Dynamic Mechanical Properties and Morphology of Styrene-Divinylbenzene Copolymer/Poly(vinyl Chloride) Systems. (II). Effect of Polymerization Temperature

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Synopsis

Effect of polymerization temperature on the phase-separated structure of the composite materials [P(St-DVB)/PVC systems] prepared by copolymerization of styrene (St) and divinylbenzene (DVB) in the presence of fine poly(vinyl chloride) (PVC) powder was studied by electron microscopy and dynamic mechanical test. P(St-DVB)/PVC systems have the two-phase nature with a styrene-divinylbenzene copolymer as the continuous phase [P(St-DVB) phase] and a PSt/PVC composite as the dispersed phase (PSt-PVC phase), in which PSt penetrates into the PVC domain. The crosslinking density of the P(St-DVB) phase is larger than that estimated from the recipe in the feed, suggesting that there exists a difference of the diffusion constants of styrene and divinylbenzene into the PVC particles on the paste formation and the polymerization process. The changes of the phase-separated structure of P(St-DVB)/PVC systems polymerized at various temperatures are also explained on the basis of the difference between the diffusion behavior of styrene and that of divinylbenzene into fine PVC particles at these temperatures.

INTRODUCTION

The P(St-DVB)/PVC systems are used as the base polymer to prepare ion-exchange membranes by the paste method,[1] that is, styrene (St), divinylbenzene (DVB), and a polymerization initiator are mixed with a fine poly(vinyl chloride) (PVC) powder to prepare a paste. This paste is coated onto a reinforcing material, and the resultant composite is heated to copolymerize monomers. Subsequently, an ion-exchange group is introduced onto the base membrane.

The ion-exchange membrane contains microheterogeneity of colloidal dimension, as elucidated by the selective decomposition of the ion-exchange resin component of the membrane and the studies of the resultant microporous membrane.[2,3] The study on the copolymerization of St and DVB in the presence of fine PVC powder by Kagiyama et al.[4] also suggested the heterogeneous structure of P(St-DVB)/PVC systems.

In the previous paper,[5] we investigated the dynamic viscoelastic behaviors and electron microscopy of P(St-DVB)/PVC systems and determined that P(St-DVB)/PVC systems consist of two phases: one is styrene-divinylbenzene copolymer as the continuous phase [P(St-DVB) phase] and the other phase is a composite of polystyrene (PSt) and PVC as the dispersed phase [PSt-PVC

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phase], in which PSt penetrates into PVC domain. The PSt-PVC phase also contains a grafting of PSt (PSt-g-PVC) onto PVC, enhancing an interaction between PSt and PVC domains. In addition, perhaps there exists a grafting of styrene-divinylbenzene copolymer onto PVC in the boundary region of the two phases. The P(St-DVB) phase has the heterogeneity in the cross-linking density due to the difference of the copolymerizability of the first double bond of DVB with St from that of the second one.[6] And the cross-linking density of this phase is much higher than that estimated from the DVB/(St + DVB) ratio in the recipe. The reason for this phenomenon was ascribed to the difference of the diffusion constants of St and DVB into PVC particles on the paste formation and the polymerization process.[5] Assuming that the phase-separated structure of P(St-DVB)/PVC systems is derived from the difference of the diffusion constants of monomers, the temperature dependences of the diffusion constants of St and DVB into PVC particles should have an effect on the structures of P(St-DVB)/PVC systems polymerized at different temperatures.

In this article, we investigated the effect of polymerization temperatures on the phase-separated structures of P(St-DVB)/PVC systems in relation to the change of monomer diffusion into PVC particles. Furthermore, the structural change of P(St-DVB)/PVC system polymerized above the glass transition temperature of PVC was observed by electron microscopy and dynamic mechanical test, which is concerned with the change of the mobility of the PVC molecular chain.

EXPERIMENTAL

Preparation of Samples

Commercial DVB and St monomers were washed successively with an aqueous NaOH solution and pure water, dried over anhydrous sodium sulfate,

TABLE I
P(St-DVB)/PVC Systems, P(St-DVB) Copolymers
and PSt/PVC Composite

Sample	No.	St	DVB	PVC	Polymerization condition[a]
P(St-DVB)/PVC systems	A-3-1	8.0	2.0	5.0	65°C for 6 h, successively 110°C for 2 h
	A-3-2	8.0	2.0	5.0	80°C for 5 h
	A-3-3	8.0	2.0	5.0	110°C for 5 h
P(St-DVB) copolymers	M-1-1	8.0	2.0	—	65°C for 6 h, successively 110°C for 2 h
	M-1-2	8.0	2.0	—	80°C for 5 h
	M-1-3	8.0	2.0	—	110°C for 5 h
PSt/PVC composite	C-1-1	10.0	—	5.0	65°C for 6 h, successively 110°C for 2 h
	C-1-2	10.0	—	5.0	80°C for 5 h
	C-1-3	10.0	—	5.0	110°C for 5 h

Compositions of St, DVB, and PVC are listed as weight parts.
[a]Polymerization at 65°C: *Bis*(4-tert-butylcycrohexyl) peroxy carbonate was used as a polymerization initiator.
Polymerization at 80 and 110°C: Benzoyl peroxide was used as a polymerization initiator.

and distilled under nitrogen atmosphere. The DVB used is composed of m- and p-diethylbenzene (2.5%), m- and p-ethylvinyl-benzene (42%), m- and p-DVB (55%), and 0.5% of other compounds. The fine PVC powder used was a commercial product by emulsion polymerization ($\overline{Pn}$ = 600, particle diameter = 0.20 − 0.55 μm). A fine PVC powder was mixed with the monomer mixtures containing polymerization initiator at room temperature with stirring (paste preparation). The paste obtained was then placed in an air-tight container, and the monomers were copolymerized at each temperature (65, 80, 110°C). Prepared samples are shown in Table I. The details of the procedure to prepare the samples were described in the previous paper.[5]

Analysis of Polymers

Dynamic mechanical tests were performed at a frequency of 11 Hz by using Rheovibron DDV-III-EA type from Toyo Baldwin, Ltd. The temperature dependences of storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) were measured between 20°C and 180°C with a heating rate of 1°C/min.

