Compatibility of Polypeptide Blends of Poly(γ-Butyl Glutamate)/Poly(γ-Benzyl Glutamate)

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Synopsis

The compatibility of poly(γ-butyl glutamate)/poly(γ-benzyl glutamate) blend was examined by the estimation of the side chain dispersion of polypeptides in terms of the condition of preparation of blend films and the blend ratio. The polypeptide blend prepared for very short casting time exhibited an apparent compatibility. On the other hand, the polypeptide blend cast for long time did show incompatibility, irrespective of the blend ratio or mole fraction. The structures of the separated phase changed around mole fraction of 0.5 with the increasing mole fraction. The poly(γ-butyl glutamate) island phase transformed into the poly(γ-benzyl glutamate) island phase with increasing mole fraction of poly(γ-benzyl glutamate) according to the calculation of the simple island-matrix model by Takayanagi et al.

INTRODUCTION

The compatibility of many flexible polymer blends is summarized by Krause.[1] Many compatible polymer blend systems have been discovered, and study on the compatibility of new blend systems has been continued. However, it focused our attention to the flexible polymer blends. It is necessary to study the compatibility on the blend of rigid rod polymer and flexible polymer and that of rigid rod polymers from the standpoint of an application of polymer materials.

Here, our trial to understand the compatibility of blends of rigid rod polymers was performed for the α helical poly(γ-butyl glutamate) (PBuG)/poly(γ-benzyl glutamate) (PBeG) blend. One has to take into account the intermolecular mixing of the side chain attaching to each α helix, when considering the compatibility of the rigid rod polypeptide blends. It is valuable to examine the side chain dispersion ascribed to the micro-Brownian motion of the side chain region in order to check the intermolecular mixing of the side chain.

One of authors reported that the ω helix of copoly(butyl-L-aspartate–benzyl-L-aspartate) could form the intramolecular stacking between the butyl group and the benzyl group.[2] The formation of the stacking suggests an intact affinity of butyl group and benzyl group, although these groups are forced to attach much nearer to a back bone α helix. One might expect the mixing of these two groups in the side chain.

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In the present paper we studied the compatibility of PBuG/PBeG polypeptide blend. Since the α helix of two-component polypeptides remains unchanged by blending, the compatibility of polypeptide blends is characterized by that of the side chain of polypeptides. Therefore, the characteristic point is whether the entire intimate mixing between the side chains belonging to each α helix is possible or not, differing from the compatibility of a segment unit of flexible polymer blends. From these standpoint, the compatibility was determined by either single or double side chain dispersion. It was found that the compatibility of these blend systems depended upon the casting condition of a blend preparation. Furthermore, structural change in incompatible phase due to compositions was proposed by the island–matrix structural model.

EXPERIMENTAL

PBuG was synthesized by an ester exchange reaction of poly(γ-methyl glutamate) by *n*-butyl alcohol. It was 98–99% butylation and density of 1.156 g/cm^3. *N*-carboxy-γ-benzyl glutamate anhydride (NCA) was obtained by Leuch's method.[3] The purified NCA was polymerized in about 5% (w/v) ethylene dichloride (EDC) solution, using triethylamine as the initiator.

PBuG and PBeG was solubilized in EDC as a cosolvent and PBuG/PBeG blend films with various compositions were cast from EDC solution (3 wt %) for different casting times at room temperature. All the polypeptide blend films were immersed in methanol after casting and residual EDC solvent was gotten rid of.

Dynamic viscoelastic measurements were carried out on Reovibron DDV-II (Toyo Baldwin Co., Ltd.) at a frequency of 110 Hz over a temperature range from -30°C to 40°C at the heating rate of about 2°C/min.

The differential scanning calorimeter (DSC) used in this study was the standard type DSC of Rigaku Denki Co., Ltd. DSC thermograms of specimens of 25–30 mg were obtained at the sensitivity of ± 0.5 mcal/s and at the scanning rate of 5°C/min.

RESULTS AND DISCUSSION

It is well known that the side chain dispersion of polypeptides behaves very similarly to the primary dispersion (glass transition) of flexible polymers.[4–9] The appearance of single or double side chain dispersion was examined in order to investigate the compatibility of polypeptide blend, as the compatibility of flexible polymers was estimated by the primary dispersion.

