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클로로포름용액 캐스팅으로 제조된 폴리메틸메타크릴레이트/폴리비닐아세테이트 블렌드의 상거동

이 원 기 · 하 창 식†
부산대학교 고분자공학과
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Phase Behavior of Chloroform Solution-cast Poly(methyl methacrylate)/Poly(vinyl acetate) Blends

Won-Ki Lee and Chang-Sik Ha†
Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea
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요 약: 클로로포름용액으로 캐스팅된 폴리메틸메타크릴레이트(PMMA)와 폴리비닐아세테이트(PVAc)블렌드의 상거동을 광산란장치, 시차주사열량계 등을 이용하여 조사하였다. 클로로포름용액으로 캐스팅된 PMMA와 PVAc 블렌드는 LCST 거동을 보였으며 PMMA와 PVAc의 상호작용에너지밀도(A, cal/cm^3)는 온도(T, Kelvin) 및 조성(Φ)에 대해 $A=-0.100304+0.00009\Phi+0.000299T$의 관계를 나타내었다. 50/50조성의 상용성블렌드를 임계상분리온도 이상으로 열처리한 뒤의 상분리거동도 연구하였다.

Abstract: The phase behavior of blend films of poly(methyl methacrylate)(PMMA) and poly(vinyl acetate)(PVAc) cast from chloroform has been investigated by light scattering, differential scanning calorimeter(DSC), scanning electron microscopy(SEM), and Fourier transform infrared(FTIR) spectroscopy. The PMMA/PVAc blend cast from chloroform exhibited lower critical solution temperature(LCST) behavior. The interaction energy density (A, cal/cm^3) between PMMA and PVAc, was given in the functional form, $A=-0.100304+0.00009\Phi+0.000299T$, where Φ is the volume fraction of PVAc and T is the temperature in Kelvin. The thermally induced phase separation behavior was also investigated at higher temperatures above the LCST of the blend at the 50/50 composition by weight.

Keywords: poly(methyl methacrylate), poly(vinyl acetate), blend, phase behavior.

INTRODUCTION

In last two decades, the miscibility of polymer blends has been one of the most important subjects in the polymer science.[1~4] Miscibility of polymer blends is often judged from specimens prepared by solution casting or melt mixing method. These two blend preparation approaches in most cases achieve an equilibrium state; however, an inappropriate choice of temperature of solvent may lead to erroneous judgement about miscibility. Particularly, the measured miscibility of the blend, when prepared by solvent casting, is strongly dependent upon the choice of solvent; A polymer blend exhibits clear film when cast from one solvent, but yields an opaque film when cast from another solvent. One of the extensive investigations to

detrmine the absolute miscibility is the blend of poly(methyl methacrylate)(PMMA) and poly (vinyl acetate)(PVAc) but much work using different solvents to obtain the blend films have reached different conclusions on the miscibility.[5,6]

Though many experimental techniques have been developed for the characterization of polymer miscibility, it is now recognized that the measured miscibility depends on the technique used.[7~10] For example, a polymer blend can be miscible using one specific method but phase-separated using another method[4~6] depending on the size of the phases and the resoluton limit of the applied technique.

In this work, the miscibility and thermally induced phase separation behavior of PMMA/PVAc blend have thus been carefully examined using several experimental techniques such as differential scanning calorimetry (DSC), coludpoint measurement, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy(SEM). For this work, the PMMA/PVAc blend films were cast from chloroform.

EXPERIMENTAL

Materials and Blend Preparations. PMMA having M_w =99,300 and M_w/M_n=1.53 was obtained from the Petroleum and Polymer Research Center of Lucky Co., Ltd. PVAc having M_w =78,800 and M_w/M_n=1.46 was purchased from Junsei Co. Chloroform was used after distillation.

Blend films containing PMMA and PVAc mixtures were dried slowly in a glass plate at room temperature and then kept in a vacuum oven at 60℃ until constant weight is reached. The thermally induced phase-separted PMMA/PVAc blends were prepared by heating the blend in a vacuum oven from room temperature to a given temperature(160, 170, and 190℃) at a rate of about 1℃/min, holding at the temperature for 10min, and then slowly cooling to room temperature. In this case, the blend composition was fixed at 50/50 by weight.