The morphological analyses of the PSt/PVC composite and P(St-DVB)/PVC systems were performed by transmission microscopy (HU-12 from Hitachi Ltd.). Ultrathin sections prepared by ultramicrotome were stained by exposure to the vapor of aqueous osmium tetraoxide solutions at room temperature for two days. Consequently, the electron micrographs show that the PVC phase is dark, and PSt and P(St-DVB) phases are bright.

Degrees of swelling of fine PVC powder by St and DVB were measured by gravimetric method at 30, 60, 80, 100°C. The range of measured temperatures corresponds to the glass transition region of PVC. One gram of fine PVC powder was mixed with 20 g of monomer containing one gram of tertbutyl-catechol as a polymerization inhibitor at 20°C with stirring (paste preparation). The concentration of tertbutylcatechol is more than enough to inhibit polymerization for 5 hours at 100°C. The paste obtained was heated at a definite temperature for a definite time. Then the paste was filtrated on the glass filter heated at a definite temperature by aspirator suctioning for a few minutes and weighed.

RESULTS AND DISCUSSION

Degree of Swelling

In recent years the self-diffusion in polymer solvent systems has been studied by free volume theories[7-11]. These theories are adapted to predict the concentration and temperature dependences of the solvent self-diffusion coefficient at low solvent concentrations above glass transition temperature of polymers and emphasize that the mobility of molecules in the mixture is sensitive to the specific whole free volume of the system. The solvent size strongly influences on the concentration dependence of polymer solvent diffusion coefficient.[12]

Thus, it is difficult to apply these theories to our study due to the restrictions in polymerization temperature and the monomer concentration. But the large effect of the monomer size and the temperature dependence on monomer diffusion process into fine PVC powder are expected from these
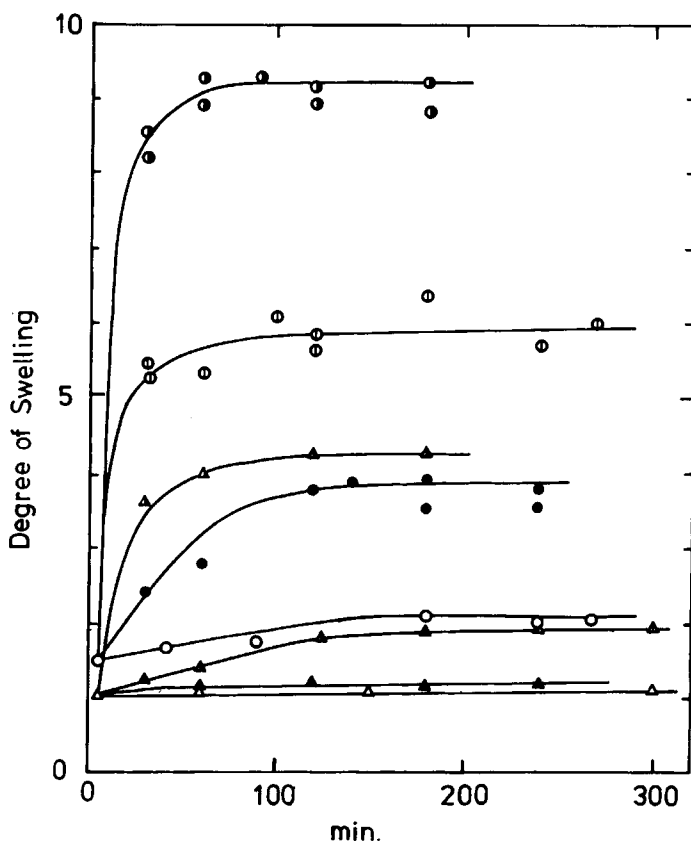
Fig. 1. Degree of swelling: Time dependences of monomer/PVC weight ratio; (○) St at 30°C; (●) St at 60°C; (◐) St at 80°C; (◑) St at 100°C; (△) DVB at 30°C; (▲) DVB at 60°C; (▲) DVB at 80°C; (▲) DVB at 100°C

works. Figure 1 shows the time dependences of the monomer/PVC weight ratio (degree of swelling). The St/PVC ratio is larger than the DVB/PVC ratio at each temperature and the swelling rate of PVC by St is larger than that of PVC by DVB from the initial gradients of each curve. The results suggest that below 80°C the diffusion constant of St into the PVC particles is much larger than that of DVB into PVC particles below due to the strong effect of monomer size. Furthermore, the swelling rates of PVC by St and DVB have strong temperature dependences. The swelling rates, especially those of PVC by DVB, increase rapidly as the temperature rises from 80°C to 100°C. Since the glass transition temperature (T_g) of PVC used is 82°C, above this temperature, the free volume of PVC chain begins to increase enormously according to the glass transition of PVC. Thus, above T_g of PVC, both the free volume of PVC chain and the free volume of monomer increase with temperature. The increase of the free volume of PVC chain also causes the increase of the system free volume above T_g of PVC. The increase of the system free volume with temperature increases the monomer diffusion coefficients and the mobility of the PVC chain. Consequently, these results suggest that the monomer diffusion constants into PVC particles increase as the temperature

rises and this depends on the increase of the system free volume with temperature.

