Morphology and Rheological Properties of High Density Polyethylene/Fluorothermoplastics Blends

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ABSTRACT: The polyolefin blends of high-density polyethylene (HDPE) with two types of fluorothermoplastics (THV500 and THV220); were prepared by melt compounding technique. The morphology, crystallization, and the viscoelastic measurements of the blends were carried out. The dispersion of THVs was studied by scanning electron microscopy (SEM) technique, and discussed. The crystallization characteristics of the blend were studied using Differential scanning calorimetry (DSC). The oscillatory shear measurement was employed for determining the rheological properties of the prepared blends. There is a significant difference in the rheological behavior of the HDPE blends with THV500 and THV220. The dynamic linear viscoelastic behavior (storage modulus and viscosity) of HDPE/THV500 was found to be higher than that of HDPE/THV220 blend. This was attributed to the molecular weight and particle size distribution of THVs. However, the molecular weight effect of THVs on the crystallization behavior of the blend is marginal. The master curves of the storage and loss modulus vs. frequency were constructed by applying the time–temperature–superposition (TTS) principle. It was established that the parsimonious and modified Cox-Merz models are fairly applicable to the storage modulus and viscosity results. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The blending of polymers is an effective way to generate materials with designed and optimized properties like morphological, chemical, structural, mechanical, and thermal stability.[1–4] During the blending process, polymers may become miscible or immiscible with each other, usually leads to a change in morphology of the blend system. It is well established that the blend properties are controlled by the morphology and phase sizes developed during the blending of two or more polymers.[5] The polymer blend processing parameters to a great extend can be controlled by understanding the rheology of the blend. Polyethylene (PE) is one of the most widely used polyolefin polymers. Blending of PE with polypropylene (PP), polyamide (PA) blends, poly(vinyl alcohol) (PVA), and/or ethylene vinyl alcohol (EVOH) have been widely investigated to improve the low-temperature toughness and barrier properties.[6–8] The success of blending depends upon compatibility between the polymer components.[9] Further investigations also reported that the stiffness and modulus properties of PP/HDPE blends depend greatly on the resulting blend morphology.[10,11] Similar investigation with PE/modified polyamide (MPA) found that the shear viscosity exhibited a significant influence on the deformation and morphology of MPA.

Fluorothermoplastic blends are considered as a cost effective replacement of engineering materials, especially in fabrication of the automobile fuel tank.[12] Fluorothermoplastic in a PE matrix is one of the well proven barrier technologies to enhance permeability resistance of PE containers. However, the concept of physically blending of high density polyethylene (HDPE) and thermoplastic fluoropolymers to obtain new products has not been studied. Therefore, it is worth for checking whether the above approach is applicable to PE blend systems.

Accordingly, the goal of this work was to produce HDPE/fluorothermoplastics blends by melt compounding technique, study the viscoelastic behavior and also to optimize the processing parameters. Two grades of fluorthermoplastics (THV500 and THV220) with different molecular weight were used to study its effect on blend properties. The THVs dispersion in HDPE was
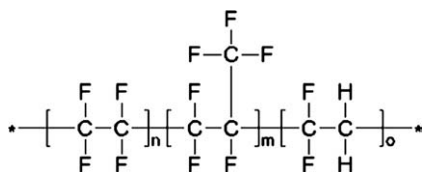
Figure 1. Chemical structure of THVs.

assessed by scanning electron microscopy (SEM). The rheological properties and the crystallization behavior of the resulting compounds were determined and compared with those of the pure HDPE.

EXPERIMENTAL

Materials and Preparation of Polymer Blend

Granulated high density polyethylene (HDPE 6914, Borealis Polymere GmbH, Burghausen, Germany) of melt flow index (MFI) of 1.6 g/10 min at 260°C/5 kg was utilized as polymeric matrix for all blend systems. Fluorothermoplastics of THV500 and 220 (tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride) were kindly supplied by Dyneon GmbH, Burgkirchen, German). The molecular weight of THV500 and THV220 are 490 and 240, respectively. The chemical structure of THV is presented in Figure 1 and their combinations of THV500 and THV200 are listed in Table I (according to suppliers' information).

