Polymer Bulletin 36, 79-86 (1996)

Polymer Bulletin

Studies on mechanism of phase transformation of carboxylated poly(phenylene oxide) and polystyrene blend by Fourier transform infrared spectrometry

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Received: 26 June 1995/Revised version: 29 August 1995/Accepted: 30 August 1995

Summary

The thermally-induced phase transformation behaviors of carboxylated poly(phenylene oxide)(CPPO)/polystyrene(PS), and PPO/PS blends were studied by using a difference-spectrum method of Fourier Transform Infrared Spectrometry (FTIR). The difference intensities(μ) and vibration frequency shifts($\Delta\upsilon$) of the characteristic infrared absorption bands in both CPPO/PS and PPO/PS increased with raising temperature. A linear temperature dependence in the band frequency vs. temperature plots was observed for PPO/PS system, while three slopes corresponding to the three temperature ranges: below 190°C, 190°-215°C, and above 220°C, appeared in frequency-temperature curves for the CPPO/PS blend. These temperature ranges are consistent with the UCST area, the miscible area and the LCST area obtained by our previous works. The mechanism of phase transformation of CPPO/PS was discussed.

Introduction

The blends of poly(2,6-dimethyl, 1,4-phenylene oxide)(PPO) and polystyrene(PS) were found to be the first miscible over the complete composition range (1-3) and successful commercial polymer alloy (4). The driving forces responsible for the miscibilities of this blend became a focus for the recent twenty years (5-9). It has been shown to have a negative excess volume of mixing relative to the pure components. This improved packing in the blend suggest that these two polymers must have the intermolecular interaction. The FTIR and UV studies indicate that is the Van der Waals interactions between the phenyl ring of PPO and those of PS (7), while NMR studies show that it is the methyl groups of PPO that interact with the phenyl group of PS (8,9).

In order to understand the factors responsible for the compatibility of polymer blends more deeply, PPO blended with PS-based copolymers, ionomers were widely investigated. The significant difference in miscibilities and phase behavior with their parent blend(PPO/PS) were observed (10-13), which were caused by the small amount of co-units attached to the PS chains. However, in the investigation of Carboxylated PPO(CPPO) and PS blend, we found that both UCST and LCST exist in the blends of

PS and CPPO with 8 to 10 mol% of carboxylation (14). The dynamics of phase separation processing of $C^{8.0}$PPO/PS blend was studied, where the coexistence of UCST and LCST behavior was further confirmed (15).

In this paper, difference-spectrum method in Fourier Transform Infrared(FTIR) technique is employed to monitor small variations of absorption intensities and vibrational frequency shifts of the characteristic IR bands in $C^{8.0}$PPO/PS and PPO/PS blends under the thermally induced condition. An attempt is made to understand the mechanism in molecular level for the specific phase behavior of $C^{8.0}$PPO/PS system.

Experimental

Materials

Atactic PS with $\overline{M_n}$=115,000 and $\overline{M_w}/\overline{M_n}$ less than 1.06 was used. It was obtained from Polymer Laboratories Ltd. PPO with $\overline{M_w}$=67,600 and $\overline{M_n}$=29,200 was used, which was received from Aldrich Chemical Co. CPPO with 8.0 mol% of carboxylation was prepared as previous report (16), and its samples are denoted as "$C^{8.0}$PPO". The blends of $C^{8.0}$PPO/PS and PPO/PS in 50/50 ratio were dissolved in chloroform then casted on a glass surface to form a film with definite thickness.

Measurement

Difference-spectrum studies were carried out on a IFS 112V FTIR Spectroscopy produced by Bruker Co. For all FTIR spectra, 128 scans were taken with a resolution of 2cm^{-1}.

Thermally Induced Procedure

The sample film was mounted to a hot-stage under vacuum and heated to 140 ℃, then annealed at 140℃ for 20 minutes. According to our previous research(14-15), the blend sample of $C^{8.0}$PPO/PS now is immiscible. In order to study how the FTIR band of the blend changed with temperature, we must detect the FTIR band of the blend at its equilibrium state of different tested temperature. When heating, the sample absorbed the heat, but needed a time to reach equilibrium state at tested temperature. It is obvious that we can't use higher rate of heating. During experiment, we used much slower heating rate(1 ℃ /min). The spectra of $C^{8.0}$PPO/PS and PPO/PS blends were taken every 5 degree with the hot stage temperature increasing at a rate of approximate 1°C/min over the 140°-250°C range. The difference-spectrum was obtained by the spectrum at testing temperature subtracted the spectrum at 140°.