Cloud Point measurements. The blend films were cut into discs of 1.2cm diameter and put on a glass microscope slide. A cover glass was applied to protect the sample. The assembly was inserted horizontally into a rectangular aluminum block, heated with resistance wires wound around its surface. The cloud point measurement equipment include the light source, detector, recorder and heating system. A lower-power 2 mW He-Ne laser was used as the light source, and a photodiode(EG & GHAV-1000) with a sensitivity of 7×10^6 V/W at R_f =20MΩ for 6328Å wevelength) was used as the detector. All measurements were performed at 1.5℃/min.

T_g Measurements and FTIR Spectroscopy. The glass transition temperatures(T_g) of samples were measured with a Perkin-Elmer DSC 7 using a heating rate of 10℃/min. The T_g value was taken as the half-hight of the heat capacity jump. The measured T_g is the value based on the second run after heating to 120℃. FT-IR spectra were obtained using a Analect FX-6160 FTIR spectrophotometer. Sixty-four scans at a resolution of $2cm^{-1}$ were signal-averaged.

Morphology. The morphology of the blend films after cryogenic fracture was examined by SEM with a JEOL CSM-35CF SEM microscope. The films were coated with gold before installation in the SEM chamber.

RESULTS AND DISCUSSION

Optical Clarity and T_g Behavior. From the standpoints of optical clarity, the PMMA/PVAc blends cast from chloroform solutions showed miscibility over the whole composition range examined in this study at room temperature, since the PMMA/PVAc blends yielded clear films when cast from chloroform solutions over all the blend compositions at room temper-

ature. The chloroform cast blend showed one single T_g on DSC thermograms over the entire blend compositions. Fig. 1 shows the dependence of T_g of the chloroform cast PMMA/PVAc blends on the blend compositions. The solid line drawn in Fig. 1 was obtained from the Gordon-Taylor equaton (1) with parameter k. The figure shows that the Tg of the PMMA/PVAc blends observe the Gordon-Taylor equation very well and k is determined as 0.52 for the blends by nonlinear regressions.

$$T_g = \frac{W_{PVAc}\, T_{gPVAc} + k\, w_{PMMA}\, T_{gPMMA}}{w_{PVAc} + k\, w_{PMMA}} \quad (1)$$

where w_{PMMA} and w_{PVAc} are the weight fractions of PMMA and PVAc, respectively, and T_{gPMMA} and T_{gPVAc} are T_g of PMMA and PVAc, respectively. k is the ratio between the volume expansion coefficients of the homopolymers of the blend. The k value (0.52) obtained in this work may be thought reasonable, considering the volume expansion coefficient of PVAc ($6.7\times10^{-4}\ K^{-1}$) and that of PMMA in the range of $2.55\times10^{-4}\sim5.80\times10^{-4}\ K^{-1}$ depending on the T_g.[11]

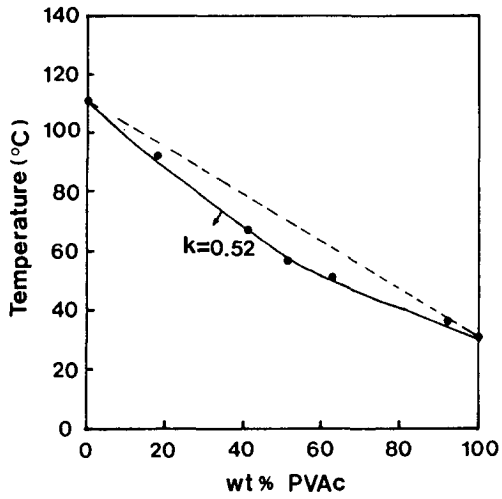

Fig. 1. Glass transition temperatures of the chloroform cast PMMA/PVAc blends as a function of PVAc compositions. The dotted line denotes simple additivity rule. The solid line shows that the dependence of T_g on the blend compositions observes the Gordon-Taylor equation with k equal to 0.52.

