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Miscibility of C_{60}-end-capped poly(ethylene oxide) with poly(vinyl chloride)

X.D. Huang, S.H. Goh*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, Singapore 117543

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Abstract

The miscibility of blends of single [60]fullerene (C_{60})-end-capped poly(ethylene oxide) (FPEO) or double C_{60}-end-capped poly(ethylene oxide) (FPEOF) with poly(vinyl chloride) (PVC) has been studied. Similar to poly(ethylene oxide) (PEO), both FPEO and FPEOF are also miscible with PVC over the entire composition range. X-ray photoelectron spectroscopy showed the development of a new low-binding-energy Cl2p doublet and a new high-binding-energy O1s peak in FPEO/PVC blends. The results show that the miscibility between FPEO and PVC arises from hydrogen bonding interaction between the α-hydrogen of PVC and the ether oxygen of FPEO. From the melting point depression of PEO, FPEO or FPEOF in the blends, the Flory–Huggins interaction parameters were found to be −0.169, −0.142, −0.093 for PVC/PEO, PVC/FPEO and PVC/FPEOF, respectively, demonstrating that all the three blend systems are miscible in the melt. However, the incorporation of C_{60} slightly impairs the interaction between PEO and PVC.

Keywords: Poly(ethylene oxide); Poly(vinyl chloride); Miscibility

1. Introduction

The fabrication of [60]fullerene (C_{60}) devices with interesting physical properties has been limited by its poor processability. Thus, from the time of its discovery, a vast amount of research has focused on the challenge to render C_{60} into tractable forms by, for example, covalently bonding it to tractable polymer chains. The C_{60} molecule can be introduced into the main chain of an organic polymer to form a 'pearl necklace' polymer, in which the C_{60} unit is part of the polymer chain, or into the side chain of a polymer as a pendant group to form a 'charm bracelet' polymer [1–3]. However, it can be difficult to incorporate C_{60} into some polymers. Blending of polymers provides a convenient way to develop new polymeric materials, which combine the desired properties of two polymers. The blending process is much less time-consuming than the conventional process of development of new monomers and their polymerization. Therefore, the use of C_{60}-containing polymers as blend components provides a simple means to impart their attractive properties to many other polymers.

Recently, we have synthesized single C_{60}-end-capped poly(ethylene oxide) (FPEO) and double C_{60}-end-capped poly(ethylene oxide) (FPEOF) by the cycloaddition reaction of azido-terminated poly(ethylene oxide) (PEO) with C_{60} [4,5]. Monoaddition of PEO to C_{60} has been demonstrated by various techniques. Both FPEO and FPEOF readily dissolve in various solvents that can dissolve PEO. PEO can be considered as a proton-accepting polymer and it is miscible with some proton-donating polymers. We have reported that the incorporation of C_{60} at the chain ends of PEO produces a significant hydrophobic effect on its complexation with poly(methacrylic acid) [5]. The miscibility of FPEO with poly(*p*-vinylphenol) was also studied [4]. Poly(vinyl chloride) (PVC) is a weak proton-donating polymer; its α-hydrogen atoms can form hydrogen-bonding with proton-accepting polymers, such as PEO. Moreover, PVC has attracted interest as a component in polymer blends due to its miscibility with other important polymers [6–8]. In this communication, we report the miscibility behavior of PVC with FPEO as well as FPEOF.

2. Experimental

2.1. Materials and samples

C_{60} (99.9% pure) was obtained from Peking University, China. Poly(ethylene glycol) monomethyl ether was obtained from Aldrich; its number-average molecular

* Corresponding author. Tel.: +65-874-2844; fax: +65-779-1691.
E-mail address: chmgohsh@nus.edu.sg (S.H. Goh).

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weight (M_n) and polydispersity are 2200 and 1.07, respectively. The synthesis of FPEO and FPEOF was reported earlier [4,5]. PVC (inherent viscosity = 1.02) was obtained from Aldrich.

All the blends were prepared by casting from 1% (w/v) THF solution. The solvent was allowed to slowly evaporate at room temperature, followed by drying in a vacuum desiccator for one week and then in a vacuum oven at 60 °C for another one week.