Dynamic Viscoelastic Behavior and Morphology P(St-DVB) Copolymers

Figure 2 shows the effect of polymerization temperature on the viscoelastic behaviors of P(St-DVB) copolymers. P(St-DVB) copolymer polymerized at 80°C (sample M-1-2) has a broad peak of loss tangent, which is ascribed to the two-phase cross-linked structure composed of tightly cross-linked network and loosely cross-linked network as described earlier.[5] This two-phase structure is in agreement with the copolymerization kinetics reported by Kagiyama et al.[4] and Popov and Schwachula[13, 14], who have deduced that DVB is more preferentially copolymerized than St in the early stage and loosely cross-linked
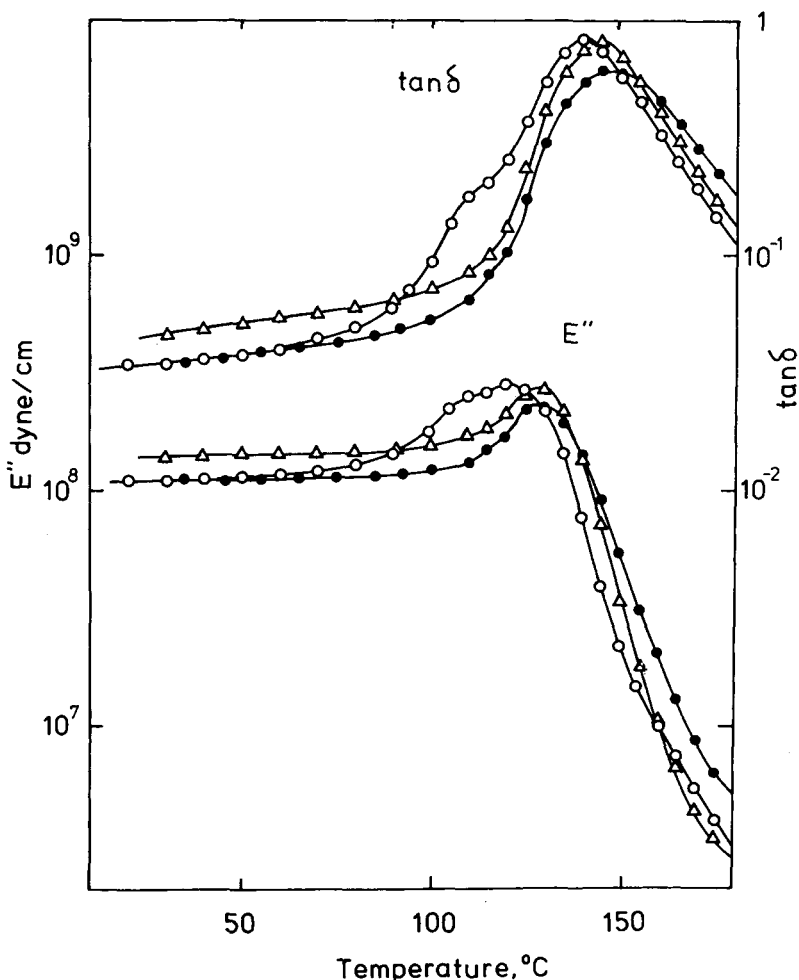

Fig. 2. Dynamic viscoelastic behaviors of P(St-DVB) copolymers polymerized at various temperatures: (○) polymerized at 80°C (sample M-1-2); (△) polymerized at 65°C and successively polymerized at 110°C (sample M-1-1); (●) polymerized at 110°C (sample M-1-3)

copolymers are formed in the latter stage due to the decrease of DVB concentration. It is noticeable that the peak of loss tangent of sample M-1-1 polymerized at 65°C and successively at 110°C is similar to that of sample M-1-3 polymerized at 110°C, and becomes narrower and shifts to a higher temperature compared with that of sample M-1-2 polymerized at 80°C. The copolymerization conversions of all the samples are high (96–98%). These results suggest that the second double bond of DVB can easily copolymerize with St at 110°C due to the higher mobility of the resultant copolymer, producing tightly cross-linked network structure.

Thus, the heterogeneity of the cross-linked structure of P(St-DVB) copolymers is deduced to depend mainly on the copolymerizability of the second double bond of DVB with St in the latter stage of copolymerization process. With an increase in polymerization temperature, the cross-linking density and the homogeneity of the cross-linked structure of P(St-DVB) copolymers increase.

The copolymerizability of the second double bond of DVB requires the further investigation of polymerization kinetics and the characterization of the resultant P(St-DVB) copolymers in detail.

