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Characterization of Interdiffusion between PVDF and Stereoregular PMMA by Using ATR-FTIR Spectroscopy

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Summary: In this study we investigated the interdiffusion between PVDF and PMMA below the melting temperature of PVDF by ATR-FTIR spectroscopy. The influence of the stereoregularity of different PMMA samples was studied. The PMMA tacticity showed a significant influence on the kinetics of the diffusion. Syndiotactic PMMA diffuses faster than isotactic and atactic PMMA which can be explained from the difference of chains stiffness between the two stereoisomers.

Keywords: diffusion; dynamic; PMMA; PVDF; tacticity

Introduction

The problem of the polymer-polymer interfaces is crucial because it plays a critical role in many fields like welding, adhesion, coextrusion and polymers mixtures. The characterization of the interface is essential because it is in many applications the essential feature of the final material mechanical properties. Interdiffusion phenomenon is strongly connected to the formation of the interphases in polymers. Interdiffusion between polymers is closely related to temperature, chemical composition, compatibility between polymers, molecular weight, distribution of the molecular weight, chains orientation and polymers microstructure.

Three classes of diffusion behaviour have been distinguished : Case I or Fickian diffusion, Case II diffusion and non-Fickian or anomalous diffusion. Experimentally, the type of diffusion can be established by the observed time dependence, t^n, where n is a constant. Case I systems are characterized by an exponent $n=½$, Case II by $n=1$ and non-Fickian systems by n taking an intermediate value between ½ and 1.

Various therories have been proposed for the diffusion of polymer in melts. The most widely accepted theory is the model of reptation proposed by de Gennes[1] and Doi and Edwards[2]. The basis of reptation is the snakelike motion of a polymer chain along its own contour

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formed by the constraint of neighbouring chains. The reptation model identifies distinct regions, which exhibit characteristic power-law time dependencies with exponents (n) equal to ¼ and ½. Interdiffusion between many polymer couples has been studied for several years[3-6].

Many studies of Poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA) blends have been carried out from both scientific and technological view points[7-14].

Several studies have been carried out on blends of PVDF and isotactic-, syndiotactic and atactic-PMMAs. Roerdink and Challa[9] reported the influence of tacticity of PMMA on the compatibility with PVDF based on observations of glass transition temperature (T_g) and melting temperature (T_m) depressions. Riedl and Prud'homme[10] evaluated the thermodynamic interaction parameter (χ_{12}) for PVDF/PMMAs with different tacticity using T_m depression data[9]. Both studies suggest that blends of PVDF and isotactic-, syndiotactic- and atactic-PMMAs are miscible. The lower value of the interaction parameter observed for the PVDF/i-PMMA system seems to indicate that the interaction of PVDF segments with i-PMMA segments is stronger than that with a-PMMA and s-PMMA segments. However, the values of χ_{12} for PMMA/PVDF blends estimated from the equilibrium melting temperature (T°_m) depression increase in the order atactic, syndiotactic and isotactic[15]. The χ_{12} value (-0.02) of PVDF/iso-PMMA suggests that the mixing state of PVDF/i-PMMA in the melt is metastable[15] which differs from the previous results. This could be due to the fact that χ_{12} values obtained by melting temperature depression using the Nishi-Wang equation yield large errors compared to values obtained by other methods[16]. Sasaki and al. have studied miscibility of PVDF/PMMA blends by crystallization dynamics[17]. The tacticity difference between at-PMMA and s-PMMA used in their study was not so large, however, both blends showed different crystallization dynamics. These results indicate that a slight difference in tacticity influences the miscibility of the blends. In contrast with previously reported results, they conclued that PVDF/i-PMMA were immiscible.

Benedetti and al. [18] investigated PVDF/PMMA blends by FTIR microspectroscopy and DSC. On the basis of the major shift of the carbonyl band of i-PMMA in the mixtures, they have observed stronger interactions for PVDF/i-PMMA compared with PVDF/s-PMMA. Strong interaction of PVDF with stereoregular PMMA have also been reported by Roerdink and Challa by infra-red spectroscopy[19].

The purpose of this study is to investigate the molecular interdiffusion across a PMMA/PVDF interface by using FTIR-ATR spectroscopy. These two polymers are known to be miscible in the molten state[7] but actually interdiffusion between these two polymers has not been observed below the melting temperature of PVDF. This is not trivial since PVDF high cristallinity (about 60%) is a limiting factor for interdiffusion.