Extrusion process with a special mixing corotating screw (Leistritz, Nuremberg, Germany) was employed for the preparation of HDPE/fluorothermoplastic blends. The length-to-diameter ratio (*L/D*) of the extruder was 32 with a screw length of 109 cm. The HDPE based blends were compounded at an output rate of 5 kg/h by setting the barrel temperatures between 100 (Zone 1) and 200 °C (from Zone 2 to 9), rotor speed of 40 rpm and pressure of 70 bar. The fluoropolymer contents in the system investigated (HDPE/THV500 and HDPE/THV220 blends) were set for 10–40 wt%. The extrudate was pelletized and compression molded in to 2 mm thick and 25 mm diameter at $T = 200$°C using a hot press. The specimens of appropriate dimensions for different analysis were cut from the compression molded sheet.

Rheology

A controlled strain rheometer (ARES of Rheometric Scientific, NJ) was utilized in parallel plate configuration (diameter of the plate: 25 mm) for the viscoelastic measurements. Oscillatory shear and step shear configurations at temperature range from 180 to 220°C was performed. Oscillatory shear measurements were performed on each sample by setting the strain amplitude for 3%. This was derived from a strain sweep test series checking the presence of the linear viscoelastic region. The gap between the plates was fixed to 1 mm. In oscillatory shear experiments, a sinusoidal shear strain $\gamma(t) = \gamma_0 \sin(\omega t + \varphi)$ was imposed. In the frequency sweep measurements, φ is the shift factor and frequency-dependent storage modulus (G') as well as loss modulus (G'') were determined.

Morphology

The dispersion of THVs in the HDPE blends was studied by scanning electron microscopy technique (SEM). The fractured surface of specimens was subjected to SEM inspection in a Leo 435 VP (Leica GmbH, Germany). The surface was carbon coated prior to SEM and the inspection performed at low acceleration voltage.

Crystallization

Differential scanning calorimetry (DSC) traces were recorded on a Thermal Analyst 2200 device (TA Instruments, New Castle, NJ) in the temperature range from 30 to 250°C at a heating and cooling rate of 10°C/min. The crystallinity (X_c) was calculated from the following equation:

$$X_c = \frac{\Delta H_m}{(\Delta H_m^0)} * 100\% \qquad (1)$$

where ΔH_m is the melt enthalpy of the HDPE in the sample (net HDPE content considered), ΔH_m^0 is the melt enthalpy of HDPE with 100% crystallinity ($X_c = 100\%$) for which 293 J/g was taken as reported.[13]

RESULTS AND DISCUSSION

Viscoelastic behavior can be determined by measuring the storage modulus and the loss modulus over a wide range of frequencies and temperatures. The storage modulus is proportional to the degree of elasticity of the system. The loss modulus is proportional to the dissipation or energy loss in a cycle deformation, reflecting the degree of viscosity of the system.[14]

The trace of the storage (G') and loss (G'') modulus as a function of the frequency at 190°C for the HDPE/THV500 and the HDPE/THV220 blends are shown in Figure 2(a,b), respectively. As expected, there is an increase in storage and loss modulus with increase in shear rate. The addition of THV500 (10 wt%) into HDPE matrix resulted in a marginal decrease in the G' and G'' [cf. Figure 2(a)], where as there is a significant decrease in the G' and G'' of the blends by the addition of THV220 [cf. Figure 2(b)]. There was only a slight change in G' and G'' at higher loading (40 wt%) of the THVs. Note that the small difference in between 10 and 40 wt% of THV220 is an interesting aspect which is an open issue whether there is a correlation between the modulus and dispersion of the particles. To contribute to this topic the first task is, however, to assess the dispersion by a suitable mathematical description. There is a clear observation from the experimental results that the molecular weight of the fluorthermoplastics is having a major role in controlling the blend properties. According to literature[15] for the higher shear modulus of the confined melt is believed to arise from high