PSt/PVC Composites

Figure 3(b) exhibits the electron microphotograph of the PSt/PVC composite polymerized at 80°C showing that the PVC phase is the dark portion and the PSt phase is the bright portion.
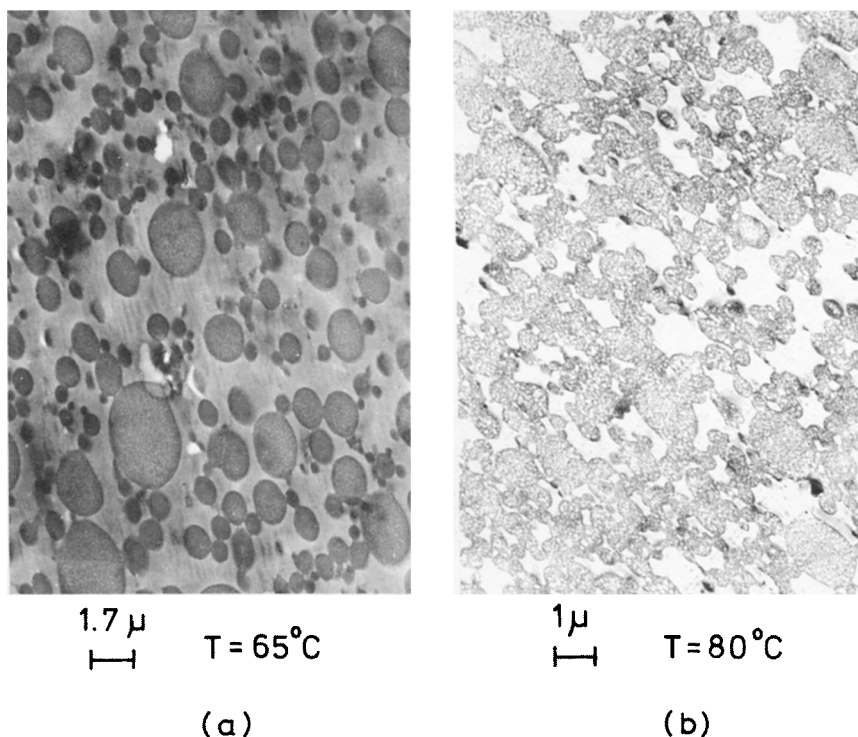

Fig. 3. Electron micrographs of PSt/PVC composites: (a) polymerized at 80°C (sample C-1-2); (b) polymerized at 65°C and successively polymerized at 110°C (sample C-1-3)
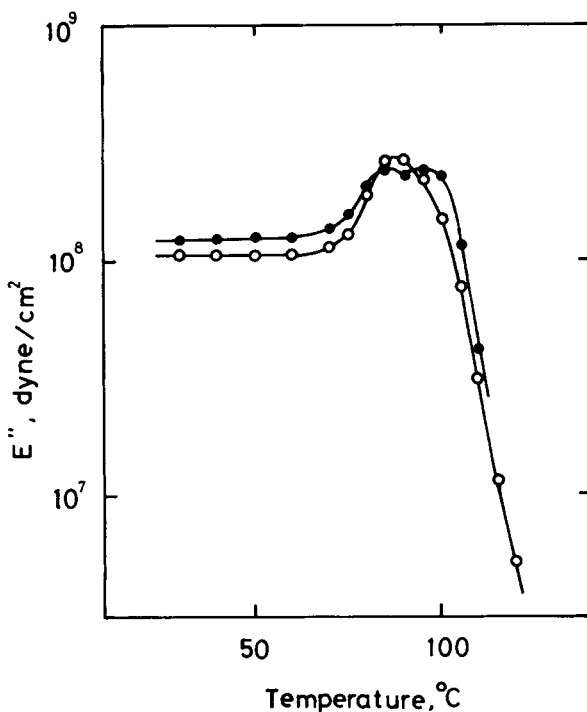
Fig. 4. Loss moduli of PSt/PVC composites: (○) polymerized at 80°C (sample C-1-2); (●) polymerized at 65°C and successively polymerized at 110°C (sample C-1-1)

Figure 4 shows the dynamic viscoelastic behaviors of the PSt/PVC composites polymerized at different temperatures. The PSt/PVC composite (sample C-1-2) polymerized at 80°C shows a single E'' peak, but electron microscopic study of this sample morphology substantiates a phase-separated structure composed of PSt domain and the domain of which is composed PVC and dispersed PSt in the PVC. The authors deduced the reason for the single E'' peak that the PSt/PVC composite contains not only grafting PSt onto PVC but also finely dispersed PSt in the PVC domain and that the glass transition temperatures of PSt and PVC are close to each other.[5] PSt/PVC composite polymerized at 110°C shows the same viscoelastic behavior as the PSt/PVC composite polymerized at 80°C. Assuming that the monomer diffusion into fine PVC particles dominates the nature of the microstructure of PSt/PVC composite on the paste formation and the polymerization process, the comparable initial swelling rates of PVC by St monomer at 80 and 100°C should derive this result.

