP} :

$$X_{PP} = \frac{\Delta H_{TPE}}{m_{PP} \Delta H_{PP}} \quad (1)$$

2.5. Dielectric relaxation spectroscopy

Samples for dielectric measurements were prepared by melt mixing the blends or the binary mixtures with 0.5 wt% of the probe, DBANS, in the internal batch mixer. In these samples, the EPDM in the TPVs and in the binary mixtures was not cured to avoid interference of the curatives with the probe molecule in the dielectric measurements. We should refer to these blends as PP/EPDM blends instead of TPVs. The DBANS was added after premixing the ternary blends for 8 min at 100 rpm. The blends were mixed for 2 min to ensure a homogenise probe distribution. The samples were subsequently compression moulded into sheets of 0.3 mm thickness at 200 °C. The same procedure was used for the PP–oil mixtures. The elastomer–oil mixtures were mixed and compression moulded at 150 °C. For the dielectric measurements, the materials were hot pressed between circular brass electrodes ($\varnothing = 2$ cm) together with 100 μ m glass fibre spacers.

Dielectric measurements were performed using a high precision dielectric analyzer (ALPHA analyzer, Novocontrol Technologies) in combination with a Novocontrol Quatro temperature control system. Isothermal frequency sweeps (10^{-1} – 10^7 Hz) were taken in the temperature range of +200––120 °C in steps of –5 K. This way, thermal and mechanical history is removed, and the measurement starts from an isotropic sample. A comprehensive description of the analysis methods for dielectric data can be found in [13,14].

3. Results

3.1. DMA and DSC

Fig. 2(a) shows the loss modulus of SEBS–oil binary mixtures as a function of temperature. The oil is present in

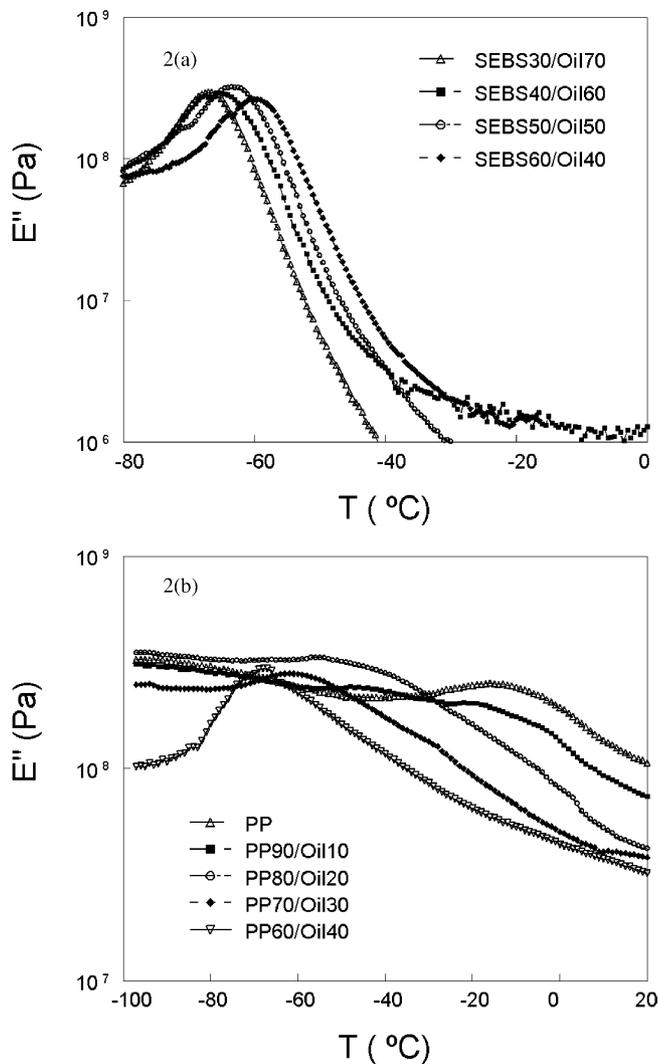


Fig. 2. Temperature dependence of the loss modulus of the binary mixtures (a) SEBS–oil (b) PP–oil.

the olefinic EB blocks and it plasticizes that phase: increasing the oil content results in a gradual decrease of the glass transition temperature, indicated by the position of the maximum in E'' , and the peak becomes narrower. Similar trends are found for the EPDM–oil vulcanisates. The effect of oil on the loss moduli of PP is shown in Fig. 2(b). Addition of oil results in a drastic decrease of the glass transition temperature. PP is semicrystalline and only the amorphous parts are accessible for the oil. Therefore, the local concentration of oil in the amorphous parts increases faster than the overall oil concentration. Moreover, even for low oil concentrations, two additional local maxima can be observed in the ranges from -20 to -30 °C and from -50 to -70 °C, which point to phase-separation in the PP–oil system. The higher temperature relaxation in Fig. 2(b) diminishes with increasing oil content and is absent above 30 wt% oil. In the range of the concentrations that should correspond to the oil in the phases of the ternary blends (25–40 wt%) only the lower

temperature transition can be observed. The presence of separate oil domains in the binary mixtures or in the blends, however, could not be proven by morphology studies on these OTPE blends [15].

The temperature dependent dynamic moduli of the OTPE blends with different composition are shown in Fig. 3. The dependence of the dynamic moduli on composition is comparable for the two blend types. Between -70 and -40 °C only one peak in E'' is observed, where two peaks should be expected, corresponding to the PP and elastomer phases. Apparently, the glass transition dynamics of the two phases are so close to each other that they overlap.