2.2. Differential scanning calorimetry measurements

Glass transition and nonisothermal crystallization measurements were carried out on a TA Instruments 2920 Differential Scanning Calorimeter. The instrument was calibrated with an indium standard and a nitrogen atmosphere (flow rate = 50 ml/min) was used throughout. Samples were first heated to 150 °C and were kept at that temperature for 2 min. They were then cooled to −120 °C at a cooling rate of 10 °C/min. After being kept at −120 °C for 2 min, the samples were reheated to 150 °C at 20 °C/min. The glass transition temperature (T_g) values of various samples were taken from the second heating scan as the extrapolated onset point of the abrupt increase in DSC curve. The apparent melting temperature was obtained from the maximum of the melting endothermic peak. The degree of crystallinity was determined by comparing the heat of fusion of the sample to that of 100% crystallized PEO (203 J/g) [9]. A Perkin–Elmer Pyris 1 DSC was used to monitor isothermal crystallization. Approximately 6 mg of sample was first heated to 100 °C and maintained at that temperature for 5 min to erase thermal history. The sample was then quenched to a specific crystallization temperature T_c at a controlled cooling rate of 120 °C/min. The sample was kept at T_c for a sufficient period to allow complete crystallization. It was then heated to 100 °C at 20 °C/min to determine the melting temperature, T_m.

2.3. X-ray photoelectron spectroscopic measurements

X-ray photoelectron spectroscopic (XPS) measurements were made on a VG ESCALAB MkII spectrometer with a Mg Kα X-ray source (1253.6 eV photons) and a hemispherical energy analyzer. Samples were ground to fine powders and then mounted on standard sample studs by means of a double-sided adhesive. The X-ray source was run at 12 kV and 10 mA. Pass energy of 20 eV and a rate of 0.05 eV/step were used for all the high-resolution XPS spectra acquisition with a binding energy (BE) width of 12 eV. The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during measurements. All spectra were obtained at a takeoff angle of 75°. Each peak was curve-fitted using the XPSPEAK3.1 software; the error between the synthesized peak and the experimental signal was less than 5%. To compensate for surface charging effects, all binding energies were referenced to the saturated hydrocarbon C1s peak at 285.0 eV.

3. Results and discussion

3.1. Thermal analysis

PVC is a weak proton donor that offers potential for hydrogen-bonding interactions with proton-accepting polymers. The existence of hydrogen-bonding interaction between PVC and PEO was reported by several authors using inverse gas chromatography and ^{13}C NMR [10,11].

The existence of a single T_g is the most widely used criterion for miscibility. As shown in Fig. 1, each of the PVC/FPEO blends containing 50% or more of PVC was found to exhibit a single and composition-dependent T_g, showing that FPEO is miscible with PVC. The glass transitions of blends containing less than 50% of PVC were difficult to detect.

In addition to the single-T_g criterion, the depression of the melting point of the crystalline polymer is also an important characteristic demonstrating the miscibility of a semi-crystalline/amorphous polymer blend system. As shown in Fig. 1 and Table 1, the apparent melting points of FPEO in PVC/FPEO blends are depressed, confirming the miscibility of the blends. Blends containing 80 wt% or more PVC are amorphous.

For PVC/FPEOF blends, single and composition-dependent T_gs were detected for blends containing 10 and 80 wt% PVC as shown in Fig. 2. However, the T_gs of the other blends were difficult to determine with certainty. Nevertheless, the apparent melting temperatures of FPEOF are also depressed in the PVC/FPEOF blends, demonstrating the miscibility of the blend system.

The melting point depression of a semi-crystalline polymer in a miscible blend can be used to determine the Flory–Huggins interaction parameter, χ_{12}. In order to separate morphological and thermodynamic factors, the equilibrium melting temperatures (T_m^0s) were determined by applying the extrapolation method according to the Hoffman and

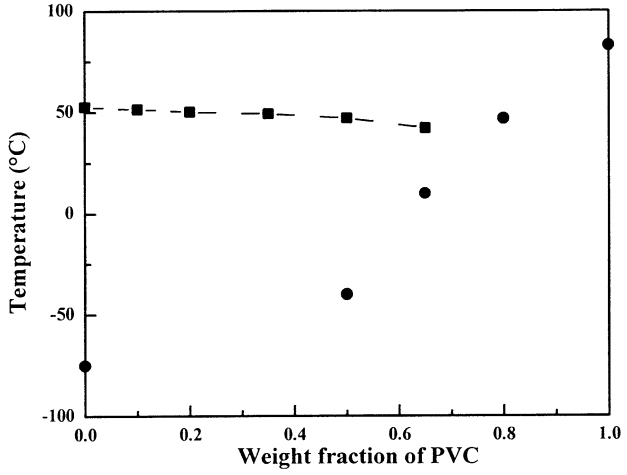

Fig. 1. Melting points (■) and glass transition temperatures (●) of PVC/FPEO blends.