Figure 3(a) shows the electron microphotograph of the PSt/PVC composite polymerized at 65°C and successively polymerized at 110°C. PSt forms the continuous phase (sea phase) and PSt is finely dispersed in the isolated PVC domain (island phase). This distinct sea–island structure corresponds to the two E'' peaks observed at 85 and 95°C as shown in Figure 4. The former peak corresponds to the island phase and the latter peak corresponds to the sea phase.[5] This result suggests that the first polymerization temperature determines the phase separation of the PSt/PVC composite and the decrease of the rate of monomer diffusion into PVC induces the change of the phase-sep-
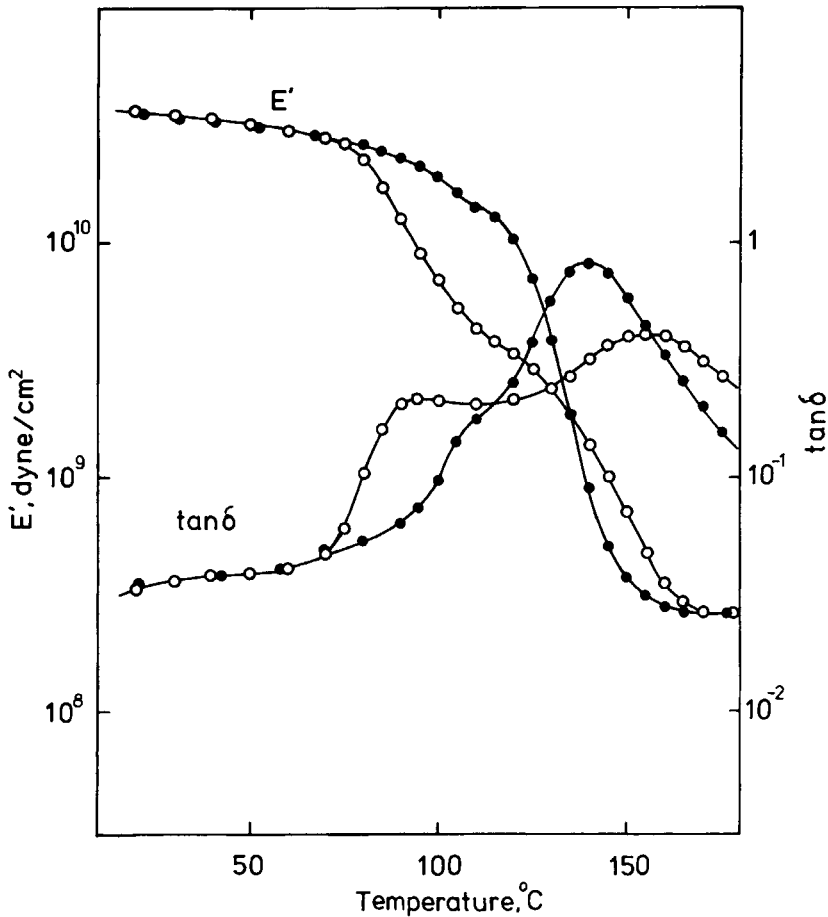
Fig. 5. Dynamic viscoelastic behaviors of P(St-DVB)/PVC system and P(St-DVB) copolymer polymerized at 80°C: (○) P(St-DVB)/PVC system (sample A-3-2); (●) P(St-DVB) copolymer (sample M-1-2)

arated structure. From these results, the polymerization temperature has a strong effect on the heterogeneity of the PSt/PVC composites, and the assumption mentioned above is applicable to the mechanism of the formation of the microphase separation.

P(St-DVB)/PVC Systems

P(St-DVB)/PVC systems have the phase-separated structure with a styrene-divinylbenzene copolymer as the continuous phase [P(St-DVB) phase] and a PSt/PVC composite as the dispersed phase [PSt-PVC phase]. Figure 5 shows the viscoelastic behaviors of the P(St-DVB)/PVC system (sample A-3-2) and P(St-DVB) copolymer (sample M-1-2) polymerized at 80°C. In spite of the same DVB/(St + DVB) ratio in the recipe, the peak positions of loss tangent at high temperatures of sample A-3-2 and sample M-1-2 are observed at 141°C and 155°C, respectively. The cross-linking density of the P(St-DVB) phase in the P(St-DVB)/PVC system is much larger than that of
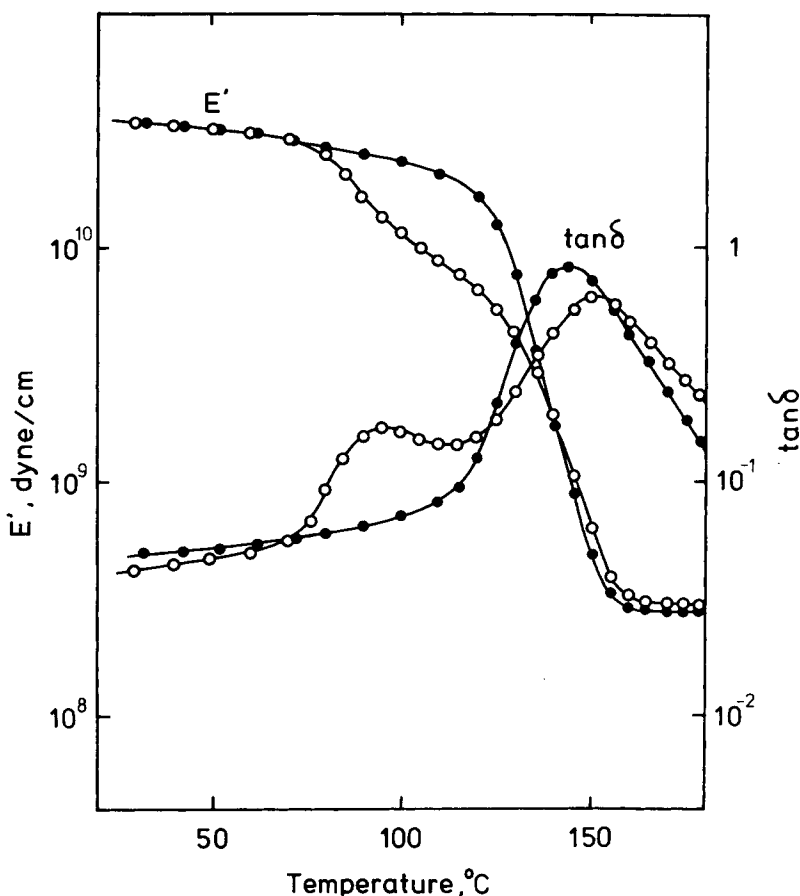
Fig. 6.   Dynamic viscoelastic behaviors of P(St-DVB)/PVC system and P(St-DVB) copolymer polymerized at 65°C for 6 h and successively polymerized at 110°C for 5 h: (○) P(St-DVB)/PVC system (sample A-3-1); (●) P(St-DVB) copolymer (sample M-1-1)