Fig. 3 shows the dynamic moduli of the OTPE blends. The behaviour of the two blends is comparable. Increasing the amount of PP in the TPVs results in a shift of the E'' peak to higher temperatures (Fig. 3(a)), while the peak becomes broader at the high temperature side. Both E' and E'' increase with increasing PP content. The PP matrix phase is the stiffer phase and an increase of its volume fraction results in an increase of the blend modulus. Fig. 3(b) shows

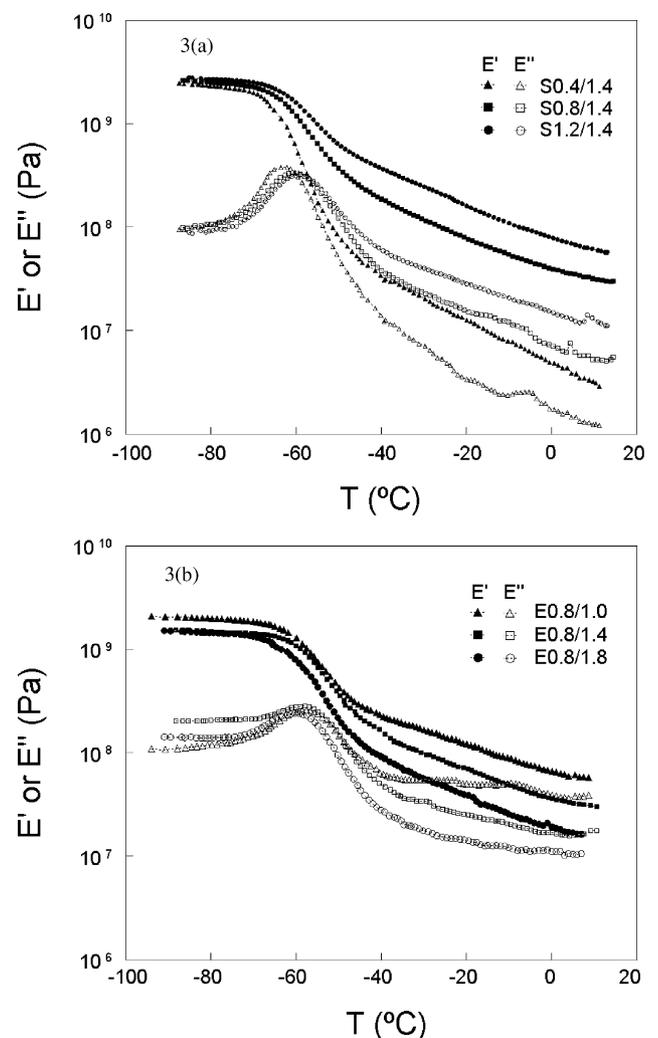


Fig. 3. Temperature dependence of the dynamic moduli of the OTPE blends (a) PP/SEBS, different PP content (b) TPVs, different oil content.

that an increasing oil content results in a shift of the single E'' peak to lower temperatures and a narrowing of the peak. E' decreases upon adding more oil because of the plasticizing effect. The extra amount of oil is distributed over the two phases and the T_g of both phases decreases.

Fig. 4 shows the T_g 's (E'' maxima) of the PP–oil and SEBS–oil binary mixtures and of the PP/SEBS/oil blends as a function of the total oil content. The double points for the PP–oil mixtures correspond to the two local maxima in E'' shown in Fig. 2(b) and are probably due to the presence of two phases: one oil-rich and one PP-rich. This ambiguity in the identification of the relaxations of the PP phases propagates into the difficulty to identify these transitions in the ternary blends. It has been mentioned that the higher temperature transition of the PP rich phase disappears above 30 wt% oil. The lower temperature transition is very close to the glass transition of the SEBS–oil mixture. As a result, the corresponding transition of the PP/SEBS/oil ternary blend falls also at the same temperature region and cannot be identified as either the transition of the PP–oil or the SEBS–oil phase. For the ternary blends, therefore, the E'' maxima of Fig. 3 are the weighted summations of the two peaks present due to the transitions of the two phases around the same temperature. To complicate matter further, the values of the dynamic moduli of immiscible blends may depend also on the morphology [16–18], which is not known a-priori.

The determination of the T_g s of the OTPE blends by DSC proved to be inaccurate. Fig. 5 shows the heat capacity of TPV E0.8/1.4 and its components measured during cooling. The T_g of pure PP is difficult to discern at around -8°C . The pure oil and elastomer components show a broad exothermic process at temperatures between -10 and -50°C . This is probably due to the crystallisation of repeating ethylene units [19,20]. The PP–oil binary blends

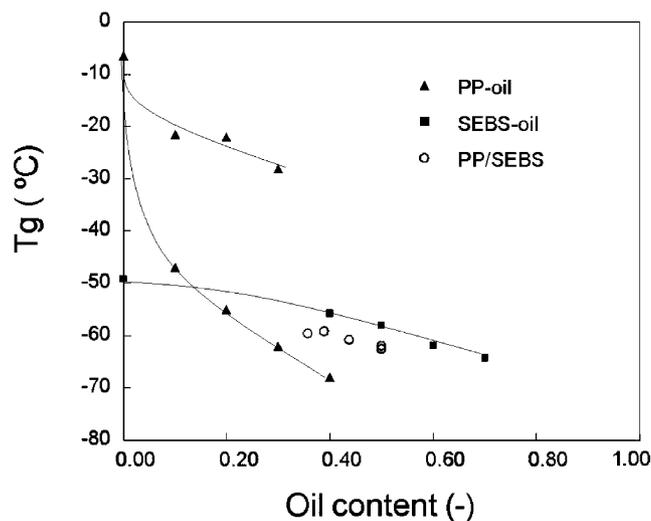


Fig. 4. Glass transition temperature of the binary mixtures as a function of the total oil content measured with DMA of PP/SEBS blends, PP/oil and SEBS/oil. The lines are a guide to the eye.