Phase Diagram. Fig. 2 shows a cloud point data as a function of PVAc composition. The chloroform cast blend showed typical lower critical solution temperature(LCST) behavior. The data were fitted by a binodal curve calculated on the basis of the Flory-Huggins free energy of mixing, given below, with Λ regarded as an adjustable parameter.[8]

$$\Delta G_M = RT\left[\left(\frac{1}{V_1}\right)\Phi_1 \ln \Phi_1 + \left(\frac{1}{V_2}\Phi_2 \ln \Phi_2\right)\right] + \Lambda\, \Phi_1\, \Phi_2 \quad (2)$$

where ΔG_M is the free energy per unit volume of the mixture, V_1 and V_2 are the molar volumes of polymer 1 and 2, and Φ_1 and Φ_2 are the volume fractions of the two polymers. The quantity Λ, denoting the polymer-polymer interation energy density, may depend moderately on both the temperature and the composition of the blend. We take the simplest functional form in-

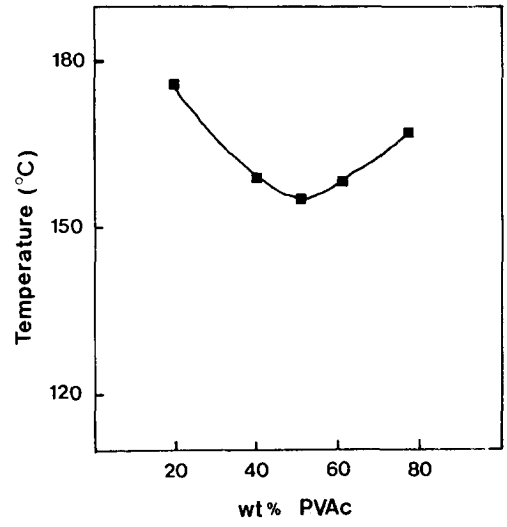

Fig. 2. Cloud-points for the PMMA/PVAc films cast from chloroform.

corporating these dependencies as

$$\Lambda = \lambda_0 + \lambda_1 \Phi_1 + \lambda_T T \quad (3)$$

The values of the constants λ_0, λ_1 and λ_T giving the best fit to experimentally determined cloud points were evaluated by the method of nonlinear least squares. The solid curve drawn for PMMA/PVAc data in Fig. 2 was calculated by equation (2) with the following Λ value:

$$\Lambda = -0.100304 + 0.00009\Phi + 0.000299T \quad (3)$$

where Λ is in cal/cm^3 , Φ is the volume fraction of PVAc, and T is in Kelvin. The equation (3) gives Λ=0.023 cal/cm^3 at 150℃ for 50/50 by weight PMMA/PVAc blend. Considering Λ= 0.011 cal/cm^3 for the well known miscible polystyrene(PS)/poly(vinyl methyl ether)(PVME) blend at the comparable temperature and composition,[12] the interaction between PMMA and PVAc is not so much strong as that between PS and PVME. The specific interaction between PS and PVME, giving rise to their miscibility, was reported to reside on the phenyl group of the styrene monomer and $COCH_3$ of PVME.[12~15]

No work has yet been reported on the exact nature of the intermolecular interaction between PMMA and PVAc. One of the difficulties comes from the similar molecular structure of PVAc and PMMA. It may be, however, thought that their electron donor/electron acceptor interaction is slightly different. PMMA behave either as a proton acceptor through the negative oxygen or as a proton donor owing to the influence of the positive carbon atoms of the carbonyl groups. The carbonyl carbons in PVAc, however, can be strongly positive and thus the methyl group on the side chains may act as a proton donor.[16] Thus, the molecular interaction between PMMA and PVAc may be presumably due to the interaction between proton donor and acceptor.

The Λ values can be utilized as a semiquantitative tool to estimate the interaction energy density between polymer pairs interaction not only through nonpolar forces but through other types of forces, such as polar or hydrogen bonding forces, as well.[8] It is interesting to note that the temperature coefficient λ_T of the interaction energy density Λ (λ_T/Λ, or more exactly, dln Λ /dT) is positive (0.013 for this work). Roe and Zin[8] applied the equation-of-state considerations to analyze the value of the polymer-polymer interaction energy density and its temperature dependence obtained in their work. They explained that the blends exhibiting a UCST behavior have a positive Λ value at low temperature, which in general decreases as the temperature is increased. Similarly, it may be assumed that blends exhibiting an LCST behavior have either a negative or a small positive Λ value at low temperature, which increases rapidly with increasing temperature. Thus, it is not surprising that the λ_T/Λ is positive for our miscible PMMA/PVAc systems.