The side chain dispersion of PBuG/PBeG (1/1) polypeptide blends which were prepared by cast method varying casting time, e.g., 7 h, 2 days, and 12 days was measured by Reovibron DDV-II at the frequency of 110 Hz and over the temperature range from -30°C to 40°C. Temperature dependence of tan δ of each polypeptide blend was shown in Figure 1. PBuG/PBeG polypeptide blend of casting time 12 days exhibited double side chain dispersion at -13 and 35°C. These temperatures correspond to the temperature of the side chain dispersion of homopolypeptides, PBuG and PBeG, -13 and 38°C, respectively. This is indicative of existence of two

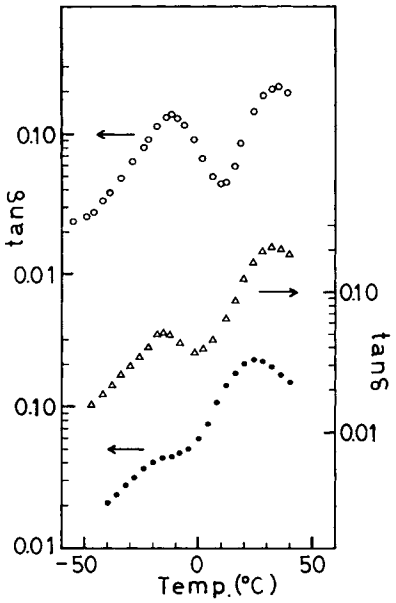

Fig. 1. Temperature dependence of tan δ of poly(γ-butyl glutamate)/poly(γ-benzyl glutamate) blend (1/1). Casting time: (●) 7 h; (△) 2 days; (○) 12 days.

separated phases which nearly consist of homopolypeptide of PBuG or PBeG. The side chain dispersion peak around −13°C decreased as casting time of polypeptide blend is shorter. PBuG/PBeG polypeptide blend of casting time 7 h exhibited a shoulder around −13°C and the rather broad dispersion around 25°C, indicating a tendency to a single side chain dispersion peak. Similar phenomena for poly(γ-methyl glutamate)/PBG polypeptide blend are observed by a dielectric dispersion method.[9] This suggests a compatible PBuG/PBeG polypeptide blend, when casting time is very short. In fact, the solution of this blend is so transparent even in concentrated solution that the blend is considered to be compatible in very concentrated solution. The PBuG/PBeG polypeptide blend became incompatible as casting time increased. Therefore, this polypeptide blend is thermodynamically incompatible system in the solid state. It is considered that the PBuG/PBeG polypeptide blend of a very short casting time is apparently compatible, but it is in unstable and nonequilibrium state. Although copoly(butyl-L-aspartate–benzyl-L-aspartate) could form the ω helix containing the stacking between the butyl group and the benzyl group and there seems to be strong interaction between them,[2] it was not so strong for PBuG/PBeG polypeptide blend; but this blend system was phase-separated.

DSC thermogram of PBuG/PBeG (1/1) polypeptide blend of casting time 7 h was demonstrated in Figure 2. An exothermic peak (ΔH = 0.1 cal/g) appeared at 121.5°C, indicating that unstable and compatible PBuG/PBeG polypeptide as-cast blend transformed into incompatible in the solid state and separated phase corresponding to the thermodynamically stable state. Such a phase transition is likely to be caused by α helix molecular motion which is enhanced above 120°C. Two kinds of viscoelastic crystalline relax-

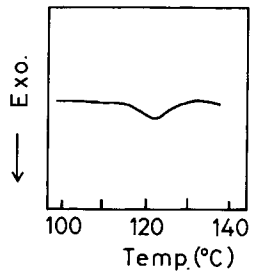

Fig. 2. DSC thermogram of poly(γ-butyl glutamate)/poly(γ-benzyl glutamate) blend (1/1) of casting time 7 h.

ation observed for poly(γ-methyl glutamate) around 140–190°C are ascribed to the migrational slip or rotational motion of α helix and to the accordionlike torsional extension or bending motion of the α helix core, respectively.[10,11] Thus the phase transition from unstable compatible phase to stable incompatible phase takes place easily under α helix molecular motions above 120°C. The exothermic peak disappeared for PBuG/PBeG polypeptide blend cast for long time. In other words, separated PBuG/PBeG polypeptide blend did not exhibit the exothermic peak any more.