Table 1
Characteristics of PVC/FPEO blends

	Blend number					
	1	2	3	4	5	6
Weight fraction of PVC in blends	0.10	0.20	0.35	0.50	0.65	0.80
Glass transition temperature (°C)	–	–	–	−40	10	47
Crystallization temperature (°C)	15.4	11.4	7.1	−9.3	–	–
Melting point (°C)	51.4	50.1	49.2	47.1	42.2	–
Degree of crystallinility	0.51	0.51	0.42	0.27	0.10	0
Weight fraction of PVC in surface	–	–	0.03	0.05	–	0.63
O1s of blends (eV)	–	–	532.8	532.8	–	532.8, 533.6
Fraction of high-BE O1s peak	–	–	0	0		0.13
$Cl2p_{3/2}$ of blends (eV)	–	–	200.1, 200.6	200.0, 200.6	–	200.1, 200.6
$Cl2p_{1/2}$ of blends (eV)	–	–	201.7, 202.2	201.6, 202.2	–	201.7, 202.2
Fraction of low-BE Cl2p doublet	–	–	0.44	0.19	–	0.08

Weeks method [12]. Fig. 3 shows the Hoffman–Weeks plots for FPEO and its blends with PVC. The T_m^0 is obtained by extrapolating the T_ms to the $T_m = T_c$ line. The determined equilibrium melting temperatures (T_m^0s) of all the samples are given in Table 2. The Flory–Huggins interaction parameter χ_{12} is determined using the Nishi–Wang equation [13]:

$$1/T^0_{m,bl} - 1/T^0_m = \frac{-RV_2}{\Delta H_u V_1}\chi_{12}\Phi_1^2 \quad (1)$$

where T_m^0 or $T^0_{m,bl}$ are equilibrium melting temperatures of the crystalline polymer in the pure state and in the blend, respectively, V_i is the molar volume of polymer repeating unit ($V_1 = 46.1$ cm^3/mol for PVC; $V_2 = 40.5$ cm^3/mol for PEO) Φ_1 is the volume fraction of PVC in the blend, and ΔH_u is the heat of fusion per mole of crystalline repeating units (8.9 kJ/mol for PEO) [9]. The application of Eq. (1) assumes that the entropic contributions are practically negligible and that χ_{12} is independent of the composition of the blend.

Plots of $(1/T^0_{m,bl} - 1/T^0_m)$ vs. $RV_2\Phi_1^2/\Delta H_u V_1$ of the three blend systems for compositions between 10 and 50% by weight of PVC are shown in Fig. 4. From the slopes of the lines, the χ_{12} values are −0.169, −0.141 and −0.093 for PVC/PEO, PVC/FPEO and PVC/FPEOF, respectively. The negative χ_{12} values show that PVC and PEO or C_{60}-containing PEOs are miscible in the melt. However, the incorporation of C_{60} at the chain end of PEO impairs the interaction between PEO and PVC as the χ_{12} values of the C_{60}-containing blends are less negative. The bulkiness of C_{60} is the most likely reason for the impairment of interaction between PVC and FPEO or FPEOF. The presence of C_{60} entities at the chain ends could have affected the close contact between the two dissimilar polymer chains. We have earlier studied the miscibility of C_{60}-containing polystyrene (PS-C_{60}) with poly(vinyl methyl ether) (PVME) [14]. PVME is miscible with PS-C_{60} containing 1.9 or 9.9 wt% C_{60}, but the lower critical solution temperature decreases with increasing C_{60} content of PS-C_{60}. PVME is

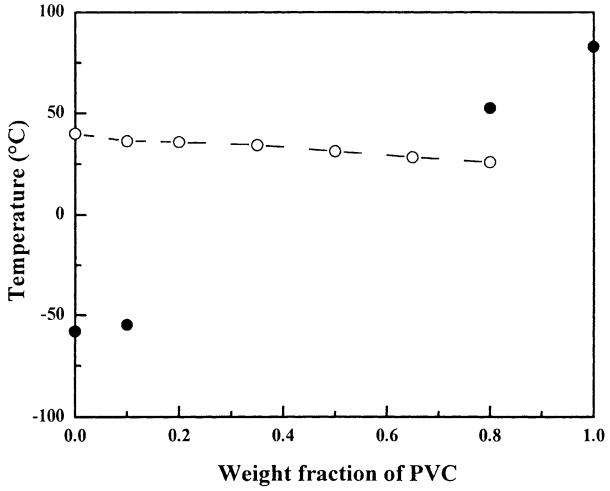

Fig. 2. Melting points (○) and glass transition temperature (●) of PVC/FPEOF blends.