Data-treating method of FTIR spectra

In IR spectroscopy, the characteristic band intensity change and vibration frequency shift provide information on possible specific interactions in polymer blend. As a tool for the discrimination of structural elements, the IR intensities are significantly more sensitive to small change in structure or bond environment than the IR frequencies are (17). Therefore, the intensity change of the characteristic band can be experimentally measured by difference-spectrum method. While the frequency shifts can not be directly measured because of the no enough sensitive resolution of IR spectroscopy.

In this study, we used a equation, that showed a relation between the variation of band intensities(μ) and vibration frequency shift($\Delta\upsilon$), for Lorentzian bands proposed by R. P. Wool (18), i.e. $\mu=[2.6(A/\Gamma)]\Delta\upsilon$ ....(1)

where, μ is peak to peak intensity difference.

A is the maximum intensity of each characteristic band.

Γ is the band halfwidth.

$\Delta\upsilon$ is the frequency shift.

A typical scheme about the relationship for the above parameters was shown in Fig. 1.

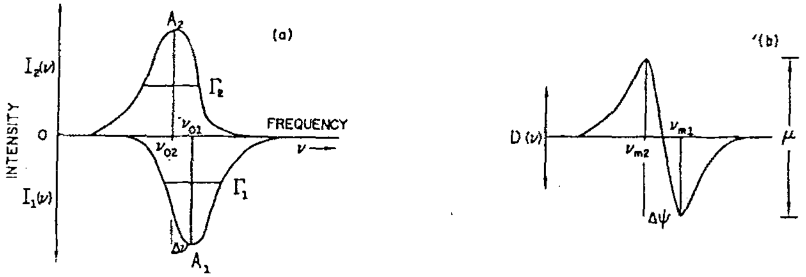
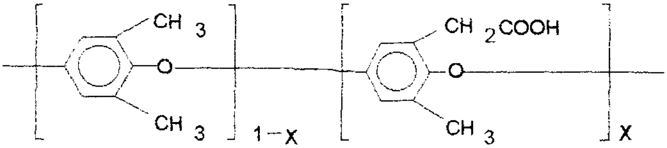


Fig. 1. (a) Frequency shift of infrared bands. (b) Typical resulting difference-spectrum intensity profile.

From equation (1), the small frequency shift ($\Delta\upsilon$) and their vibration frequency of each characteristic band can be accurately measured.

Results and discussions

Based on the ^{1}H NMR measurement, the carboxylated PPO has the following chain structure(16):



(C^x PPO)

As our previous studies, the blend of $C^{8.0}$PPO/PS is miscible when it is annealed at 190-210°C temperature range, while out of this annealing temperature ranges, the blend is immiscible (14). This particular phase behavior should be caused by the different temperature dependence of intermolecular interactions between the blend components. It could be expected to result in a regular variations in absorption intensities and vibrational frequencies of characteristic infrared absorption bands. In this paper, the temperature dependence of difference-spectrum of characteristic bands for phenylene ether bond(~1200cm^{-1}), phenylene ring band(~1600cm^{-1}) and aromatic -C-H- out of plane bending vibration band(~700cm^{-1}) in $C^{8.0}$PPO/PS blend were studied. For comparing with the typical miscible blend of PPO/PS, the mentioned above absorption bands in PPO/PS are also studied.

1. The variations of bands of phenylene ether bond with temperature in the 50/50 $C^{8.0}$PPO/PS and PPO/PS blends.

The difference spectrum intensities(μ), which were obtained by the spectra at testing temperature subtracted the spectra at 140°C, were shown in Fig.2.

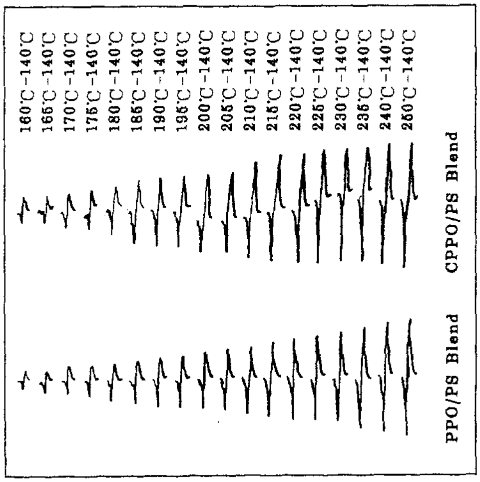


Fig.2. Difference-spectrum of phenylene ether bond IR band of $C^{8.0}$PPO/PS and PPO/PS blends.