The compatibility of PBuG/PBeG (1/1) polypeptide blend was determined by casting condition and casting time. This blend system was thermodynamically incompatible. Next we study the compatibility of PBuG/PBeG polypeptide blend with various compositions prepared with a casting time of 4 days. Temperature dependence of the storage modulus E' and tan δ of PBuG/PBeG polypeptide blend with mole fractions of PBeG, 0.1, 0.3, 0.5, and 0.8, is shown in Figure 3. All the polypeptide blends exhibited two dispersion peaks corresponding to the respective side chain dispersion of PBuG and PBeG. This suggests the existence of two separated phases close to the pure component of PBuG and PBeG, irrespective of the mole fraction of the polypeptide blend. The dispersion temperature corresponding to maximum tan δ was almost the constant, −13°C, while the dispersion temperature around 35°C lowered gradually with increasing mole fraction of PBuG, indicative of the compatibility of a small amount of PBuG to the PBeG-rich separated phase. The storage modulus of the blends ranges from that of PBeG to that of PBuG at the temperature range −30–30°C.

A trial to interpret the structure of the separated phase was performed by using the mechanical model of Takayanagi et al.[12] and the value of the storage modulus obtained here. Two separated phases of PBuG/PBeG polypeptide blend are treated as the so-called island–matrix model as shown in Figure 4. The storage modulus of phase-separated PBuG/PBeG polypeptide blend is calculated as follows;

$$E' = \lambda_1 E'_B + \frac{\lambda_2 E'_A E'_B}{f_1 E'_A + f_2 E'_B} \tag{1}$$

where λ is the volume fraction of the series part in the mechanical model as shown in Figure 4(b), f is the volume fraction of parallel part, and E'_A and E'_B represent the storage modulus of phase separated A and B phase,

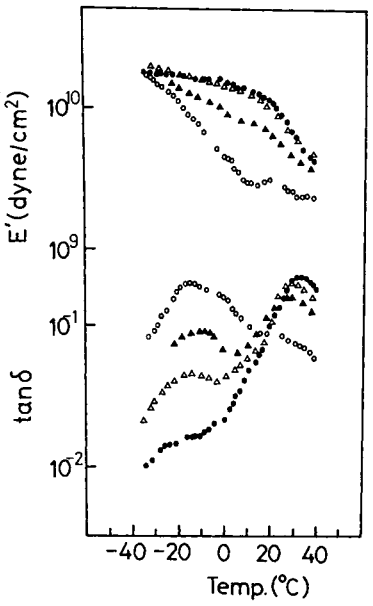

Fig. 3. Temperature dependence of storage modulus E' and tan δ of poly(γ-butyl glutamate)/poly(γ-benzyl glutamate) blend with mole fraction φ of poly(γ-benzyl glutamate): (○) 0.1; (▲) 0.3; (△) 0.5; (●) 0.8.

respectively. The values of λ and f are evaluated by the mole fraction and those of E'_A and E'_B at certain temperatures were experimentally obtained from Figure 3. Figure 5 shows the calculated storage modulus of polypeptide blend studied here, where the PBuG island phase in the PBeG matrix phase is represented by broken lines and, vice versa, the PBeG island phase in the PBuG matrix phase by solid lines. Experimental results of the storage modulus at −10, 10, and 30°C (○, ●, and △) represent roughly the inverse sigmoidal shape. On the other hand, the calculated curve is the monotonous increasing function against the mole fraction. It might be concluded that the PBuG island phase in the PBeG matrix phase (---) is formed in a small mole fraction region up to 0.5 and inversely it transforms into the PBeG

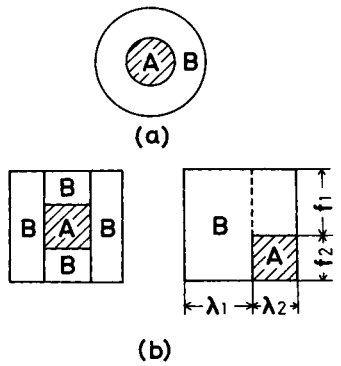

Fig. 4. (a) Island-matrix model and (b) equivalent mechanical model; λ-volume fraction of series part, f-volume fraction of parallel part.