Table I. Combinations of THV500 and THV200

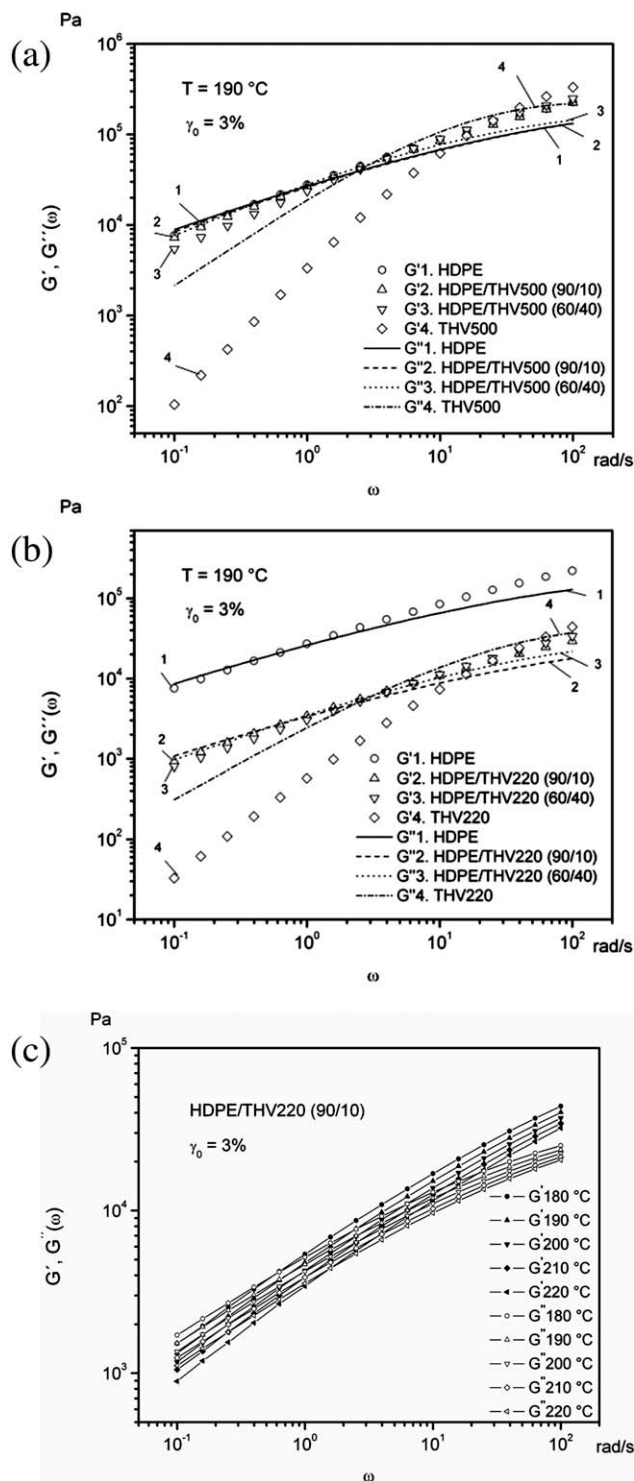| Monomer	Structural formula	THV 500 fraction (%)	THV 220 fraction (%)
Tetrafluoroethylene	[CF$_2$—CF$_2$]$_m$	55.5	40
Hexafluoropropylene	[C$_2$F$_4$—CF$_2$]$_n$	12	10
Vinylidene fluoride	[CH$_2$—CF$_2$]$_o$	32.5	50

Figure 2. G' and G'' vs. ω traces at 190°C for the HDPE/THV500 (a), HDPE/THV220 (b) blends and effect of temperature for HDPE/THV220 (90/10) blend (c).

G'' for the HDPE/THV220 blend. The G' and G'' of the blend was decreased with increase in temperature, as expected.