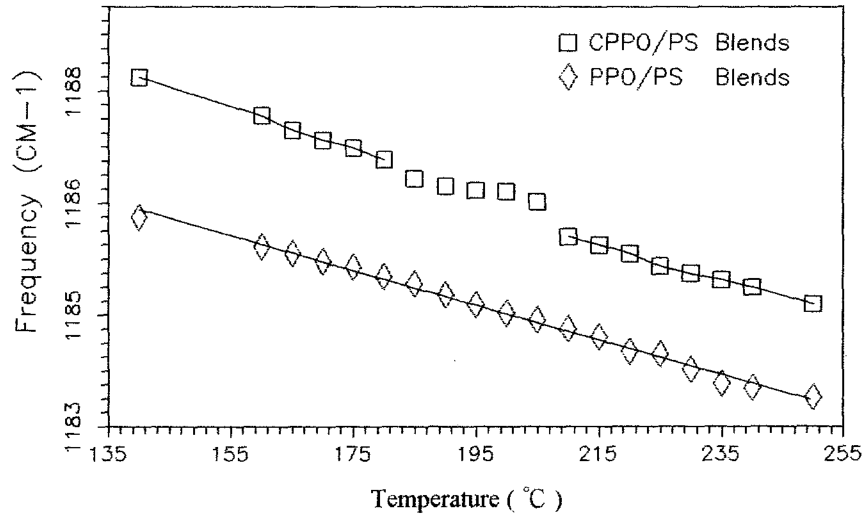


Fig.3. Effect of temp. on ether bond FTIR band of $C^{8.0}$PPO/PS and PPO/PS blends

Based on equation(1) and using the intensity difference μ, the vibrational frequency shifts($\Delta\upsilon$) and band frequency corresponding to the testing temperatures can be calculated, which were shown in Fig.3.

It is obvious that the peak-to peak intensity difference (μ) of phenylene ether bonds for both $C^{8.0}$PPO/PS and PPO/PS blends in Fig.2 increase with the raise of temperature. This is similar to those of many polymers in the stressed state (18). In comparing the difference-spectra of $C^{8.0}$PPO/PS and PPO/PS, the μ of phenylene ether bands of

PPO/PS blend are more monotonous increase with increasing temperature than those of $C^{8.0}$PPO/PS system.

We found in Fig.3, the curve of temperature vs. band frequency for $C^{8.0}$PPO/PS blend display three slopes corresponding to three temperature ranges, i.e., below 190°C, 190-215°C, and above 215°C. These are just consistent with the temperature ranges of UCST area, miscible area, and LCST area in phase diagram of $C^{8.0}$PPO/PS blend obtained by DSC and Light Scattering Measurements (14). Therefore, we can think that the slope changes of temp.-frequency(T-f) curve are responsible for the phase transformation of polymer blend. Nevertheless, a good linear line of T-f curve in PPO/PS blend indicated that no phase transformation happened in the whole studying temperature range.

It was noticed that the slope of band frequency curve in immiscible area of low temperature (below 190°C, UCST) is different from that in the immiscible area of high temperature (above 215°C, LCST). This may imply that the mechanism of phase separation in UCST is different from that in LCST. It will be discussed below.

In the miscible temperature range, 190-215°C, the band frequency shifts is somewhat random with temperature elevated and the extent of frequency shift become small. Because in this miscible area, the band of phenylene ether bond of $C^{8.0}$PPO/PS is affected by two molecular interactions, one is the chief interaction between blend components, the other is the interaction between $C^{8.0}$PPO moleculars. While in unmixing areas, the phenylene ether bond environment is quite simple, its spectrum is affected only by the interactions of aggregated $C^{8.0}$PPO molecules. Moreover, with temperature elevated, the molecular motion become stronger, which results in the spectrum band shift to lower frequency.

2. The variations of bands of phenylene ring (~1600cm^{-1}) and -C-H out of plane vibration band of phenylene ring (~700cm^{-1}) with temperature increasing.

According to the same treating procedure with those of phenylene ether bands described above, the temperature dependence of spectra of phenylene ring and C-H bands in $C^{8.0}$PPO/PS and PPO/PS blends were shown in Fig.4 and Fig.5, respectively.