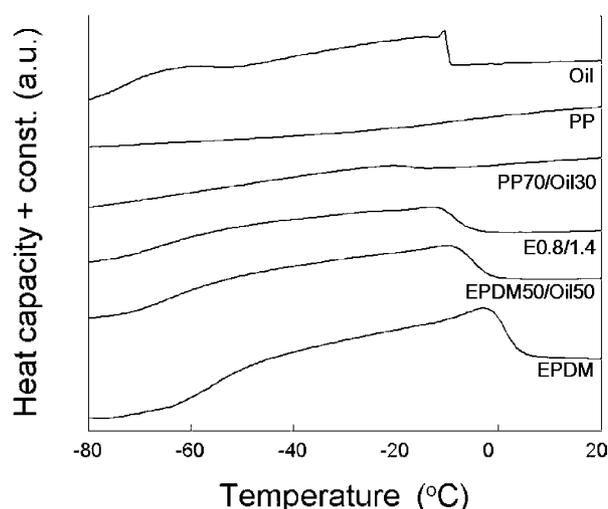


Fig. 5. Heat capacity of TPV E0.8/1.4 and its two phases and its components measured by DSC (cooling at $10^\circ\text{C}/\text{min}$).

also show this transition, which overlaps with their T_g . The shifting of the T_g in these blends cannot be quantified as a function of the oil content with sufficient reliability. Similarly, the same transition is present in the EPDM–oil blends. Because of this transition, the determination of the T_g s of the PP and the elastomer phases using DSC is inaccurate. The problem becomes worse in the OTPE blends, where the glass transition temperatures that are found cannot be directly related to each one of the two constituting phases (Fig. 6).

DSC could be used, however, to estimate the crystallinity of the PP in the blends. This was found to vary between 0.45 and 0.49 (Table 1). The crystallinity of PP was slightly higher in the PP/SEBS blends than in the TPVs.

Summarising the above, the distribution of oil in the TPVs and the PP/SEBS blends cannot be calculated from

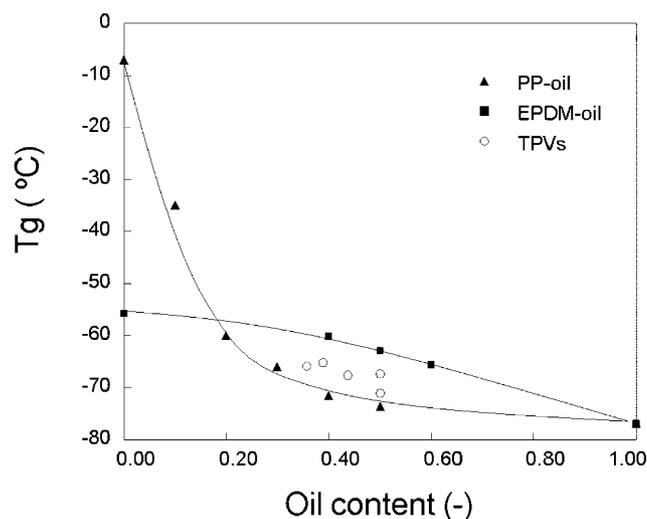


Fig. 6. Glass transition temperature as a function of the total oil content measured with DSC of TPVs, PP/oil and EPDM/oil. The lines are a guide to the eye.

the determination of the glass transition temperatures measured by DMA or DSC. The glass transition dynamics overlap in the blends and only a single T_g is found, which cannot be related specifically to one of the phases. Therefore, a new method is introduced using dielectric spectroscopy, which enables the separation of these two relaxation processes and the determination of the oil distribution in the two phases of the blends.

3.2. Dielectric relaxation spectroscopy

Dielectric relaxation spectroscopy (DRS) is a well-known technique to study polymer dynamics but is used mainly for polar polymers [21]. In Refs. [10,11], a method was proposed that allows to perform DRS also on apolar polymer systems, which have been sensitised by doping them with 4,4'-(*N,N*)-(dibutylamino)-(*E*)-nitrostilbene (Fig. 1). This probe molecule has a strong permanent dipole being almost in parallel to the molecular axis. The attached aliphatic tails enhance the solubility in olefinic media and prevent crystallisation of the probe. Because the dipole moment is parallel to the molecular axis, the orientation dynamics of the dipole is directly coupled to the rotation dynamics of the molecule. The rotation dynamics, for its part, depends on the microviscosity of its direct surrounding. The dielectric response of the probe, therefore, is affected by changes in the viscosity of the host in the region of the glass transition.

When this method is applied to blends of two polyolefins, then the probe is present in both phases because the polarity difference of the two polymers is small [21]. In addition, the values of the relative permittivity, ϵ^* , of the two polymers are comparable. For this reason, the total dielectric loss of the blend, ϵ'' , can be described as the sum of the individual loss contributions from the two polymers weighted by their respective volume fractions.

When DBANS is added to the OTPE blends, a homogeneous distribution of the probe over the PP and the elastomer phases are expected. Fig. 7 shows a typical result of the DRS measurements for the blend S0.8/1.4, where the dielectric loss, ϵ'' , is plotted as a function of frequency and temperature. The peaks in ϵ'' correspond to changes in the mobility of the surroundings of the probe. The increase of ϵ'' at high temperatures and low frequencies is due to Ohmic conduction. The peak of ϵ'' between 100 and 150 °C at high frequencies corresponds to the glass transition dynamics of the PS blocks within the SEBS. The probe molecules are also present in this phase and enhance its dynamics, so that the peaks are visible even though the total PS content in the PP/SEBS blend is only about 9 wt%. As shown by DMA and DSC, the glass transition dynamics of the PP and the elastomer phase overlap. This is also found in the DRS experiments. The overlapping glass transitions of the PP and elastomer phases appear as a single peak between –50 and 30 °C, depending on the frequency.