P(St-DVB) copolymer, which is ascribed to the difference of the diffusion constants of St and DVB into PVC particles on the paste formation and the polymerization process.[5]

As shown in Figure 1, we investigated the swelling behaviors of fine PVC particles and deduced that the diffusion constant of St into PVC is much larger than that of DVB at 80°C. Assuming that our deduction is applied to the paste formation and the polymerization process of P(St-DVB)/PVC system (sample A-3-2), the concentration of St diffused into the PVC particles is larger than that of St in the recipe due to the larger swelling rate of PVC by St than that of PVC by DVB, and the resultant DVB concentration in P(St-DVB) phase is much larger than that estimated from the recipe. The increase of the cross-linking density in P(St-DVB) phase approves our consideration of the formation process of the phase-separated structure of P(St-DVB)/PVC system polymerized at 80°C.

Figure 6 shows the viscoelastic behaviors of P(St-DVB)/PVC system (sample A-3-1) and P(St-DVB) copolymer (sample M-1-1) polymerized at 65°C and

TABLE II
Peak Temperatures of Loss Moduli and Loss Tangent

Sample	No.	Ta[a], °C	Tb[b], °C
P(St-DVB)/PVC systems	A-3-1	88	150
	A-3-2	87	155
	A-3-3	83	152
P(St-DVB) copolymers	M-1-1		145
	M-1-2		141
	M-1-3		146

[a] Peak temperatures of loss moduli observed at 80–90°C.
[b] Peak temperatures of loss tangent observed above 140°C.

successively polymerized at 110°C. Table II shows the peak temperatures of loss tangent of P(St-DVB)/PVC systems and P(St-DVB) copolymers. The peak temperatures (Tb) of loss tangent observed at temperatures above 140°C correspond to the glass transition of P(St-DVB) phase in the P(St-DVB)/PVC systems and P(St-DVB) copolymers. The Tb of sample M-1-1 polymerized at 65°C and successively polymerized at 110°C is higher than the Tb of sample M-1-2 polymerized at 80°C. The result shows that the cross-linking density of sample M-1-1 is larger than that of sample M-1-2 due to the increased copolymerizability of the second double bond of DVB at higher temperature as the P(St-DVB) copolymers described above. But the Tb of sample A-3-1 is lower than that of sample A-3-2, indicating that the cross-linking density of the sample A-3-1 is smaller than that of the sample A-3-2. This fact is interpreted as follows, the diffusion rate of St into PVC particles is much larger than that of DVB at 65°C, and the diffusion rates of St and DVB into PVC particles decrease as the polymerization temperature falls from 80°C to 65°C, thus the amount of St diffused into PVC particles decreases and the resultant DVB concentration at 65°C of the P(St-DVB) phase is smaller than that at 80°C. In this case, the effect of the decreased monomer diffusion into PVC particles decreased the cross-linking density of P(St-DVB) phase, though the second polymerization temperature (110°C) of sample A-3-1 increases copolymerizability of the second double bond of DVB. Thus the effect of the decreased monomer diffusion dominates the cross-linking density of P(St-DVB) phase of P(St-DVB)/PVC system (sample A-3-1) polymerized at 65° and successively polymerized at 110°C. The difference of Tb between P(St-DVB)/PVC system (sample A-3-1) and P(St-DVB) copolymer (sample M-1-1) is also smaller than the difference of the Tb between sample A-3-2 and sample M-1-2.

Figure 7 shows the viscoelastic behaviors of P(St-DVB)/PVC systems polymerized at different temperatures. The peak of loss tangent based on the P(St-DVB) phase of sample A-3-1 has the higher intensity compared with that of sample A-3-2. The peak of loss tangent based on the PSt-PVC phase of sample A-3-1 has the lower intensity compared with that of sample A-3-2. These results also show that the amount of St diffused into PVC particles decreases as the polymerization temperature falls from 80°C to 65°C, and
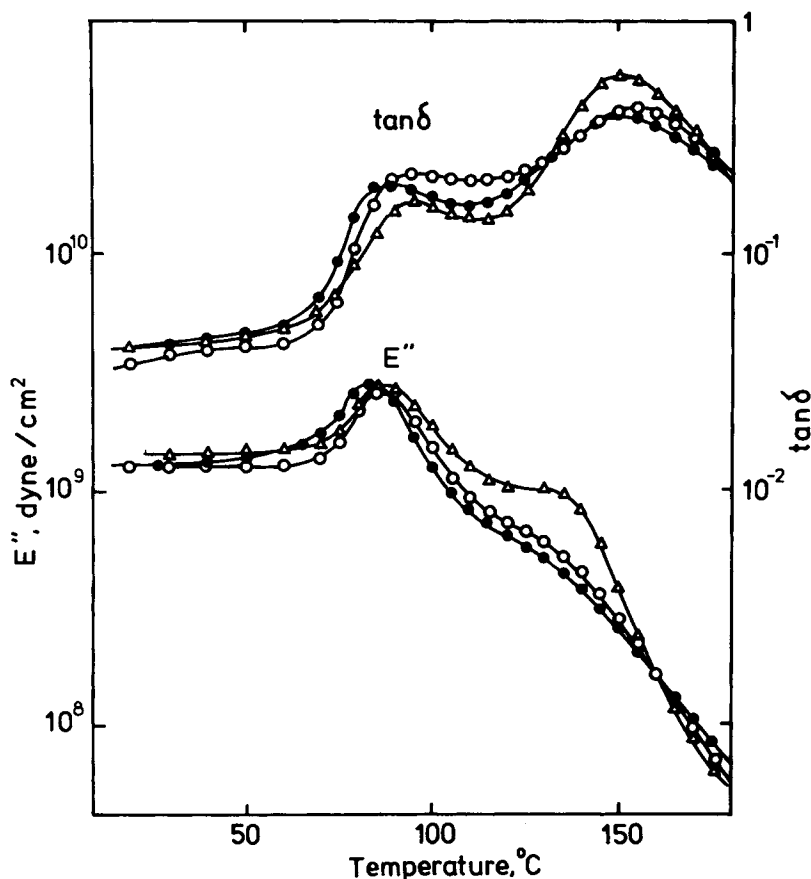
Fig. 7. Dynamic viscoelastic behaviors of P(St-DVB)/PVC systems polymerized at various temperatures: (○) polymerized at 80°C (sample A-3-2); (△) polymerized at 65°C and successively polymerized at 110°C (sample A-3-1); (●) polymerized at 110°C (sample A-3-3)