Studies on crossover frequencies between storage and loss modulus of blends and composites are extremely important to understand the transition from a liquid-like to a solid-like behavior. Figure 3(a,b) depicts the crossover as function of frequency for HDPE/THV500 and HDPE/THV220 blends, respectively. It can be seen that the transition of pure HDPE from liquid to a solid-like behavior occurs at crossover frequency of apparently 0.8 s^{-1}. The crossover for the fluorothermoplastic blends was shifted toward a higher frequency with increasing fluorothermoplastic content. Note that the transition dependence of shear rate is increasing remarkably at blends containing higher molecular weight THV500 due to the increase in entanglement among the macromolecular chains.

Figure 4(a,b) depicts the master curves of the storage and loss modulus at the reference temperature of 200°C. The time temperature superposition principle (TTS) on frequency sweep data obtained at temperature varying from 180 to 220°C. The shift factors were determined for each curve using the related software package (Rheology Advantage Data Analysis). The shift

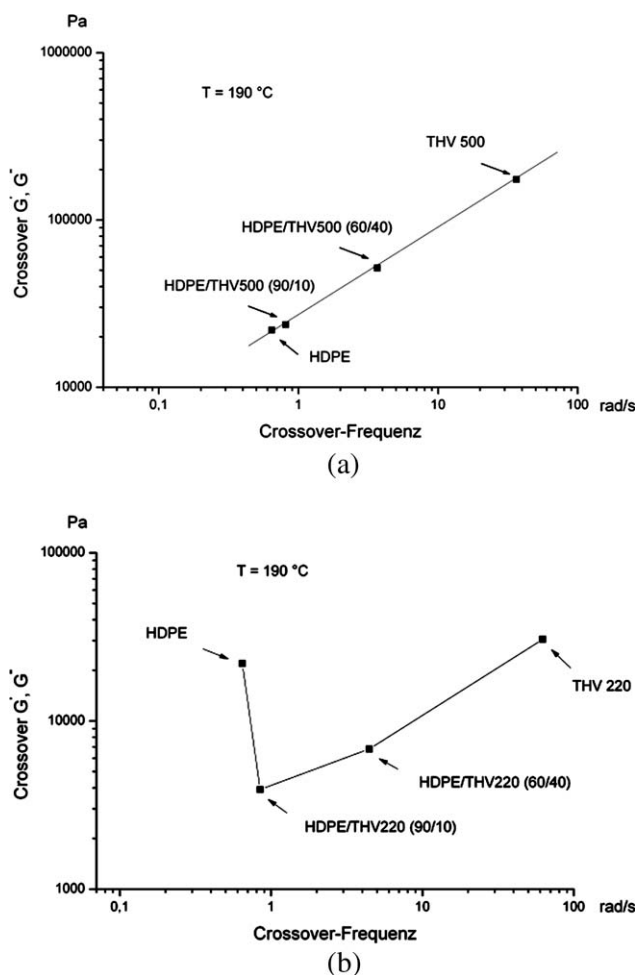**Figure 3.** Crossover frequencies between storage and loss modulus of HDPE/THV500 (a) and HDPE/THV220 (b) blends at $T = 190$°C.