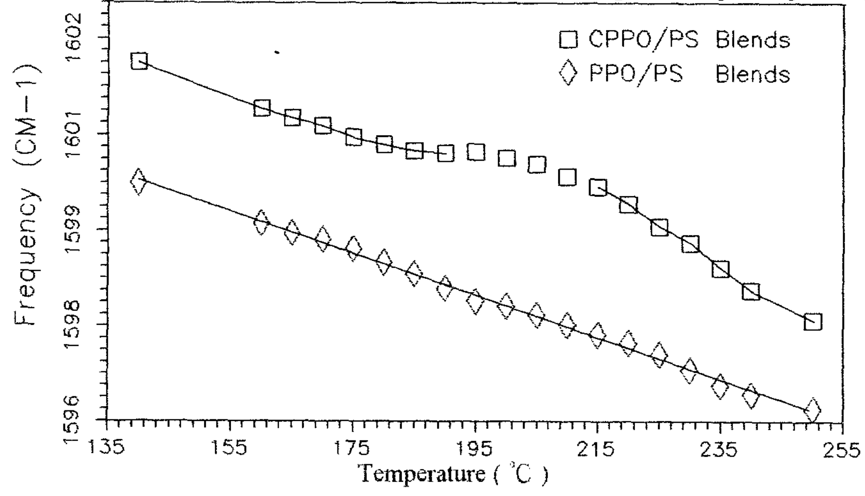


Fig.4. Effect of temp. on phenylene ring FTIR band of $C^{8.0}$PPO/PS and PPO/PS blends

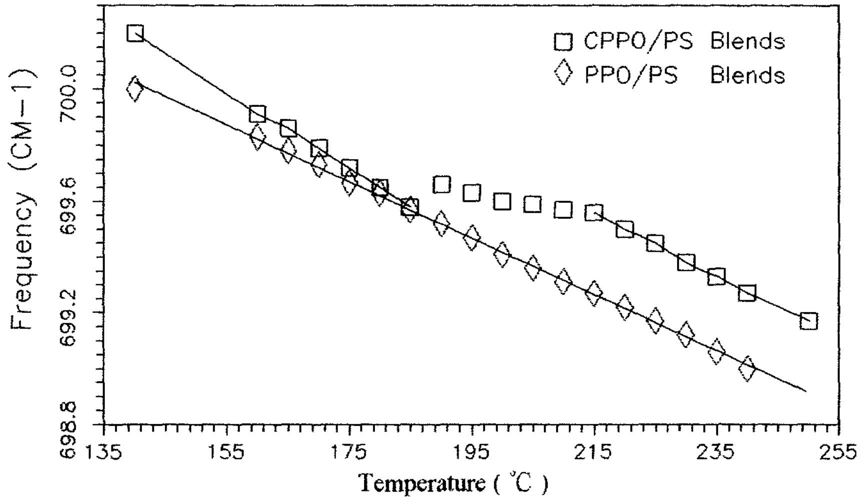


Fig.5. Effect of temp. on -CH- FTIR band of phenylene ring of $C^{8.0}$PPO/PS and PPO/PS blends

It is obvious that all the temperature dependence of vibrational frequencies of phenylene ring and C-H bands in $C^{8.0}$PPO/PS and PPO/PS blends are about the same tendencies with phenylene ether band discussed above. These gave further evidences that the variations of rate of frequency shifts were resulted from the phase transformation in $C^{8.0}$PPO/PS blend. In other words, these proved that the coexistence of UCST and LCST phase behavior existed in $C^{8.0}$PPO/PS blends.

