Polymer Bulletin 29, 97–103 (1992)

Polymer Bulletin

Miscibility and lower critical solution temperature type phase behavior of poly(ethyl acrylate)/poly(vinylidene fluoride-co-hexafluoro acetone) blends

Yoshihisa Kano and Saburo Akiyama

Laboratory of Chemistry, Faculty of General Education, Tokyo University of Agriculture and Technology, 3-5-8, Saiwai-cho, Fuchu-shi, Tokyo 183, Japan

SUMMARY

The miscibility of mixtures of poly(ethyl acrylate) (PEA) with poly (vinylidene fluoride-co-hexafluoro acetone) (P(VDF-HFA)) was investigated with optical microscopy and differential scanning calorimetry (DSC). In PEA/P(VDF-HFA) blends with P(VDF-HFA) content of 50 and 70(wt%), the heterogeneous phase morphology was observed on optical micrographs at 210℃. It was found that PEA/P(VDF-HFA) blends showed the lower critical solution temperature type (LCST) phase behavior. The endothermic peak for PEA / P(VDF-HFA) blend observed on DSC thermogram near 200℃ corresponded to the liquid-liquid phase transition temperature as shown in the heterogeneous phase morphology with optical microscopy. It was expected that the endothermic peak is the transition temperature from miscibility to immiscibility.

INTRODUCTION

For the last decades, the polymer blend has been applied in the various fields (rubber, fiber, adhesives, medicine and electronic devices) and its miscibility has been elucidated with the statistical thermodynamics [1-3]. The polymer blend is very important to the pressure sensitive adhesive (PSA) industry. In general, polyacrylate is utilized as base polymer of adhesives and its PSA properties, such as tackiness, peel adhesion and holding power, are adjusted by blending of dissimilar polymer, copolymerization of polar monomer and physical crosslinking[4-6]. It is well known that the controlling of PSA properties are carried out with the dynamic mechanical properties, surface tension and surface morphology.

We[7] found that the blend of poly(ethyl acrylate) (PEA) with poly(vinylidene fluoride-co-hexafluoro acetone) [P(VDF-HFA)] can be used as the adhesive component and examined effects of morphology, surface tension and dynamic mechanical properties on PSA properties. Following results were obtained.

1)In PEA/P(VDF-HFA) blends with P(VDF-HFA) contents from 0 to 50(wt%), the PSA properties, such as tack, peel adhesion and holding power, were controlled by P(VDF-HFA) content.

2)In the PEA/P(VDF-HFA) blends, homogeneous morphology was observed by a scanning electron microscopic (SEM) study.

3)The critical surface tensions γ_c of PEA / P(VDF-HFA) blends were unchanged against P(VDF-HFA) content.

4)The PSA properties were influenced by dynamic mechanical properties, such as storage modulus G', loss modulus G" and glass transition temperature Tg.

Recently, it is reported that the blends of P(VDF-HFA) with poly(methyl methacrylate) (PMMA)[8], poly(ethylene-co-vinyl acetate)[9] exhibit lower critical solution temperature type (LCST) phase behavior.

In this study, the heterogeneous morphology and LCST phase behavior for PEA/P(VDF-HFA) blends were investigated with optical microscopic study and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

The poly(ethyl acrylate) (PEA) was prepared by solution polymerization method at 70℃ for 8h using benzoyl peroxide (0.5mol%) as initiator and ethyl acetate / toluene = 95 / 5 (wt%) as mixed solvent. The molecular weights of PEA is Mn=46700, Mw=312000 and Mw/Mn=6.7. The molecular weights of poly(vinylidene fluoride-co-hexafluoro acetone) [P(VDF-HFA)] (HFA content : 8.0(mol%)) supplied by Central Glass Co. Ltd., are Mn=52000, Mw=130000 and Mw/Mn=2.5. Molecular weights of the copolymers were detected using a Toso CP8000 GPC in 0.1(wt%) THF solution.