The main advantage of the dielectric technique for the

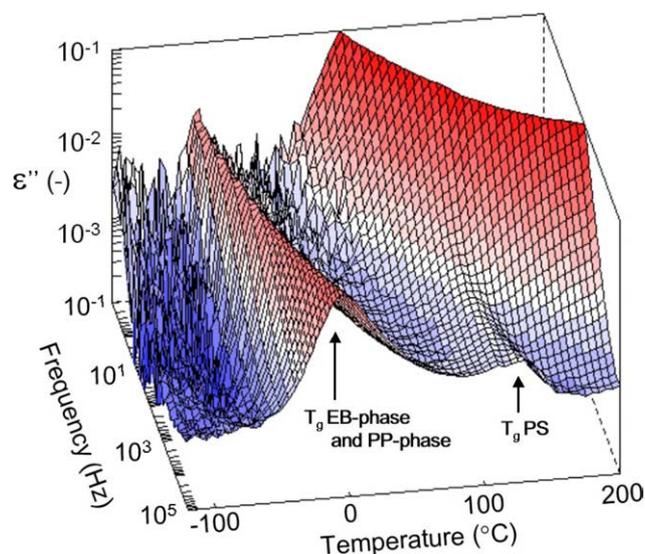


Fig. 7. Dielectric loss, ϵ'' , as a function of frequency and temperature for S0.8/1.4.

separation of the relaxation peaks and the eventually determination of the oil distribution, is that the samples can be measured isothermally over a wide frequency range (7 decades). This enables the analysis of the dielectric losses also in the frequency domain, $\epsilon''(\omega)$. The overlapping peaks in $\epsilon''(\omega)$ of the ternary blends can then be reconstructed from the peaks of the two phases.

To model the loss peaks in $\epsilon''(\omega)$ of the binary PP–oil and elastomer–oil mixtures we have used the imaginary part of the empirical Havriliak Negami (HN) function:

$$\epsilon'' = \text{Im} \left\{ \frac{\Delta\epsilon}{(1 + (i\omega\tau)^a)^b} \right\} + \frac{\sigma}{\epsilon_0\omega} \quad (2)$$

where $\Delta\epsilon$ and τ are the relaxation strength and the mean relaxation time of the corresponding transition. The shape parameters a and b are the logarithmic slopes of the curve determined by the underlying distribution in relaxation times. The parameter a corresponds to the logarithmic slope at low frequencies and ab is the logarithmic slope at high frequencies. The second term in Eq. (2) accounts for possible Ohmic conduction.

The effect of the oil content in the binary mixtures on the shape and position of the $\epsilon''(\omega)$ peak can be described by the HN-parameters, $\Delta\epsilon$, τ , a and b , if they are considered as functions of the oil content. By interpolation of these parameters, the dielectric losses of the two phases can be predicted for any oil concentration. The dielectric response of the ternary blends is then reconstructed by a weighted addition of the losses of the two phases. The oil distribution coefficient is found for each temperature in the range of –40–10 °C by an optimal fit of the ternary blend.

3.2.1. Binary mixtures

Fig. 8 shows the loss permittivity for three binary polymer–oil mixtures as a function of the frequency at

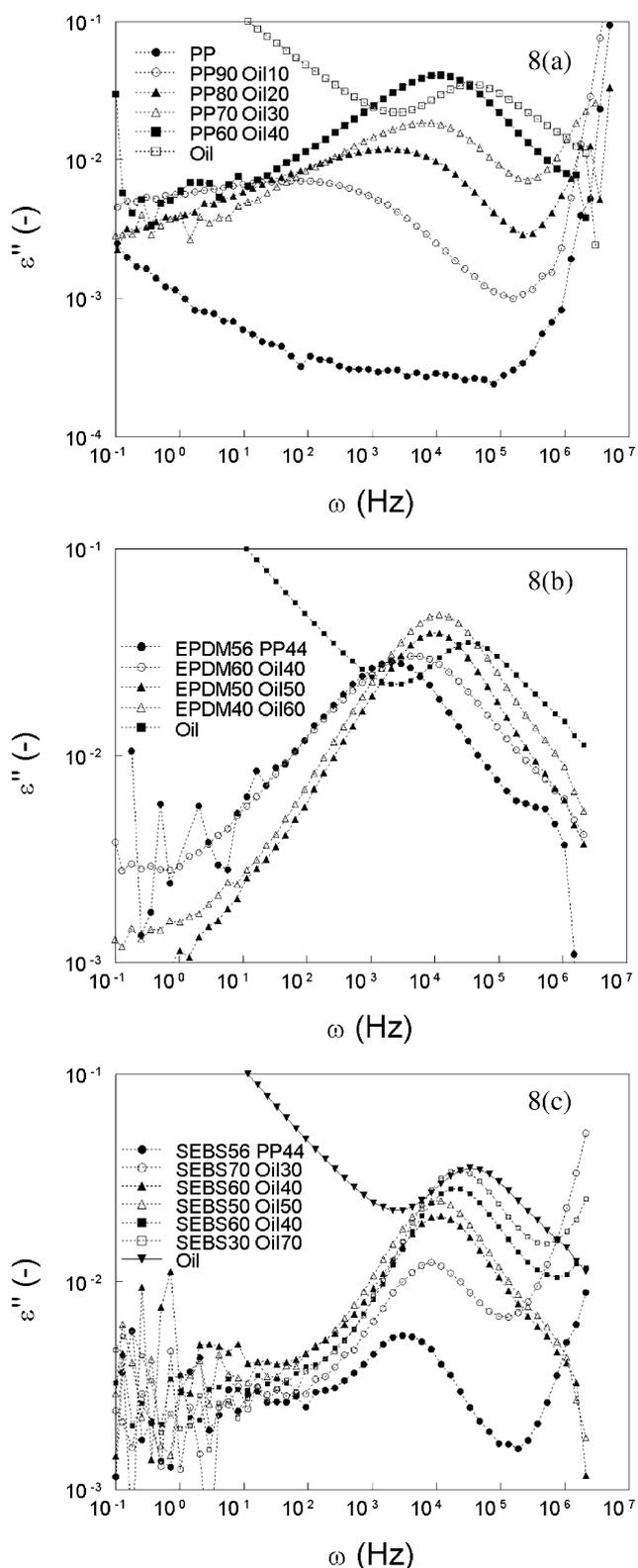


Fig. 8. Dielectric loss, ϵ'' , of the binary mixtures as a function of frequency at $-20\text{ }^{\circ}\text{C}$. (a) PP/oil (b) EPDM/oil and (c) SEBS/oil.