suggest that the domain size of P(St-DVB) phase increases and the domain size of PSt-PVC phase decreases. As shown in Figure 8(a), (b), the electron micrograph of sample A-3-1 exhibits the decrease of the dispersed PSt-PVC domain and also exhibits that the sea (P(St-DVB) phase)–island (PSt-PVC phase) structure of sample A-3-1 becomes more distinct than that of sample A-3-2.

Figure 9 shows the viscoelastic behaviors of P(St-DVB)/PVC system (sample A-3-3) and P(St-DVB) copolymer (sample M-1-3) polymerized at 110°C. The Tb of sample M-1-3 polymerized at 110°C is higher than the Tb of sample M-1-2 polymerized at 80°C. This result shows that the cross-linking density of sample M-1-3 is larger than that of sample M-1-2 due to the increased copolymerizability of the second double bond of DVB at higher temperature. But the Tb of sample A-3-3 is lower than that of sample A-3-2, indicating that the cross-linking density of sample A-3-3 is smaller than that of sample A-3-2. This is interpreted as follows, the diffusion rate of St into PVC particles at 110°C is larger than that of DVB, but the diffusion rate of DVB at 110°C is much larger than that at 80°C. The difference of the
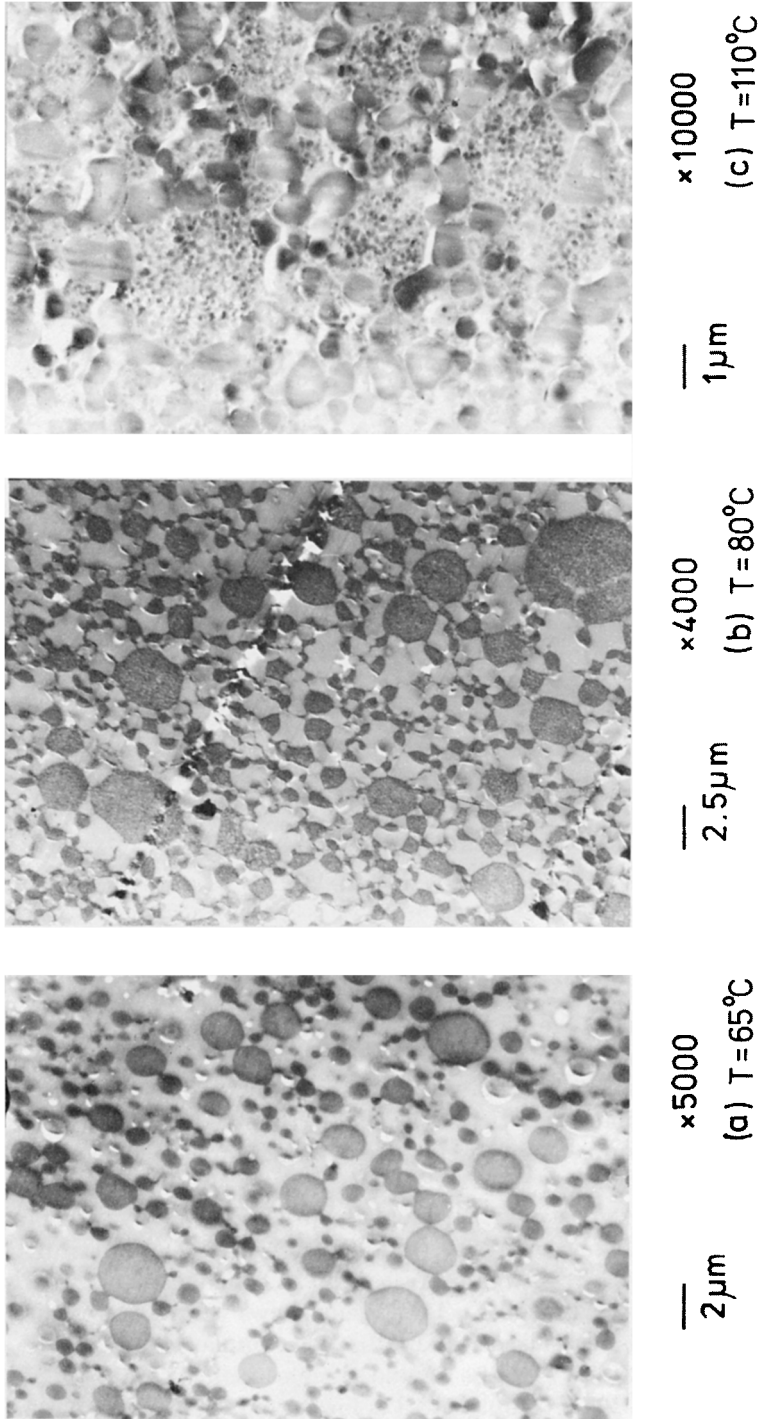
Fig. 8. Electron micrographs of P(St-DVB)/PVC systems polymerized at various temperatures: (a) polymerized at 80°C (sample A-3-2); (b) polymerized at 65°C and successively polymerized at 110°C (sample A-3-1); (c) polymerized at 110°C (sample A-3-3)
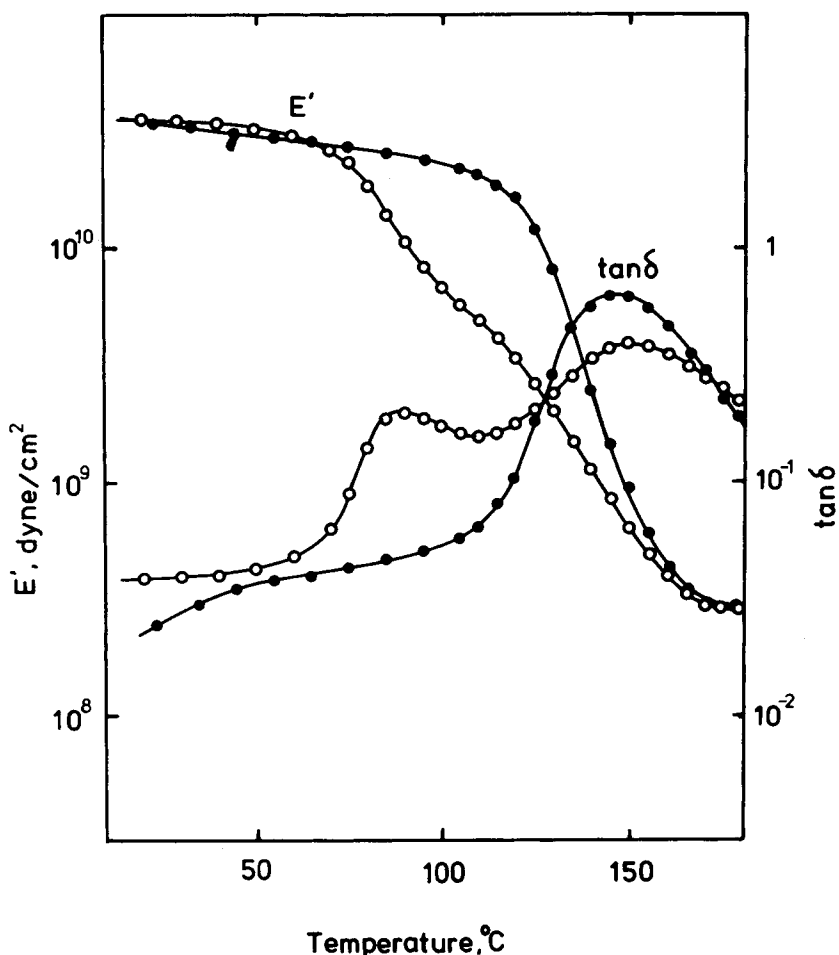
Fig. 9.   Dynamic viscoelastic behaviors of P(St-DVB)/PVC system and P(St-DVB) copolymer polymerized at 110°C: (o) P(St-DVB)/PVC system (sample A-3-3); (●) P(St-DVB) copolymer (sample M-1-3)