molecular weight of polymer chain. This indicates that the effect of modulus is realized strongly on the HDPE blend systems with high molecular weight of fluorothermoplastic. Figure 2(c) demonstrate the effect of increase in temperature on the G' and
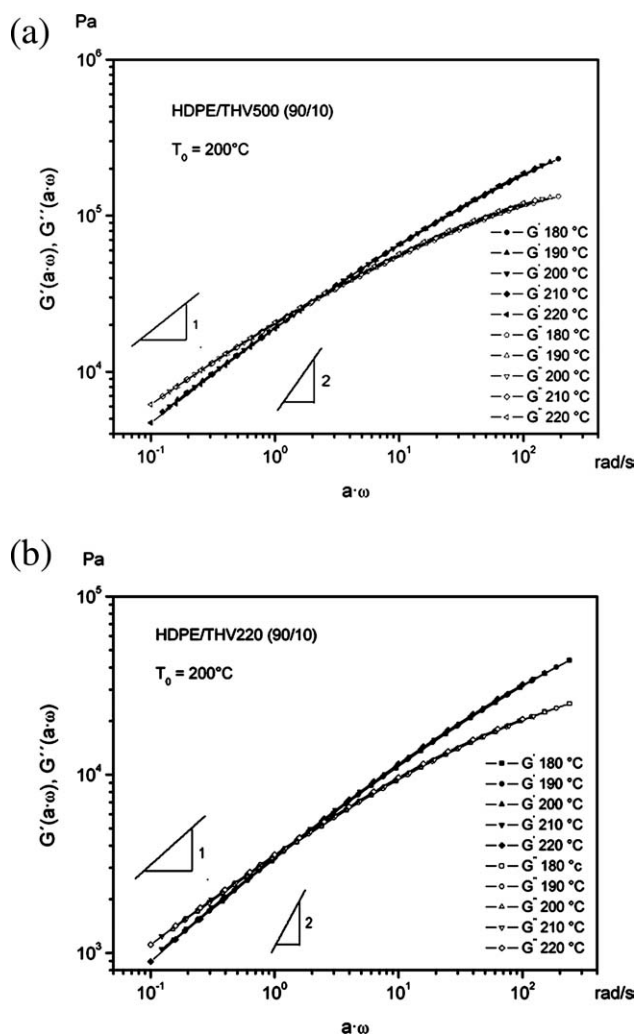
Figure 4. Master curves (storage and loss modulus versus frequencies) constructed by considering $T_{ref} = 200°C$ for HDPE/THV500 (90/10) blend (a) and HDPE/THV220 (90/10) blend (b).

factor as a function of temperature calculated from Arrhenius equation was found to adequately describe the experimental data.

$$\ln a_T = \frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \qquad (2)$$

where ΔH is the activation energy, R is the universal gas constant, T is the given temperature and T_0 is reference temperature, respectively.

One can see in Figure 4, that this superposition fits very well to the storage modulus data for all blend systems. It is noted that

the selected temperature of 200°C seems to be high enough for residual crystals to completely melt. Results of the calculated ΔH are given in Table II. The flow activation energy of HDPE/THV220 (90/10) blend was derived by Arrhenius type and equal to 37 KJ/mol. This is higher than the value of HDPE/THV500 (90/10) blend within 29 KJ/mol. The increase in flow activation energy with THV220 blend suggests that the relaxation of the fluorothermoplastic blends–chains was reduced, which again indicates the molecular weight dependency.

In general, the dynamic modulus of material can be predicted by parsimonious model.[16] The dynamic modulus of a discrete relaxation spectrum proved to hold for many polymers; therefore, their applicability has checked in this work. The experimental data was analyzed by a discrete form in terms of Maxwell modes. Accordingly, for the mathematical representation of the dynamic modulus for the generalized Maxwell model is given by the following equation:

$$G'(\omega) = \sum_{i=1}^{N} g_i \frac{(\omega\lambda_i)^2}{1 + (\omega\lambda_i)^2} \qquad (3)$$

where λ_i is i-th relaxation time, g_i is the i-th relaxation strength, and N is the number of Maxwell modes.

To achieve a more complete picture, and thereby a better understanding of the way this parsimonious model can represent a blend of high density polyethylene, it will be essential to evaluate a range of fluorothermoplastic blends with widely differing molecular weight combinations. The related curves, viz. storage modulus as a function of frequency, selecting the temperature of 190°C are depicted in Figure 5(a,b). It is clear from this figure that the best overall theoretical fit to the experimental $G'(\omega)$ data is achieved with the simplified generalized Maxwell rule, which is specific to these HDPE/THV220 blends. The relatively low molecular weight of THV220 allows it to relax largely by fluctuation in an entangled path length, and therefore the contribution to cooperative relaxation within HDPE blend is simplified.

For the theory of viscosity (η) under applied shear rate ($\dot{\gamma}$), the material response is given by:

$$\eta = \frac{\tau}{\dot{\gamma}} \qquad (4)$$

where τ is the shear stress.