$-20\text{ }^{\circ}\text{C}$. The peak in $\epsilon''(\omega)$ corresponds to the dynamic glass transition process of pure oil and the plasticized polymer–oil phase, respectively. In Fig. 8(a), the plasticizing effect of oil on

the primary relaxation of PP is demonstrated, which expresses in the increase of the loss peak intensity and its shift to higher frequencies. Since pure PP has a glass transition temperature around $-10\text{ }^{\circ}\text{C}$, no corresponding loss peak is discernible for unplasticized PP. In addition, the peak shape becomes narrower as the oil content increases.

The change in relaxation behaviour of the SEBS–oil and the EPDM–oil mixtures is presented in Fig. 8(b) and (c). Note that the pure elastomers ($c_{\text{oil}}=0$) were too viscous and elastic for melt mixing and they were blended with PP to make them processable. The dielectric response arising from the glass transition dynamics of the elastomer phase is not affected by the addition of PP because the PP does not show any dielectric process at this temperature and frequency range. Fig. 8(b) shows the dependence of $\epsilon''(\omega)$ on oil content for the EPDM–oil mixtures. The behaviour is comparable to that of the PP–oil mixtures: increasing the oil content increases the value of the maximum in $\epsilon''(\omega)$ and shifts the peak to higher frequencies. The peak narrows, especially on the low frequency side. Similarly to the SEBS–oil mixtures (Fig. 8(c)), the loss peaks shift to higher values and higher frequencies with increasing amount of oil. In these mixtures, the shape of the peaks does not change significantly with oil content. This is possibly due to the low polydispersity of the EB chains as compared to the high molecular weight PP and EPDM.

To quantify the dielectric response of the binary mixtures, the relaxation peaks were fitted with the HN-function (Eq. (2)). It was found that the shape parameter b of the mixtures did not change significantly with changing oil content and it has been kept constant for each temperature in the following analysis. As shown in Fig. 7, the peaks of PP–oil and EPDM–oil mixtures become steeper with increasing oil content. This results in an increase of the shape parameter a . For the SEBS–oil mixtures, the parameter a had a constant value of 0.77, independent of temperature and composition.

The values of the HN-parameters for the T_g dynamics of the binary mixtures at $-20\text{ }^{\circ}\text{C}$ are summarised in Fig. 9. The relaxation strength, $\Delta\epsilon$, increases linearly with the oil content (Fig. 9(a)). This increase is faster for the PP–oil mixture because PP is semi-crystalline and the oil is only present in the amorphous part. The local oil concentration, and thus the relaxation strength, increases faster than the overall oil content in the total PP phase.

The relaxation times, τ , (Fig. 9(b)) and the shape parameter a , (Table 2) of the PP–oil mixtures are different from the ones of the elastomer–oil. The two elastomer–oil mixtures show comparable behaviour of the relaxation times: they scale exponentially with the oil content. The relaxation times of the PP–oil mixtures decrease faster because of the faster increase of the local oil concentration in the amorphous parts of PP. The shape parameter, a , also increases with increasing oil content (Table 2).

The lines in Fig. 9 are empirical equations correlating the HN parameters with the oil concentration. These equations are listed in Table 2 for $T = -20\text{ }^{\circ}\text{C}$. Similar fit equations

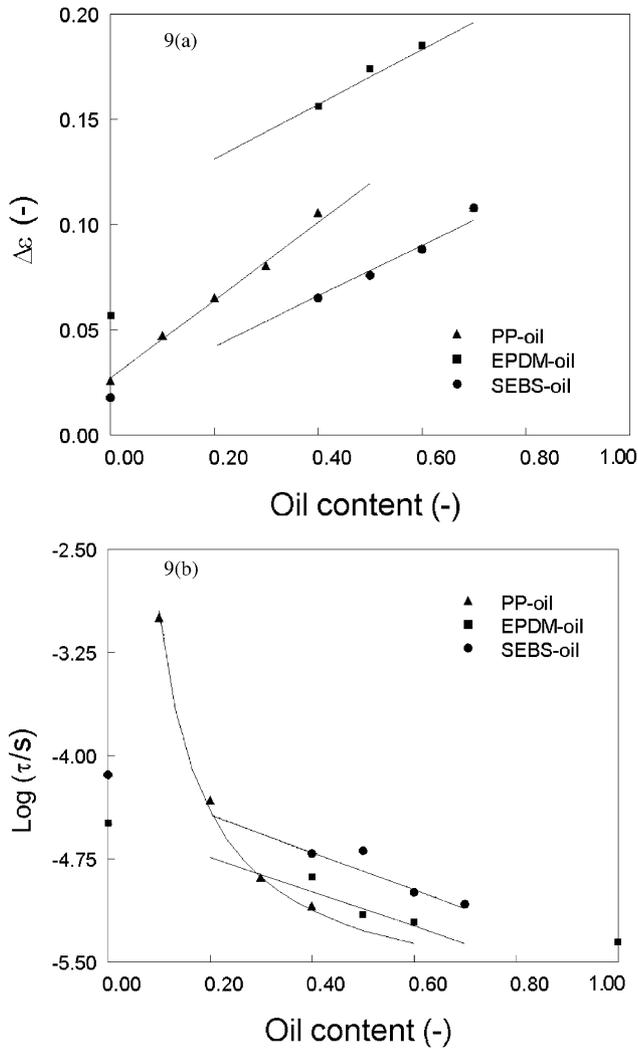


Fig. 9. Dependence of the HN parameters of the binary mixtures on the oil content (a) relaxation strength and (b) relaxation time at $-20\text{ }^{\circ}\text{C}$. See Table 2 for the drawn fitting curves.

are found for the other temperatures. These equations are used in Section 3.3 to interpolate the values at any oil content and to reconstruct the relaxation peaks of the two phases in the TPE blends.