Measurements

The blends of PEA with P(VDF-HFA) dissolved in THF to form 10(wt%) solution, were prepared by casting onto cover glass or release liner. The specimens for microscopy and DSC were allowed to dry in a vacuum oven for more than 7days at 40~60℃, and then samples for the optical microscopy were annealed at 150℃ for 1h before observation, and the blend samples for DSC measurements were annealed at 150℃ for 2h and quenched in liquid N_2. The morphology of blend samples was observed by use of an Olympus optical microscopy BH-2. The morphology of PEA / P(VDF-HFA) blends were taken on the hot-stage (Mettler FP 84HT TA Microscopy Cell) at various temperatures (heating rate:2℃·min^{-1}). DSC thermograms of blend samples were measured using a Rigaku Thermoflex DSC 8240 with heating rate of 10℃·min^{-1}.

RESULTS AND DISCUSSION

Morphology

In the previous paper[7], PEA/P(VDF-HFA) blends showed to be homogeneous morphology by SEM observation at room temperature. The change of phase morphology of the PEA/P(VDF-HFA) blend with 70(wt%) P(VDF-HFA) content for 200-220℃ under heating rate of 2℃·min^{-1} is shown in Figure 1.

The modulated structure[10,11] of the early stage of demixing by spinodal decomposition is observed at 207.5, 210 and 212.5℃. The phase morphology changes with risng temperature, then, 'sea-island structure' is seen at 220℃. It is thought that the change of phase morphology with temperature is affected by the interfacial tension between two components. Figure 2 shows the morphology of PEA / P(VDF-HFA) blend with 50(wt%) P(VDF-HFA) content at 200, 205 and 210℃. The blend sampledisplays the homogeneous phase morphology at 200℃, whereas the blend at 210℃ appears the heterogeneous phase morphology. The domain size of blend with 50(wt%) P(VDF-HFA) content is smaller than that of PEA/P(VDF-HFA) = (30/70) blend. It is clear from these results that PEA / P(VDF-HFA) blends exhibit the LCST type phase behavior.

By the way, PEA / P(VDF-HFA) blends exhibited a faint blue near 200℃ and opacity on further high temperature by visual observation. Moreover, the reversible of the rapid phase transition behavior (miscible~ immiscible) was observed in PEA / P(VDF-HFA) blends. This behavior was found in the blends of P(VDF-HFA) with PMMA[8] and poly(ethylene-co-vinyl acetate)[9], poly(styrene) / poly(vinylmethylether)[12] and PMMA/poly (vinylidene fluoride-co-tetrafluoro ethylene)[13]. It is thought that the faint blue film was attributed to Rayleigh scattering on 'sea-island structure'.

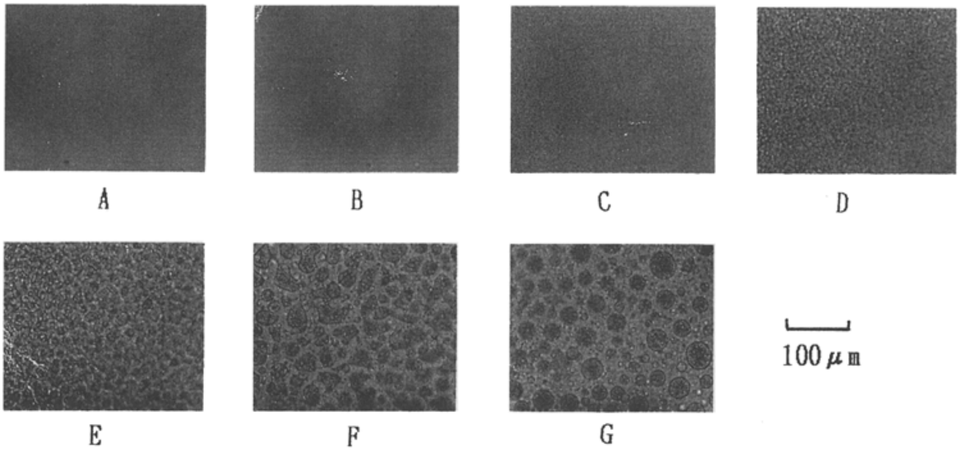

Figure 1
Optical micrographs of PEA/P(VDF-HFA)(30/70) blend. The micrographs were taken on heating rate of 2℃·min^{-1} ; A)200, B)205, C)207.5, D)210, E)212.5, F)215, and G)220℃.