Fig. 3 shows T_g behaviors for 50/50 by weight PMMA/PVAc blends after heating to various temperatures. It can be seen that the two separated T_gs of the blend shifts toward that of each component polymer when annealing temperature is above 170℃, being higher by about 15℃ than the LCST(The LCST for 50/50 by weight PMMA/PVAc blend was measured as 156℃, as shown in Fig. 2). The degree of shift in T_g can be utilized as an indirect measure of the degree of phase separation.

SEM Micrographs. The miscibility of the 50 /50 by weight PMMA/PVAc blend cast from choloroform is more clearly seen in SEM micrograph. Fig. 4(a) shows a typical SEM micrograph of the 50/50 by weight blend casting from chloroform. The chloroform cast blend showed very fine morphology implying miscible blend. The phase separation behavior of the initially miscible chloroform cast blends with different heat treatment temperatures are also

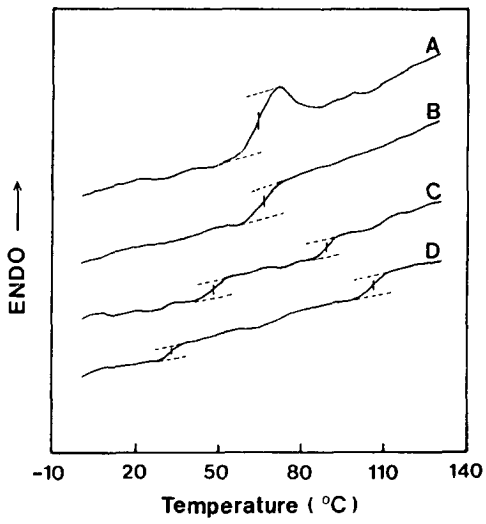

Fig. 3. DSC thermograms for 50/50 by weight PMMA/PVAc blends cast from chloroform solution after heating to various temperatures; A : as-cast, B : 160℃, C : 170℃, and D : 190℃.

seen in Fig. 4. The result is in accordance with the DSC thermograms shown in Fig. 3. Thus, the PVAc domain size of the thermally induced phase separated blend becomes larger as the heat treatment temperature increases. In this case, PMMA forms continous phase and PVAc consists of domain. It is more easily seen if one take the SEM micrographs of the blend after extraction with methanol which is a good solvent for PVAc only.

FT-IR spectroscopy has long been recognized as a powerful tool for the elucidation of structural information.[13~15,17,18] The position, intensity, and shape of vibrational bands are useful in clarifying conformational and environmental changes of polymers at the molecular level. When two polymers are completely miscible, there is a chemical interaction between the two different polymers. This interaction leads to a considerable difference between the spectrum of