Table 2
Dependence of HN fit parameters of binary mixtures on oil content at $-20\text{ }^{\circ}\text{C}$

HN parameter	Fit function
PP-oil	
$\Delta\epsilon$	$\Delta\epsilon = 0.19 c_{\text{oil, PP}} + 0.027$
τ	$\log(\tau) = 0.28/c_{\text{oil, PP}} - 5.85$
a	$a = 0.69 c_{\text{oil, PP}} + 0.27$
b	$b = 1.5$
SEBS-oil	
$\Delta\epsilon$	$\Delta\epsilon = 0.13 c_{\text{oil, SEBS}} + 0.011$
τ	$\log(\tau) = -1.36 c_{\text{oil, SEBS}} - 4.16$
a	$a = 0.77$
b	$b = 0.8$
EPDM-oil	
$\Delta\epsilon$	$\Delta\epsilon = 0.23 c_{\text{oil, EPDM}} + 0.056$
τ	$\log(\tau) = -1.25 c_{\text{oil, EPDM}} - 4.49$
a	$a = 0.076 c_{\text{oil, EPDM}} + 0.57$
b	$b = 1.64$

3.2.2. OTPE blends

Fig. 10 shows the effect of the composition on $\epsilon''(\omega)$ for the OTPE blends at $-20\text{ }^{\circ}\text{C}$. As also observed in the DMA results, the $\epsilon''(\omega)$ of the OTPE blends reveals a single peak that corresponds to the overlapping glass transition processes of the two phases. Fig. 10(a) shows the loss permittivity of PP/SEBS blends with different PP content. The spectra of the two binary mixtures, PP with 30 wt% oil and SEBS with 50 wt% oil, are also included. The maximum of the relaxation peak of the blends is close to the one of the SEBS-oil binary mixture. The curve of the blend has a shoulder at the frequencies where the PP phase relaxation should be. The peak decreases in height and shifts to lower frequencies, while the low frequency shoulder increases with increasing PP content. The peak in $\epsilon''(\omega)$ changes, thus, from elastomer-like to PP-like behaviour.

Changing the oil content also affects the position of the relaxation peaks in the blends (Fig. 10(b)). The relaxation strength of the loss permittivity of the PP/EPDM blends increases and the maximum shifts to higher frequencies with increasing oil content. This is due to the plasticizing effect of the oil, as observed also in the binary mixtures. The reduction of the low frequency shoulder is due to the change in shape of the PP phase peak. Similar to the PP-oil binary mixtures, the relaxation time and the relaxation strength increase with increasing oil content. In addition, the peak of this phase becomes sharper.

From the above we can conclude that the curves of $\epsilon''(\omega)$ of the OTPE blends consists of the peaks of the two phases that partially overlap. Increasing the PP content, the relaxation behaviour changes gradually from elastomer-like to PP-like. When the oil content is increased, both phases are plasticized and the peak in loss permittivity shifts to higher frequencies.

3.3. Determination of the oil distribution coefficient

The trends in the dielectric response of the OTPE blends can be correlated to the changes in the phase volume fractions and in the concentration levels of oil in the two phases. Therefore, the spectra of the OTPE blends can be

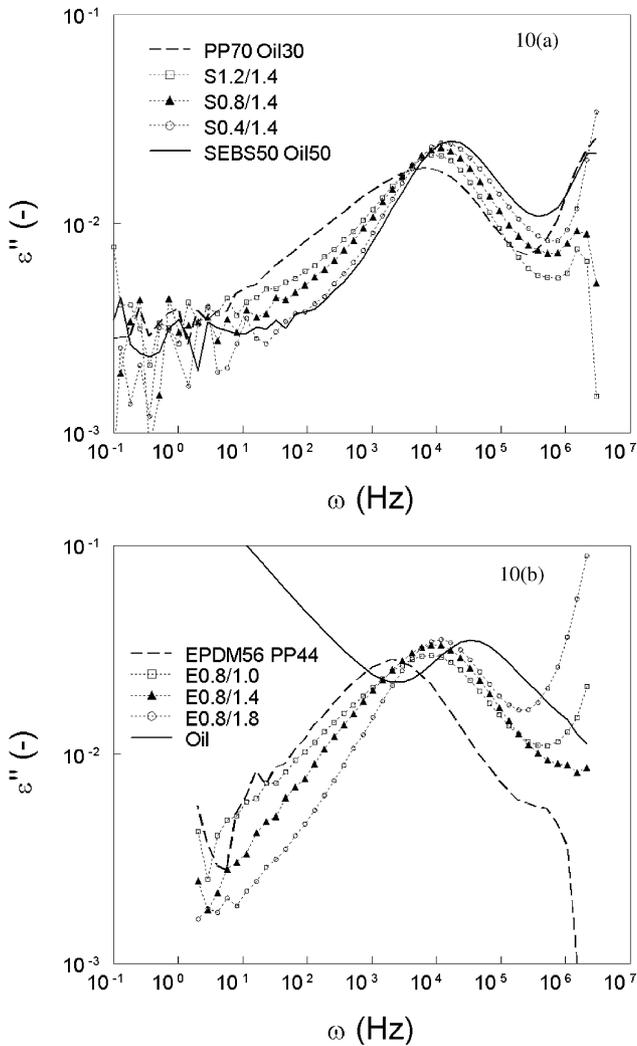


Fig. 10. Frequency dependence of the dielectric loss, ϵ'' , of the OTPE blends at $-20\text{ }^\circ\text{C}$. (a) PP/SEBS with different PP content (b) PP/EPDM with different oil content.

reconstructed by adding the ones of the binary mixtures. The determination of the oil concentrations in the two phases can, thereby, be achieved.