The Cox-Merz principle is a widely used tool to fit the experimental data for a given property as a function of shear rate or time-related quantities like frequency. For the resulting complex viscosity vs. shear rate curves we have the adapted the Cox-Merz model.

Table II. Results of the Calculated Activation Energy of the Systems Studied

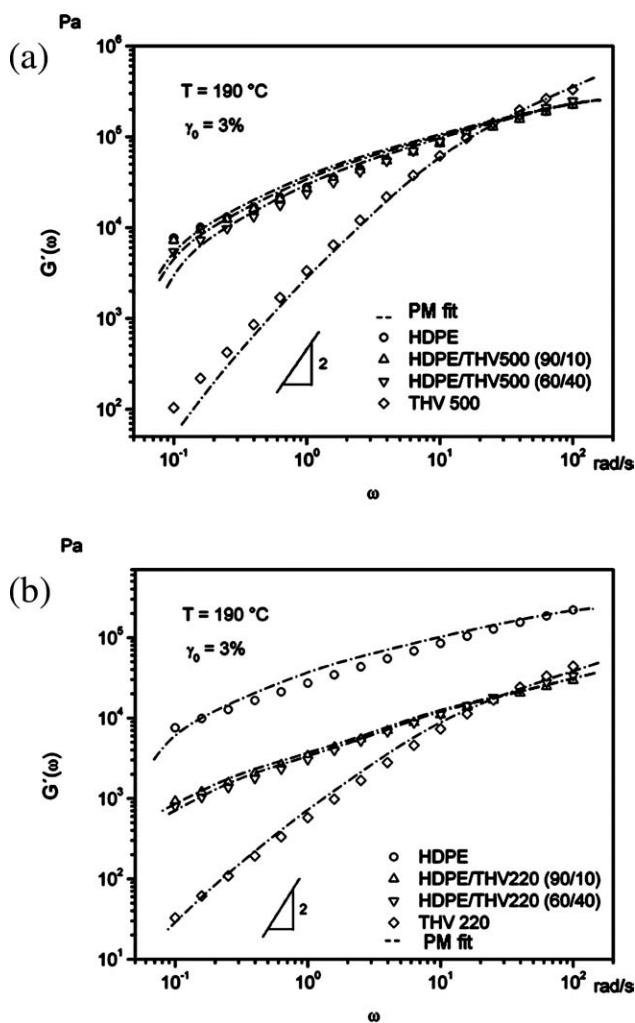| Materials	HDPE	Blend 90/10 (THV220)	Blend 60/40 (THV220)	THV220
ΔH (kJ/mol)	27	37	41	47
		Blend 90/10 (THV500)	Blend 60/40 (THV500)	THV500
		29	36	51

Figure 5. Storage modulus versus frequencies at $T = 190°C$ and their fitting by the parsimonious equation for HDPE/THV500 blends (a) and HDPE/THV220 blends (b).

$$|\eta^*| = \frac{G''}{\omega} \sqrt{1 + \left(\frac{G'}{G''}\right)^2} \quad for\ \omega = \dot{\gamma} \quad (5)$$

In many cases, the modified Cox-Merz rule has been determined that the polymers follow the same general behavior as when a factor is applied[17]:

$$|\eta^*|(\omega) = \eta(c\,\dot{\gamma})|_{\omega = c\dot{\gamma}} \quad (6)$$

where c is the shift factor.

Figure 6(a,b) displays the complex viscosity and simulated fits according to the modified Cox-Merz model for the HDPE/THV500 and HDPE/THV220 blends, respectively, at temperature of 190°C. The solid lines in each curve represents the calculated data using the modified Cox-Merz model. It can be seen from both figures that the viscosity curves of neat THV500 and THV220 exhibited a Newtonian behavior of essentially constant viscosity at the low frequencies since zero-shear viscosity