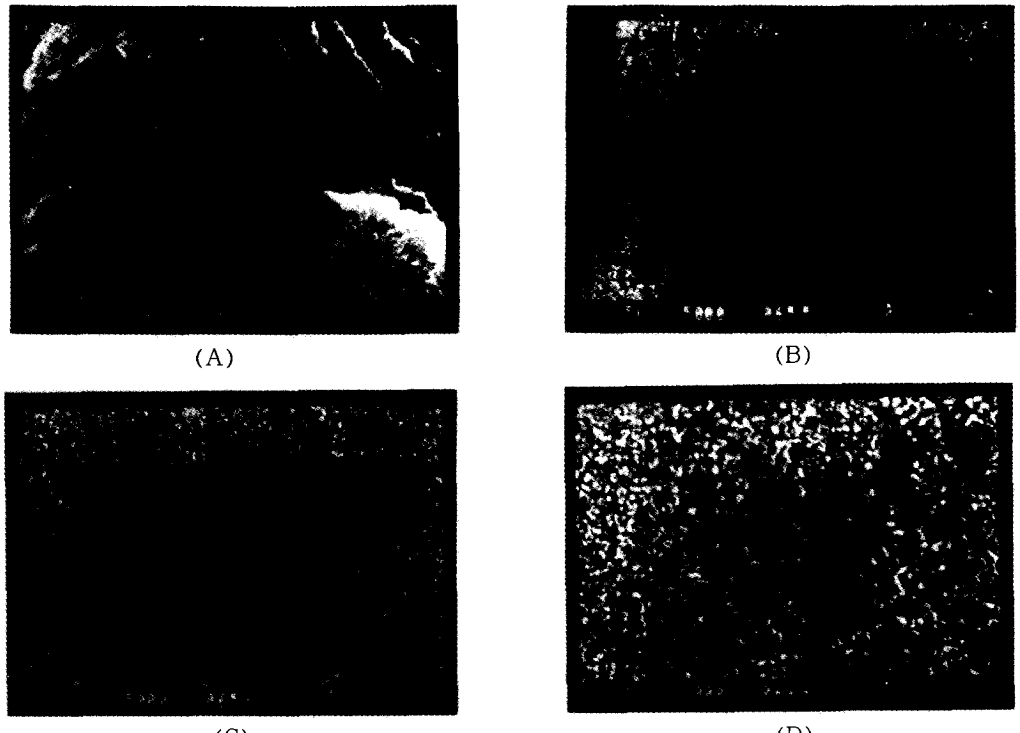

Fig. 4. SEM micrographs of chloroform cast films after heating to various temperatures; A:as-cast, B:160℃, C:170, and D:190℃.

the polymer in the blend and that of a pure component. This interaction leads to considerable difference between the spectrum of the polymer in the blend. Fig. 5 shows the FTIR spectra of the (a) as-cast 50/50 by weight blend and (b) 50/50 by weight blend after heated at 170℃. The frequency of the C-O band of PMMA was observed in a little different position for the as-cast blend, which showed miscibility based on the optical clarity and T_g behaviors.

The frequency shift of the peak due to the C-O band of PMMA around 1146.9cm^{-1} (Δ_ν=4.5cm^{-1}) for the as-cast miscible blend implies that there is a specific interaction between PMMA and PVAc, which is already discussed above. The small frequency shift, however, means that the intermolecular interaction is not strong. The frequency shift of the peak due to the C-O band of PMMA became smaller as Δ_ν =2.5cm^{-1} for the thermally induced phase separated blend by heating it at high temperature when compared to that of the as-cast blend. As a reference, Fig. 5 also shows the FTIR spectra of the (a) as-cast 50/50 by weight blend and (b) 50/50 by weight blend after heated at 170 ℃ before substracting the contribution of PVAc from that of the blend system.

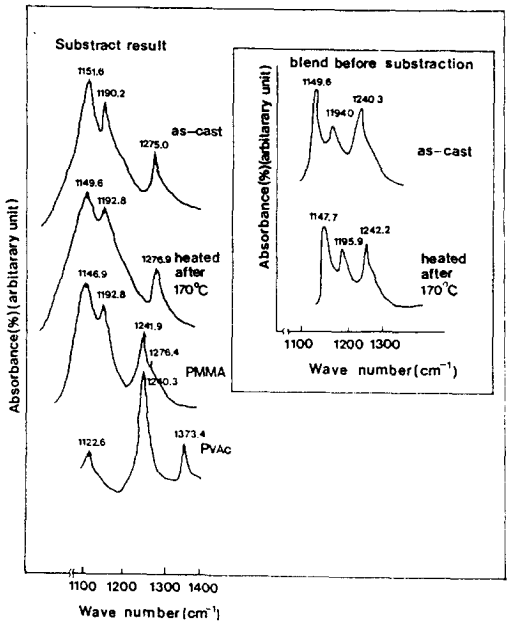

Fig. 5. FTIR spectra of the as-cast 50/50 by weight PMMA/PVAc blend and the blend after heated at 170℃ for 10 min. As a reference, the FTIR spectra of the same blends before substracting the contribution of PVAc from that of the blend system are also illustrated.

CONCLUSIONS

In this work, the PMMA/PVAc blends were found to be miscible and exhibited LCST behavior over the entire composition ranges when they are cast from chloroform. The miscibility of the blends was determined in terms of optical clarity, T_g behavior, SEM micorgraphs, and FTIR spectroscopy within the resolution limits ranging from ca. 10^{-3} to ca. 10^{-1} μm.[19] It was found that the interaction energy density(Λ, cal /cm^3) between PMMA and PVAc, was given in the functional form, Λ= -0.100304+0.00009 Φ +0.000299T, where Φ is the volume fraction of PVAc and T is the temperature in Kelvin. The FTIR spectral results showed that PMMA and PVAc had weak molecular interactions. When the 50/50 by weight PMMA/PVAc blend was annealed at higher temperature than the LCST, the thermally induced phase separation became larger as the annealing temperature increased.

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