To quantify the preference of the oil in one of the phases, the distribution coefficient, K , is used [3]. This is the ratio of the oil concentration of the PP phase, $c_{oil, PP}$, over the one of the elastomer phase, $c_{oil, EI}$:

$$K = \frac{c_{oil, PP}}{c_{oil, EI}} \quad (3)$$

These concentrations are interrelated via the mass balance of the system, where the oil is distributed over the two phases:

$$m_{PP} + m_{oil, PP} + m_{oil, EI} + m_{EI} = 1 \quad (4)$$

and $m_{oil, PP} + m_{oil, EI} = m_{oil}$

where m_i is the mass fraction of component i . The oil concentrations are related to the phase mass fractions of the

components:

$$c_{oil, PP} = \frac{m_{oil, PP}}{m_{oil, PP} + m_{PP}} \quad \text{and} \quad c_{oil, EI} = \frac{m_{oil, EI}}{m_{oil, EI} + m_{EI}} \quad (5)$$

The dielectric losses of the ternary blends are calculated at a constant temperature by adding the losses of the PP and elastomer phases. This is done by an iterative technique. An initial value of K is chosen for the specific ternary blend and the oil concentrations are calculated using Eqs. (3)–(5). The parameters $\Delta\epsilon(c_{oil})$, $\tau(c_{oil})$, $a(c_{oil})$ and b for the two phases are calculated by the equations listed in Table 2 and the two peaks of the phases, $\epsilon''_{PP}(\omega, c_{oil, PP})$ and $\epsilon''_{EI}(\omega, c_{oil, EI})$ are calculated from Eq. (2). Finally, The dielectric loss of the ternary blend, $\epsilon''_{TPE}(\omega)$, is reconstructed by the addition of $\epsilon''_{PP}(\omega, c_{oil, PP})$ and $\epsilon''_{EI}(\omega, c_{oil, EI})$:

$$\epsilon''_{TPE}(\omega) = x_{PP}\epsilon''_{PP}(\omega, c_{oil, PP}) + x_{EI}\epsilon''_{EI}(\omega, c_{oil, EI}) \quad (6)$$

with $x_{PP} = m_{PP} + m_{oil, PP}$ and $x_{EI} = m_{EI} + m_{oil, EI}$ the phase mass fractions. The curve is compared to the measured one and the value of K is obtained by a least squares fit.

An example of this calculation is given in Fig. 11, which shows the loss permittivity curve for the blend S0.8/1.4 at $-20\text{ }^\circ\text{C}$. The graph shows the measured peak, the calculated individual peaks of the two phases (dashed lines) and the reconstructed peak for the blend using the above procedure for an estimated value of $K=0.62$. The values of K for the two TPE blends do not change significantly with temperature in the range of $-40\text{--}0\text{ }^\circ\text{C}$. The averaged values are listed in Table 3. Within experimental error, the oil distribution in the PP/SEBS blends is comparable to that in the PP/EPDM blends. The average value of K in all the blends is smaller than one, indicating that the oil concentration in the elastomer phase is higher than in the PP phase. The composition has a minor effect on the value of K : in both the OPTPE blends K decreases slightly with increasing PP content. The total

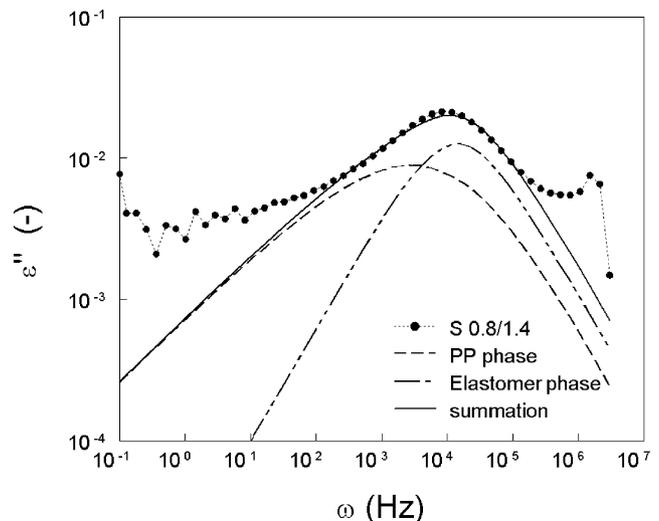


Fig. 11. Fit of ϵ'' for the blend S0.8/1.4 at $-20\text{ }^\circ\text{C}$.

Table 3
Oil distribution coefficients in OTPE blends

Blend	DRS -40 – 10 °C		Veenstra D 190 °C	
	K	$K_{\text{corrected}}^a$	K^b	$K_{\text{corrected}}^c$
S0.4/1.4	0.63 ± 0.02	0.79	0.97	0.77
S0.8/1.0	0.61 ± 0.02	0.78	0.36	0.30
S0.8/1.4	0.62 ± 0.03	0.77	0.63	0.53
S0.8/1.8	0.57 ± 0.03	0.73	0.65	0.56
S1.2/1.4	0.57 ± 0.03	0.74	0.48	0.40
E0.4/1.4	0.67 ± 0.03	0.96	1.14	1.14
E0.8/1.0	0.65 ± 0.04	0.86	0.04	0.04
E0.8/1.4	0.63 ± 0.06	0.85	0.60	0.60
E0.8/1.8	0.63 ± 0.03	0.88	0.94	0.94
E1.2/1.4	0.60 ± 0.04	0.84	0.34	0.34

^a $K_{\text{corr}} = c_{\text{oil, amorphPP}}/c_{\text{oil, EB}}$; $K_{\text{corr}} = c_{\text{oil, amorphPP}}/c_{\text{oil, EPDM}}$.

^b Obtained from Ref. [8].

^c $K_{\text{corr}} = c_{\text{oil, PP}}/c_{\text{oil, EB}}$; $K_{\text{corr}} = c_{\text{oil, PP}}/c_{\text{oil, EPDM}}$.

amount of oil does not affect the oil distribution coefficient significantly.