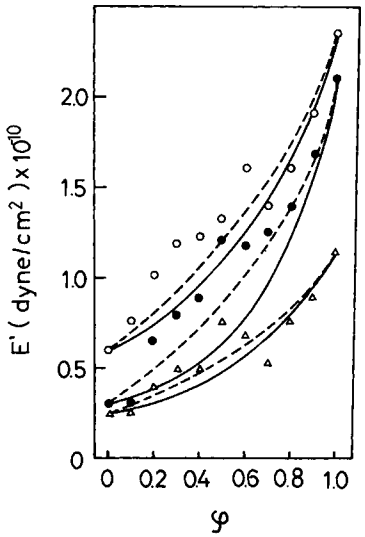

Fig. 5. Plot of the calculated storage modulus of poly(γ-butyl glutamate)/poly(γ-benzyl glutamate) blend against mole fraction of poly(γ-benzyl glutamate); (---) PBuG island in PBeG matrix phase; (——) PBeG island in PBuG matrix phase; (○) −10°C; (●) 10°C; (△) 30°C.

island phase in the PBuG matrix phase (—) in a larger mole fraction region, when the experimental and calculated curves of the storage modulus are compared. Namely, the reversal in island–matrix phase was considered to take place around the mole fraction of 0.5.

In a real PBuG/PBeG polypeptide blend, a separated phase is likely to be very complicated. Although the present island–matrix model can qualitatively interpret the storage modulus–mole fraction curve by the mechanical model of Takayanagi et al.,[12] it is necessary to consider that we do not treat only two separated phases as the each pure component of PBuG and PBeG, but also those as the PBuG-rich and the PBeG-rich phases. Moreover, as a further study, we will have to confirm the existence of the separated phase and also the reversal in the island–matrix phase by electron microscopic observation.

CONCLUSIONS

PBuG/PBeG polypeptide blend was thermodynamically in the incompatible system in the case of the blend prepared by the relatively long casting time. Apparently compatible polypeptide blend could be obtained when cast by a very short casting time.

The PBuG/PBeG polypeptide blend prepared by a long casting time was phase-separated, irrespective of mole fraction. The storage modulus of the phase-separated PBuG/PBeG polypeptide blend vs. the mole fraction was qualitatively well explained by the simple island–matrix model of Takayanagi et al.[12] The reversal in the island–matrix separated phase was expected to take place around the mole fraction of 0.5.

References

1. Krause, in *Polymer Blends*, D. R. Paul and Seymour Newman, Eds., Academic, New York, 1978, Vol. 1, Chap. 1.

2. Y. Tsujita, M. Fukagawa, and I. Uematsu, *Polym. J.*, **14**, 773 (1982).

3. H. Leuchs, *Ber.*, **39**, 857 (1906).

4. A. J. McKinnon and A. V. Tobolsky, *J. Phys. Chem.*, **70**, 1453 (1966).

5. A. Tsutsumi, S. Isozaki, K. Hikichi, and M. Kaneko, *Rep. Progr. Polym. Phys. Jpn.*, **16**, 591 (1973).

6. G. Pezzin, G. Ceccorulli, M. Pizzoli, and E. Peggion, *Macromolecules*, **8**, 762 (1975).

7. Y. Oohachi, H. Hamano, T. Yoshida, Y. Tsujita, and A. Takizawa, *J. Appl. Polym. Sci.*, **22**, 1469 (1978).

8. Y. Yamashita, A. Tsutsumi, K. Hikichi, and M. Kaneko, *Rep. Progr. Polym. Phys. Jpn.*, **15**, 607 (1972).

9. A. Tsutsumi, K. Hikichi, T. Takahachi, Y. Yamashita, N. Matsushima, M. Kanke, and M. Kaneko, *J. Macromol. Sci.*, **B8**, 413 (1973).

10. T. Kajiyama, M. Kuroishi, and M. Takayanagi, *J. Macromol. Sci. Phys.*, **B11**, 195 (1975).

11. K. Koga, T. Kajiyama, and M. Takayanagi, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 401 (1976).

12. M. Takayanagi, H. Harima, and Y. Iwata, *Zairyo (Japanese)* **12**, 389 (1963).

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