of HDPE was observed at this temperature. The slope of shear viscosity at high frequency increases with addition of THV500. The modified Cox-Merz fit are also plotted in Figure 6(a,b). It can be seen that it describes well all the experimental data of HDPE, THV500, THV200, and blend systems. The viscosity of HDPE/THV500 blend is always higher than that of HDPE/THV220 blend. SEM was used to compare the blend morphology between HDPE/THV500 and HDPE/THV220 blends [cf. Figure 7(a,b), respectively]. Note that the mechanism of deformation in extruder followed by break-up is an effective way of dispersing two polymers. A homogenous distribution of THV500 and THV220 particles was achieved on the fracture surface as shown in Figure 7(a,b). It can be also observed that the THV220 particles are mostly smaller dispersed in HDPE matrix compared to incorporation of THV500 [cf. Figure 7(c)]. The increase in viscosity at higher molecular weight THV500 can be explained by considering the large particles. As molecular weight increased the viscosity also increased and the particles of larger size may be formed. This viscosity of the continuous
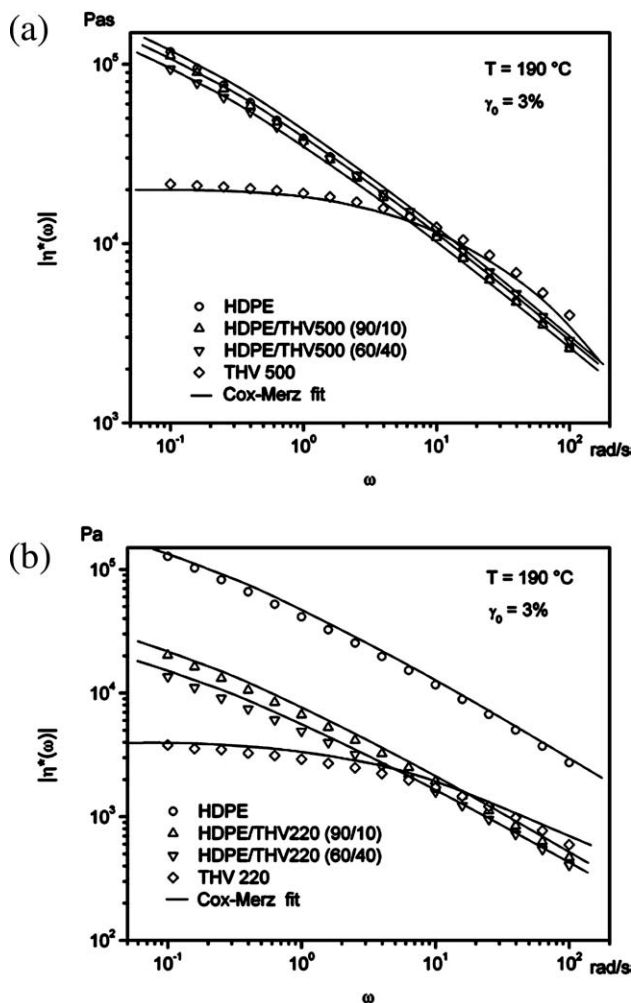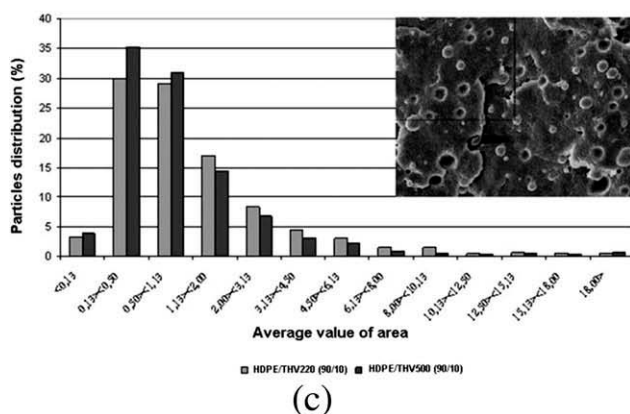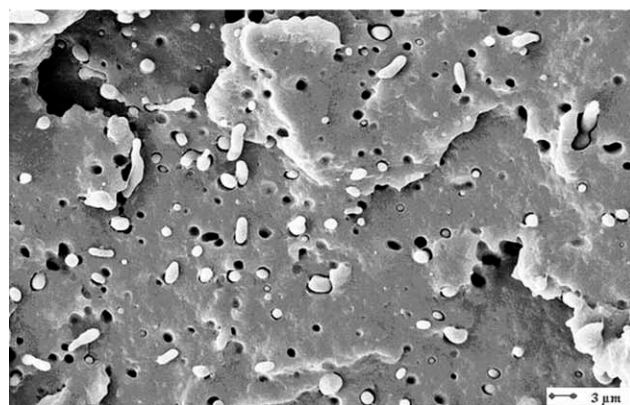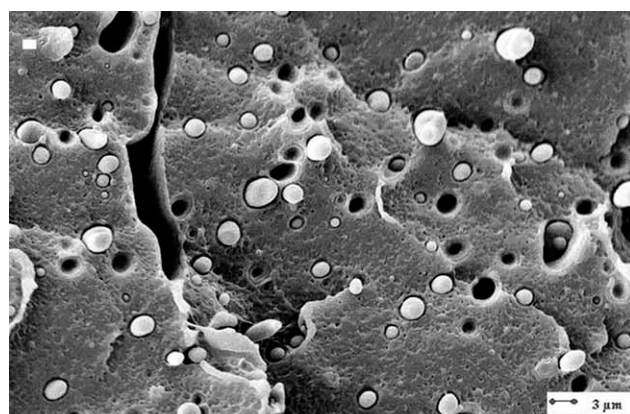