To test the validity of the present results we fitted also the dynamic moduli using the Veenstra model D [8]. This model has been used successfully to describe the frequency dependence of the dynamic moduli in the melt state. We applied this model to the ternary blend S0.8/1.4, where the concentrations of oil in the phases (31 wt% oil in the PP phase and 53 wt% in the SEBS phase) are close to two of the binary mixtures in the series made here: 30 wt% oil in PP and 50 wt% oil in SEBS. The values of the dynamic moduli in the latter binary mixtures are used to calculate the dynamic moduli of the blend using the Veenstra-D model. Fig. 12 shows the temperature dependent dynamic moduli of blend S0.8/1.4 and the results of the model. The moduli of the PP and the elastomer phases are also included. The calculated E' underestimates the values of the blend in the glassy state slightly, but the calculated E'' values describe the blend values well. It is noted that the curve calculated using the Veenstra model D gives a remarkable agreement

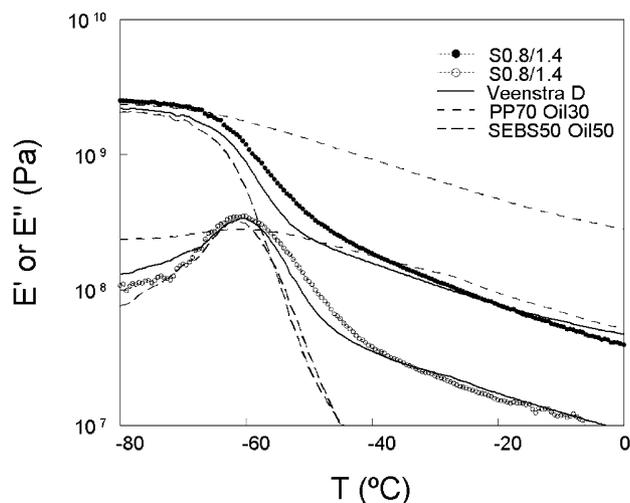


Fig. 12. Calculated DMA response of the blend S0.8/1.4 using Veenstra model D, compared to the experimental results.

with the measured peak of the PP/SEBS blend at the glass transition. The model predicts that the E'' peak of the blend is indeed a weighted summation of two overlapping glass transition processes and that the maximum in E'' does not correspond to the T_g of only one of the individual phases. The peak height of the blend is broad at the low temperature side because of the contribution of the glass transition of the elastomer phase. At the high temperature side, it is broad because of the contribution of the T_g of the PP phase.

4. Discussion

There is a small difference in polarity between the PP and the elastomers that could affect the solubility parameters and the oil distribution. This difference is small and a value of K close to 1 should be expected. The oil, however, is paraffinic in nature and could be considered as an EP oligomer with an ethylene content of 70% [7]. Since both elastomers contain ethylene as co-monomer, it is likely that a small preference of the oil for the elastomer phase exists, resulting in a value of K slightly less than 1.

The distribution of the oil in the compounds was found in the present work to favour the elastomer phase: the average value of K was 0.60 for the PP/SEBS blends and 0.63 for the TPV, which is lower than the ones expected theoretically. The distribution coefficient seems to be relatively insensitive to the blend composition.

Non-uniform oil distribution has been previously observed in comparable PP/SEBS systems by Ohlsson et al. [3], who found a value of $K \approx 0.35$ in the solid state. This is lower than what was found here, indicating that the oil preferred the elastomer phase much stronger in their case. However, Ohlsson et al. used different oil and PP and it is expected that the chemical structure and the molecular weight of the components will affect their affinity. The values of K for the PP/SEBS blends found for the melt state in [8] were around 0.36 and 0.97. These values are comparable to the values found here for the solid state, but depend on the composition. The values for K in the melt were obtained from modelling and not by direct measurements. Furthermore, increasing the PP content for these blends has a larger effect in the melt state than in the solid state.

The values of K for the TPVs were also found in general to be less than 1. Jayaraman et al. [6] reported values in the range of 0.65–0.68 for the solid state, the same as in the present work. The concentration of oil in the PP phase was found to decrease with increasing PP content in the blend. These results are similar to what was reported in [6] for the TPVs in the melt state and do not agree fully with what is found here for the solid state, where K depends on the PP/elastomer ratio. The oil distribution was evaluated in [6] by comparing the domain areas in the transmission electron micrographs. In the present DRS experiments, the elastomer phase in the blends was not cured. The swelling behaviour

of a polymer network differs from a freely entangled polymer. Entropic contributions to the swelling due to constraints imposed by the cross links may account for the greater composition dependence of the distribution of oil between the two phases in the TPVs.

A final point concerns the proportion of the mass in the phases that is available for the oil to diffuse. As outlined above, K was calculated based on the total mass fractions of the components. There is, however, 45–49% crystallinity in the PP phase in the blends (Table 1). The oil cannot be present in the crystalline regions [5]. Further, the paraffinic nature of the oil will prevent it from diluting the aromatic PS domains of the SEBS phase. The crystalline parts of PP and the PS domains of the SEBS can, thus, be considered as hard fillers and are not available for the oil. Therefore, they should be excluded from the calculation of the oil distribution coefficient and only the amorphous PP and the EB part of the SEBS should be considered.

New values of the oil distribution coefficient were, therefore, calculated from the data by considering only these amounts of PP and elastomer that were actually available for the oil. These ‘corrected’ values of K are listed in Table 3. For the PP/SEBS blends, the average value of K is now 0.51 in the melt and 0.76 in the solid state. The average corrected value of K for the TPVs is 0.89 in the solid state. These values for K are closer to an equal distribution than the uncorrected values, but the oil has still a preference for the elastomer phase.

5. Conclusions

Three experimental techniques for the determination of the distribution of oil in the PP/SEBS and PP/EPDM blends were tested and evaluated. Although DMA and DSC results revealed the plasticizing effects on the glass transitions in the PP and the elastomer phase, there was no unambiguous way to determine the phase-specific oil concentration from the depression of the T_g s due to the strong overlap in the glass transition regions. The third approach, dielectric relaxation spectroscopy (DRS) using dielectric probes, turned out to be successful in analysing and separating the glass transition processes related to the two individual, oil containing, phases. The oil distribution coefficient is determined by modelling the imaginary part of the permittivity of the blend from those of binary PP–oil and

elastomer oil mixtures. Both in the TPVs and in PP/SEBS blends the values for K are lower than one, indicating that the oil prefers the elastomer phase. The composition has minor effect on the values of K . Based on the oil distribution calculated from the DRS experiments the mechanical properties of the blends can be modelled successfully.

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