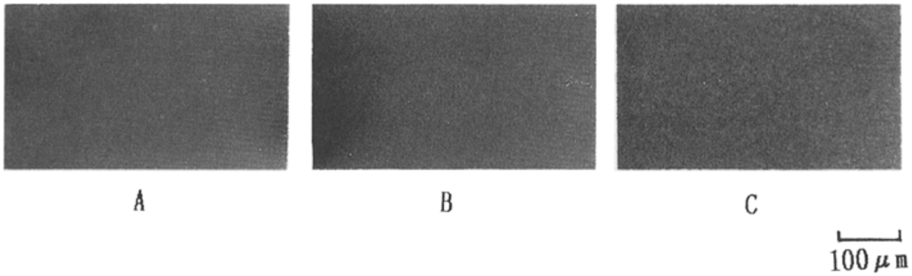

Figure 2
Optical micrographs of PEA/P(VDF-HFA)(50/50) blend. The micrographs were taken on heating rate of 2℃·min^{-1} ; A)200, B)205, and C)210℃.

Thermal Analysis

Recently, Hamazaki et al.[13] found the PMMA/poly(vinylidene fluoride-co-tetrafluoro ethylene) blends to reveal endothermic peak on DSC thermograms near phase separation temperature be corresponded to the cloud point. Then, they calculated the interaction parameter χ_{12} by enthalpy change

(ΔH) obtained with the area under DSC thermogram. The agreement between the endothermic peak temperature and phase separation temperature was also reported in the blends of PEA with poly(vinylidene fluoride) (PVDF)[14]. Therefore, it is expected that the LCST type phase diagram in PEA/P(VDF-HFA)blends is obtained with the DSC measurement.

The DSC thermograms for PEA, PEA / P(VDF-HFA) = 70/30, 50/50 and 30/70 blend and P(VDF-HFA) are shown in Figure 3. In the range of -100℃ to 250℃, the peaks based on the glass transition temperature Tg, the crystal temperature Tc, the melting temperature Tm and the demixing temperature Td are observed on the DSC thermograms, respectively. The phase diagram is shown in Figure 4. In the previous paper[7], the peak temperature of the dynamic loss tangent tan δ (T_{Dmax}) increased with increasing P(VDF-HFA) content (0~50wt%) about 8℃. On the other hand, Tg obtained by DSC measurement in this study drops with increasing P(VDF-HFA) content (0~100 wt%) about 7℃. As the blend samples of DSC measurement was annealed above Tm, then, was quenched in liquid N_2, the blends completely maintained the amorphous state around Tg. Then, the exothermic peak (crystal temperature Tc) appears above Tg in PEA/P(VDF-HFA) blends. However, it is suggested that the crystal phase structure exists because samples of tan δ measurement was not annealed above Tm[7]. Therefore, it was thought that the difference of Tg behavior between tan δ and DSC measurements was caused by the crystal state of P(VDF-HFA). The crystal temperature Tc based on the exothermic peak is observed in PEA/P(VDF-HFA) blends [P(VDF-HFA) content: 40~80(wt%)] and decreases with increasing P(VDF-HFA) content. The melting temperature Tm is seen in the blends of 40~100(wt%) P(VDF-HFA) content and increases with increasing P(VDF-HFA) content. The melting depression behavior reveals the blends of PEA with P(VDF-HFA) to consist of amorphous polymer and crystal polymer. Nishi and Wang[15] found PMMA/PVDF blends to exhibit the melting depression and calculated the interaction parameter χ_{12} = -0.295 at 160℃. As the χ_{12} is negative, they pointed out that PMMA/PVDF blends have the miscible region above Tm. Therefore, it is expected that the χ_{12} in PEA/P(VDF-HFA) blend also is negative.

The endothermic peak Td of PEA/P(VDF-HFA) blends observed near 200℃ as shown in Figure 3 corresponds to the temperature for the homogeneous to heterogeneous transition in the morphology on optical microcopes, suggests that the endothermic peak Td ≈ 205~210℃ (Tm+80℃) is the transition temperature from miscibility to immiscibility and the PEA / P(VDF-HFA) blend is a liquid-liquid phase separation system.