In this paper, the influence of tacticity of PMMA on interdiffusion process will be described, espcially concerning the composition of the interface, in order to compare it with classical PMMA/PVDF blends. Analysis of selected infrared specific absorption bands permitted the tracking of diffusion of both components.

Experimental

The infrared spectra were obtained on a Perkin Elmer spectrometer. Spectra were collected at a resolution of 4 cm^{-1} with 32 averaged scans. An electrically heated 6 reflections trough ATR cell bought from Specac LTD. was used. The cell can be heated up to 200°C. The temperature of the sample is measured with a thermocouple and regulated to ± 0.5°C with a Specac 3000 Series^{TM} RS232 controller. The internal reflection element crystal was made from zinc selenide (ZnSe), having a refractive index of 2.42. The angle of incidence was chosen as 45°C. The extinction coefficients [$\varepsilon_i(\mu m^{-1})$] of the PMMA C=O stretching mode at 1724 cm^{-1} and PVDF C-F bending mode at 1402 cm^{-1} were determined as the slopes of plots of absorbance against film thickness from the transmission spectra of a series of DMF or toluene-cast homopolymer films. Least squares slopes give ε_{PVDF}= 0.1562 μm^{-1} and ε_{PMMA}= 0.105 μm^{-1}.

Poly(metylmethacrylate) (PMMA) was supplied by Polymer Source, Inc.. The Poly(vinylidene fluoride) (PVDF) was provided by Solvay. The main characteristics and origin of the polymers used in this study are shown in table 1.

The thin film of PVDF was cast directly from solution onto the ATR crystal, in order to achieve a good contact between the polymer and the ATR crystal. Since PVDF was soluble in dimethylformamide (DMF), a small amount of PVDF was dissolved into DMF at a concentration of 4,5 gram per liter. The system was stirred for 2h at 100°C to ensure complete mixing. 1 mL of the solution was cast in the ATR cell and then the film was dried at 80°C under vacuum for 12 hours. The thickness of the PVDF film was typically on the order of 1 μm which corresponds to the penetration depth[22], *dp*, of the infrared ray for the carbonyl pic (1724 cm^{-1}). A thick film of PMMA of about 0.5 mm thick was pressed against the PVDF film under a pressure of 10 MPa.

Table 1. Main characteristics of polymers.

Polymer	Source	M_w (g.mol^{-1})	M_w/Mn	T_m (°C)	T_g (°C)
PVDF	Solvay	125000	1.2	174	-32
at-PMMA-76	Atofina	76000	2.08	-	100
at-PMMA-48,5	Polymer Source	48500	1.66	-	121
iso-PMMA-46	Polymer Source	46000	1.27	-	59
syn-PMMA-37,5	Polymer Source	37500	1.25	-	129

Results and Discussion

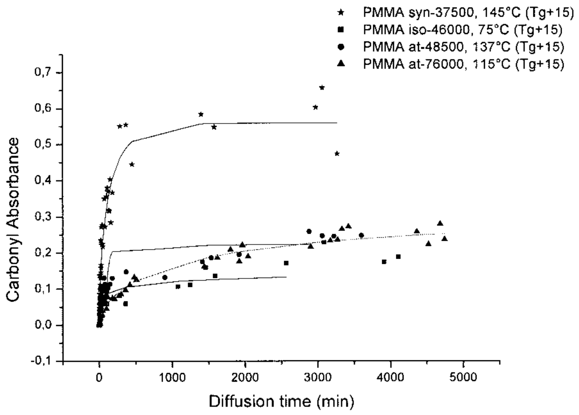

Figure 1. Plot of carbonyl absorbance versus diffusion time for PMMAs with different tacticities at T=Tg +15°C.

The evolution of the carbonyl absorbance with the diffusion time at T_{gPMMA}+15°C is shown in Figure 1. The ATR-FTIR measurements reveal a significant diffusion of PMMA in PVDF. Figure 1 shows that PMMA tacticity influences the diffusion. The absorbance of syndiotactic PMMA reaches 0.55 at the plateau at T_g+15°C (145°C) whereas absorbances of atactic and isotactic PMMAs are about 0.18. We assume that the chain mobility in the amorphous phase of PVDF is constant within the temperature range of 75°C to 145°C. T_g of PVDF is about –32°C so the difference of temperature between all the experiments is very low compared to the difference with the T_g of PVDF. Experiments were also carried out at T=T_{gPMMA}+20°C and we observe the same differences of diffusion with the tacticity as it is shown on Figure 2.