Figure 6. Viscosity versus frequencies at $T = 190°C$ and their fitting by the modified Cox-Merz rule for HDPE/THV500 blends (a) and HDPE/THV220 blends (b).

phase increase making the drainage of the blends separating two droplets more difficult. A similar trend has been reported for PP/EPDM blends that the size of EPDM dispersed phase in these blends can be related to its melt viscosity.[18]

DSC is an important method to study the crystallization behavior of polymer blends. Figure 8(a) shows the degree of crystallinity (X_c) of HDPE/THV500 and HDPE/THV220 blends. The crystallinity (X_c) of HDPE was about 78%. The THV500 and THV220 present in the matrix altered the degree of perfection

(a)

(b)

(c)

Figure 7. SEM picture taken HDPE/THV500 (90/10) blend (a), HDPE/THV220 (90/10) blend (b) and particle distribution of blends (c).

(a)

(b)

Figure 8. Degree of crystallinity (a) and melting characteristics (b) of the systems studied.

of HDPE crystals resulted in a close to linear decrease of X_c. However, it does not much influence on molecular weight. There is only a marginal effect on the overall melting temperature of HDPE in the related blend systems [cf. Figure 8(b)]. It was also justified that the temperature range selected for rheology experiments was acceptable, since there is no residual crystallinity observed at the selected temperatures, as evident from the DSC plots.

CONCLUSIONS

HDPE blends with two types of fluorothermoplastics (THV500 and THV220) were prepared and their rheological characterization has been carried out. The SEM results have shown that THV220 particles are well dispersed in HDPE matrix compared to that of THV500. The storage modulus and viscosity of the HDPE/THV500 blend was higher than the HDPE/THV220 blend. The related rheology results exhibited a strong dependence on the defined molecular weight and particle size distribution of blend partners. Master curves in form of storage and

loss modulus vs. frequency, constructed by considering dynamic linear viscoelastic data, could be well described by the TTS principle. The flow activation energy of HDPE/THV220 blend was found to be higher than that of HDPE/THV500 (90/10) blend. Moreover, the results were also fitted by means of parsimonious and modified Cox-Merz models. The parsimonious model satisfactorily described the storage vs. frequency traces. The value of viscosity recovered from modified Cox-Merz law were close to experimentally data for all systems studied. THV blends had a marginal effect on the overall melting temperature of HDPE in the related systems according to DSC measurement and no clear trend in the molecular weight effect of THVs was found in the crystallization behavior.

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