diffusion constants between St and DVB at 110°C is smaller than that at 80°C. Thus, as the amount of DVB diffused into PVC particles increases with increased polymerization temperature, the resultant DVB concentration of the P(St-DVB) phase at 110°C is smaller than that at 80°. In this case, the increased DVB diffusion into PVC particles decreased the cross-linking density of P(St-DVB) phase, though the copolymerizability of the second double bond of DVB increases at a higher polymerization temperature of sample A-3-3. Consequently, the effect of the increased monomer diffusion dominates the cross-linking density of P(St-DVB) phase in the P(St-DVB)/PVC system (sample A-3-3) polymerized at 110°C. The difference of Tb between P(St-DVB)/PVC system (sample A-3-3) and P(St-DVB) copolymer (sample M-1-3) is smaller than the difference of Tb between sample A-3-2 and sample M-1-2. Figure 7 and Table II show that Ta of sample A-3-3 decreased by 5°C compared with that of sample A-3-2. This result suggests that the second

double bond of DVB diffused into PVC particles does not copolymerize and plasticizes the PSt-PVC phase.

As shown in Figure 8(c), electron micrograph of sample A-3-3 exhibits that the phase-separated structure is obscure and the domain sizes of the P(St-DVB) phase and the PSt-PVC phase decrease. The result of electron microscopy suggests that the difference between the DVB concentration of the P(St-DVB) phase and that of the PSt-PVC phase decreases, and corresponds to the accelerated diffusion of DVB into PVC particles due to the effect of polymerization temperature above the glass transition temperature of PVC.

The effect of polymerization temperature on the phase-separated structure of P(St-DVB)/PVC systems is based on the temperature dependence of monomer diffusion into PVC particles. Thus the polymerization temperature is one of the most important factors to dominate the formation process of the phase-separated structure of P(St-DVB)/PVC systems.

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