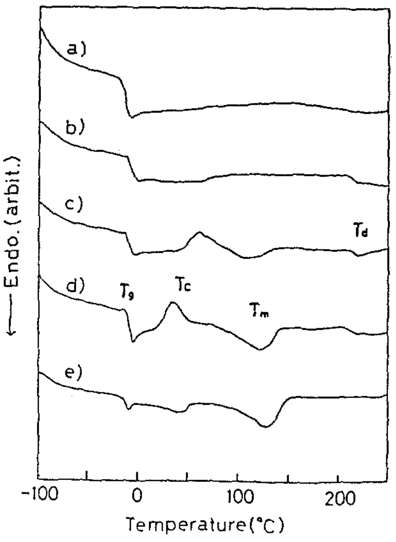

Figure 3
DSC thermograms of PEA/P(VDF-HFA) blend. a)PEA,b)PEA/P(VDF-HFA)=70/30,c)50/50 and d)30/70 blend, e)P(VDF-HFA).

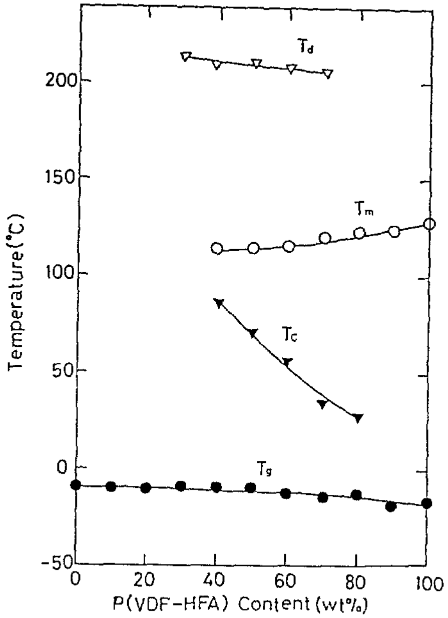

Figure 4
Phase diagram of PEA/P(VDF-HFA) blends.

CONCLUSION

The miscibility of blends of PEA with P(VDF-HFA) was investigated with optical microscopy and DSC. The heterogeneous phase morphology for PEA/P(VDF-HFA) blends observed on the optical micrograms around 210℃. It was suggested that PEA / P(VDF-HFA) blends had a LCST type phase behavior. From the results obtained by DSC measurements, we expected that the endothermic reaction around 205-210℃ on DSC thermogram is related to phase transition from miscibility to immiscibility in PEA/P(VDF-HFA) blends.

REFERENCES

1. D.R.Paul and S.Newman, (Ed.), "Polymer Blends", Vols. 1 and 2, Academic Press, New York, 1978.
2. S.Akiyama, T.Inoue, and T.Nishi, "Polymer Blends - Compatibility and Interface", 1979 (R&D report) and 1981, CMC Press, Tokyo.
3. O.Olabishi, L.M.Robeson and M.T.Show, "Polymer-Polymer Miscibility", Academic Press, New York, 1979.
4. M.A.Krenceski, J.F.Johnson, and S.C.Temin, Macromol.Chem.Phys., C26(1), 143(1986).
5. K.Fukuzawa, "Nenchaku Gijyutsu", Kobunshi Kankokai, Kyoto, 1987.
6. M.Toyama, "Kanatsu Setchakuzai (Nenchakuzai)", Kobunshi Kankokai, Kyoto, 1991.
7. Y.Kano, N.Sato, and S.Akiyama, Polym.J., 23, 1489(1991).
8. S.Kobayashi, T.Tasaka, and S.Miyata, Kobunshi Ronbunshu, 44, 695(1987).
9. M.Hasegawa, S.Akiyama, Polym.J., 20, 471(1988).
10. T.Inoue, T.Ougizawa, O.Yasuda, and K.Miyasaka, Macromolecules, 18, 57(1985).
11. T.Ougizawa, T.Inoue, and H.W.Kammer, Macromolecules, 18, 2089(1985).
12. T.Nishi, T.T.Wang, and T.K.Kwei, Macromolecules, 8, 227(1975).
13. N.Hamazaki, J.W.Cho, and S.Miyata, Polym.J., 23, 333(1991).
14. M.Ebert, R.W.Garbella, and J.H.Wendorff, Macromol.Chem., Rapid Comun., 7, 65(1986).
15. T.Nishi, T.T.Wang, Macromolecules, 8, 909(1975).

Accepted June 11, 1992 S