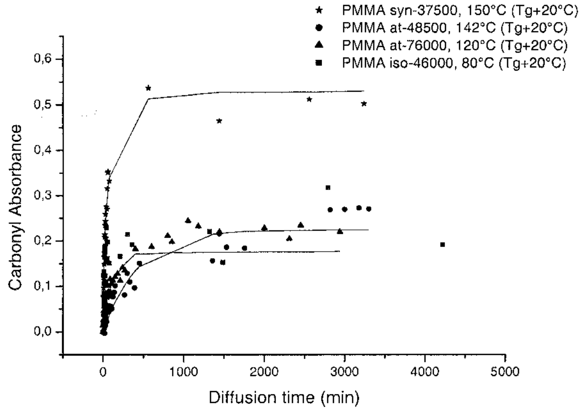

Figure 2. Plots of carbonyl absorbance versus diffusion time for PMMAs with different tacticities at T=Tg +20°C.

With ε_i in μm^{-1}, the measured apparent surface volume fraction of PMMA (ϕ_{PMMA}) within the sampling depth of the ATR technique is given by[21] :

$$\phi_{PMMA}=C_{PMMA}/(C_{PMMA}+C_{PVDF})\approx A_{PMMA}/(A_{PMMA}+\lambda A_{PVDF})$$

where $\lambda=dp_{PMMA}\varepsilon_{PMMA}/dp_{PVDF}\varepsilon_{PVDF}$. The respective depths of penetration are calculated according to Harrick[22] at 1724 cm^{-1} for PMMA and at 1402 cm^{-1} for PVDF. With $n_1=2.4$ and $n_2=1.42$ (the refractive index of PVDF), $dp_{PMMA}=0.993$ µm and $dp_{PVDF}=1.22$ µm. Values of ε_i were found a little higher than reported in the literature [21].

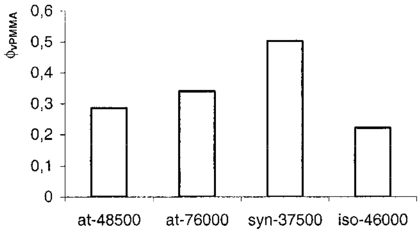

Figure 3. ϕ_v of PMMA in PMMA/PVDF interface after diffusion at $T=T_{gPMMA}+15°C$.

Figure 3 shows the evolution of the apparent surface volume fraction of PMMA in the measurement depth of the infrared evanescent beam. For syndiotactic PMMA, approximately 50% in volume of PMMA in the probed region is reached after two days of diffusion whereas only 30% is reached for atactic PMMA and 20% for isotactic PMMA. If we consider that the miscibility of the two polymers is the only parameter which influences the diffusion, these results would indicate that the interaction of syndiotactic PMMA segments with PVDF is stronger than the interaction with isotactic and atactic PMMAs. This is not in agreement with the literature data concerning the calculated Flory-Huggins interaction parameter[9]. High cristallinity of PVDF reduces considerably the mobility of the amorphous phase and the PMMA is only able to diffuse in 41% of the PVDF film. We can conclude from these results that the diffusion of PMMA chains in PVDF amorphous phase is more directly driven by dynamic phenomenons than by blend thermodynamics.

An important property that needs to be mentioned is the critical molecular weight for entanglements, M_c. Chain entanglement, a key concept in the dynamics of polymer chains in the melts, is affected by the polymer chain's flexibility. Chain entanglement, therefore, varies with chain tacticity in PMMA. In other words, M_e, hence M_c decreases with increasing syndiotacticity of the polymer samples. This reveals that PMMA actually has a range of M_c from about 11,650 for highly syndiotactic to about 40,000 for purely isotactic polymer[23]. Regarding these values, the reptation time of the isotactic chains might be lower than the one for syndiotactic chains which is obviously not the case[24]. Even though we consider the slight molecular weight difference of our samples, the reptation model is not consistent with the previous observations. Nevertheless, at the plateau where an equilibrium is reached, the large stiffness of isotactic PMMA[25] may also partially hinder its diffusion between the PVDF cristallites. The tortuous pathway of the amorphous regions of PVDF may prevent diffusion of stiff chains.

Conclusion

In this study, diffusion of PMMA chains in PVDF has been shown below the melting temperature of PVDF. Despite of the high cristallinity of PVDF, PMMA diffuses into amorphous phase of PVDF. The tacticity of PMMA has a significant influence on the diffusion which is not in agreement with the interaction parameters found in the literature. The stiffness of the PMMA chains is suggested to be relevant to the diffusion process. Further investigations are in progress to confirm the relevance of this parameter in polymer diffusion processes.

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