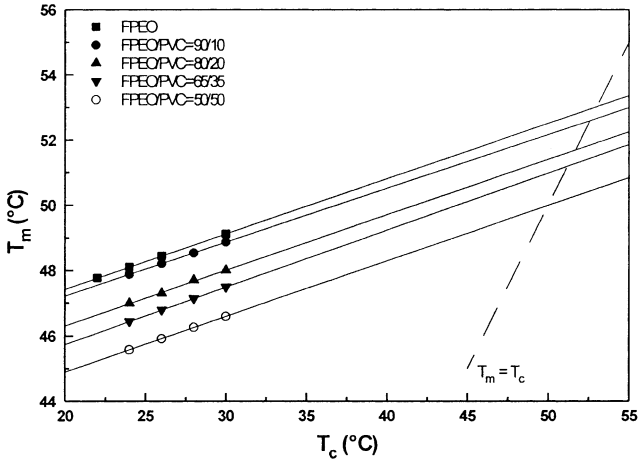

Fig. 3. Hoffman–Weeks plots for FPEO and its blends with PVC.

Table 2
Equilibrium melting temperatures for PVC/PEO, PVC/FPEO and PVC/FPEOF blends

PVC (wt%)	Equilibrium melting temperature (°C)		
	PVC/PEO	PVC/FPEO	PVC/FPEOF
0	54.6	53.0	43.4
10	54.2	52.6	43.0
20	53.5	51.7	42.7
35	53.1	51.2	42.2
50	51.2	50.0	41.5

immiscible with PS-C_{60} when the C_{60} content is further increased to 13.6 wt%. However, it should be noted that in aqueous solutions, C_{60} produces a significant hydrophobic effect which facilitates the complexation between poly(methacrylic acid) and FPEO or FPEOF [5].

3.2. X-ray photoelectron spectroscopic characterization

XPS has been used to study intermolecular interactions in polymer blends and complexes [15–22]. Since the BE of a core-level electron depends on its chemical environment within the molecule, the XPS spectrum provides information on the type and number of different species of a given atom in the molecules. Generally, the core-level BE increases as the electron density around the atom decreases. PVC/FPEO blends were chosen for the study of intermolecular interaction by XPS. The Cl2p spectra of PVC and PVC/FPEO blends are shown in Fig. 5. PVC exhibits a spin–orbit split doublet $Cl2p_{3/2}$ and $Cl2p_{1/2}$ at 200.6 and 202.2 eV, respectively. The Cl2p peaks in the blends are slightly broader and cannot be curve-fitted by the original doublet with unchanged peak position and peak width. Instead, the Cl2p peaks of the blends can be fitted by two doublets with one doublet remaining in the original position and a new doublet in a low-BE region. The need of using two doublets for curve fitting is particularly obvious for the blend containing 65% FPEO (Fig. 5d). The development of low-BE doublet shows that the α-hydrogen of PVC is interacting with the ether oxygen of FPEO, and the chlorine atom becomes more electron-rich. The fraction of the PVC units that participate in the hydrogen bonding can be estimated from the peak areas of the two doublets and the results are given in Table 1. The results show that the fraction of interacting PVC units increases substantially with increasing FPEO content.

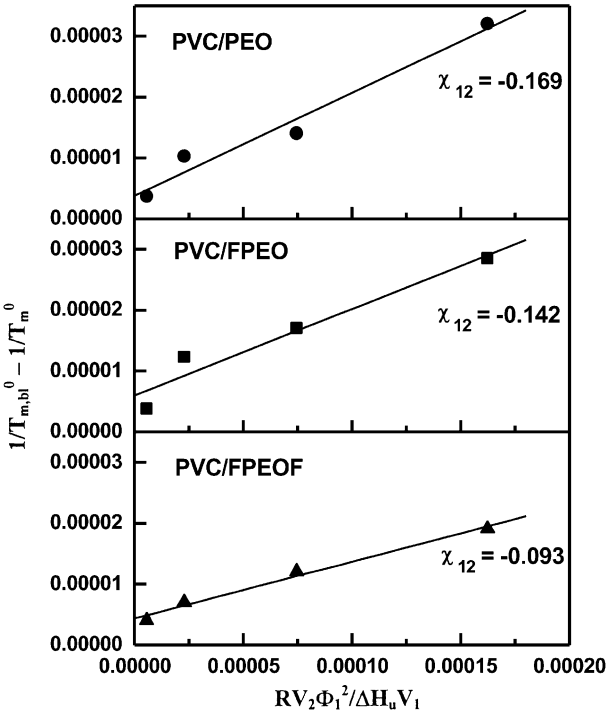

Fig. 4. Melting point depression plots of PVC/PEO, PVC/FPEO, PVC/FPEOF based on Nishi–Wang equation.