3. The analysis of the mechanism of phase transformation for $C^{8.0}$PPO/PS blend.

The phase behavior of blends at constant pressure and temperature is governed by the Gibbs free energy of mixing ΔG_m. Only if ΔG_m is negative, the blend is miscible. According to the more recent theories of polymer mixing such as the equation of state(19) and co-workers(20) and the lattice-fluid theory(21), the Gibbs free energy of mixing contains three different contributions: the combinatorial entropy of mixing, the exchange interaction and a so-called free volume term. For high molar mass polymer, the combinatorial entropy of mixing in polymers becomes insignificant. So, ΔG_m is mainly governed by the exchange interaction and a so-called free volume term. The free volume contribution is always positive and increases as a function of temperature. So, only a specific interaction, resulting in a negative or positive exchange interaction, contribution to the free energy of polymer mixing, is usually said to be a prerequisite for the phase transformation of polymer pairs. By studying the IR characteristic bands of $C^{8.0}$PPO/PS blend, we found bands changed with temperature regularly, it means the interaction between two polymer molecules changed with temperature. In addition, the miscible mechanism of PPO/PS to be as an attractive project was studied in the world up to now. M.B.Djordjevic based on the NMR measurement suggested that the driving force responsible for the formation of miscible blend of PPO/PS is the π-hydrogen bond between the electrondeficient methyl groups in PPO and π-orbitals in PS (8). In comparison with this suggestion, we consider that the UCST behavior in carboxylated PPO and PS blend may be caused by that one hydrogen in methyl group was substituted for a carboxyl group, and result in a steric hindrance between the electrodeficient methyl groups in $C^{8.0}$PPO and π-orbitals in PS. With the energetic molecular motion by raising the temperature, the increase of collision probability among the residual $-CH_3$ and π-orbitals caused the miscible blend of $C^{8.0}$PPO and PS. For understanding the cause of LCST behavior, the $C^{8.0}$PPO/PS blend was annealed at higher temperature, the variations of -COOH IR absorption band(~1710cm^{-1}) depending on the temperature were measured as shown in Fig.6.

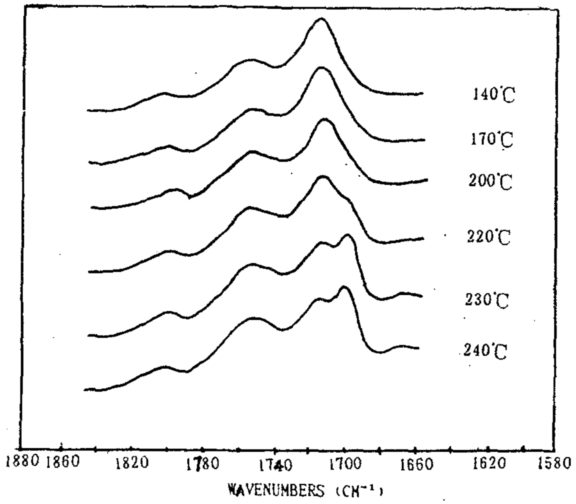


Fig.6. Annealing temp. dependence of carboxyl FTIR band of $C^{8.0}$PPO/PS blend

It is obvious that when the annealing temperature is higher than 210°C, a small band at 1696cm^{-1} was splitted out from the carboxyl band(1710cm^{-1}), and stronger with the temperature increasing.

The appearance of this new band could be attributed to the formation of carboxylic acid dimers. In addition, at high temperature, free volume change on mixing palys an important role for LCST phase behavior. Therefore, we can think that $C^{8.0}$PPO chains aggregated by the formation of carboxylic acid dimers and free volume change result in the LCST behavior for $C^{8.0}$PPO/PS blend.

Conclusion

The studies of FTIR on $C^{8.0}$PPO/PS blends confirmed the previous results that $C^{8.0}$PPO/PS blend coexist UCST and LCST, UCST area is below 190°C, LCST area is above 215°C.

In the miscible area, the characteristic FTIR bands of $C^{8.0}$PPO/PS blend, such as:

phenylene ether bond IR band(near 1200cm^{-1}); phenylene ring IR band(near 1600cm^{-1}), and -CH- group IR band of phenylene ring(near 700cm^{-1}), all shift to the higher frequency.

The phase transformation mechanism in UCST area is different from that in LCST area. In UCST area, the hydrogen in methyl group of $C^{8.0}$PPO/PS is replaced by a big carboxyl group, which change the electronegativity of the methyl and cause the steric hindrance between the unreplaced electrondeficient methyls in $C^{8.0}$PPO and phenylene ring of PS, weaken the interaction between the molecules of $C^{8.0}$PPO and PS, so the blend is immiscible. In LCST area, as the molecular motion is more violent, $C^{8.0}$PPO molecules in a high free motion state, the carboxyl groups in $C^{8.0}$PPO are easy to form the carboxylic acid dimer, which cause the aggregation of $C^{8.0}$PPO molecular chains, weaken the interaction between the molecules of $C^{8.0}$PPO and PS. In addition, at high temperature, free volume contribution to the Gibbs free energy of mixing become important and it is always positive, the phase is separated. In miscible area, the unreplaced methyl of $C^{8.0}$PPO and π orbitals of phenylene ring of PS can form the hydrogen bond, it make two polymers miscible.

The author is grateful to The National Key Projects for Fundamental Research "Macromolecular Condensed State", The State Science and Technology Commission of China.

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