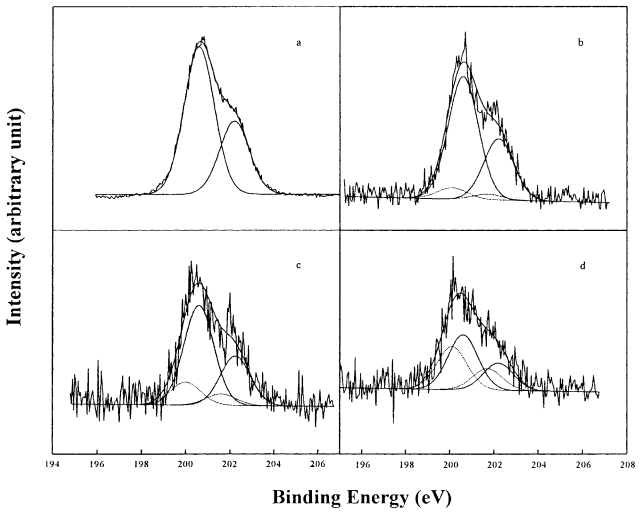

Fig. 5. Cl2p spectra of PVC (a) and PVC/FPEO blends: (b) 80/20; (c) 50/50; (d) 35/65.

From the XPS results, the surface composition of the blends can be estimated from the peak areas of O1s and Cl2p (Table 1). The PVC content of a PVC/FPEO blend in the surface region is always far lower than that in the bulk. The surface enrichment of FPEO shows that it has a much lower surface energy than PVC.

Fig. 6 shows the O1s spectra of FPEO and its blends with PVC. The O1s spectrum of FPEO features a symmetrical peak at 532.8 eV with a full width at half maximum (FWHM) of 1.6 eV. The O1s spectra of blends containing 35 and 50% PVC does not show distinct difference from that of FPEO, because the PVC content in the surface region is too low. However, the O1s spectrum of the blend containing 80% PVC is broader with an FWHM of 1.8 eV. The peak can be resolved into two different oxygen environments using a curve-fitting software with the FWHMs of both

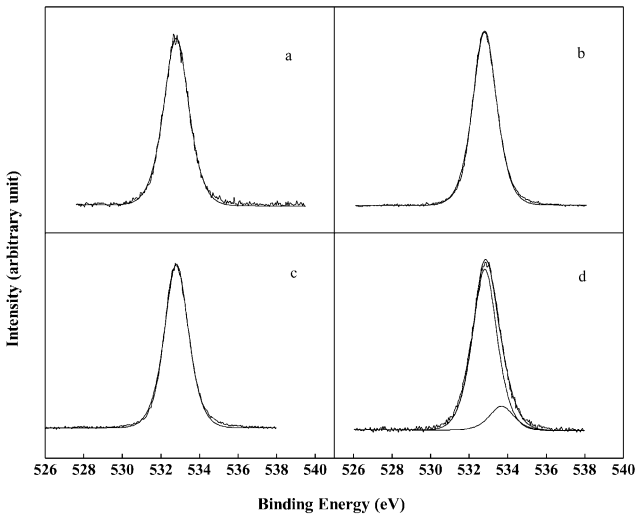

Fig. 6. O1s spectra of FPEO (a) and PVC/FPEO blends: (b) 35/65; (c) 50/50; (d) 80/20.

peaks fixed at 1.6 eV. The low-BE component is characteristic of the original ether oxygen in pure FPEO, and the high-BE component at around 533.6 eV is a result of hydrogen-bonding interaction with the α-hydrogen of PVC.

4. Conclusions

PEO is miscible with PVC. When one or both chain ends of PEO have been capped with C_{60}, the resulting polymers are still miscible with PVC. From the melting point depression results, the Flory–Huggins interaction parameters were found to be −0.169, −0.141, −0.093 for PVC/PEO, PVC/FPEO and PVC/FPEOF, respectively, demonstrating that the introduction of C_{60} slightly impairs the interaction between PVC and PEO. XPS studies showed the existence of specific interaction between the α-hydrogen of PVC and the ether oxygen of FPEO.

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