

Dynamic Mechanical Properties and Morphology of Styrene-Divinylbenzene Copolymer/Poly(vinyl Chloride) Systems

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Synopsis

The morphology and dynamic mechanical properties of the composite materials [P(St-DVB)/PVC systems], prepared by copolymerization of styrene and divinylbenzene in the presence of fine PVC powder, were studied by electron microscopy and the dynamic mechanical test. The composite material (PSt/PVC composite), prepared by the polymerization of styrene in the presence of fine PVC powder, contains grafting polystyrene (PSt) onto PVC, which improves the compatibility of PSt and PVC. This result also suggests the formation of the graft copolymer of styrene-divinylbenzene onto PVC in the P(St-DVB)/PVC systems. Electron microscopy and the dynamic mechanical test indicate that 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 domain size of the dispersed phase is 0.5–2 μ . The crosslinking density of the P(St-DVB) continuous phase is larger than that estimated from the recipe. One of the reasons for this is ascribed to the difference of the diffusion constants of styrene and divinylbenzene into the PVC particles on the paste formation and polymerization process.

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 PVC powder to prepare a paste. This paste is coated onto a reinforcing material, and then 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} Kagiya et al.⁴ have also studied the copolymerization of St and DVB in the presence of fine PVC powder and suggested that P(St-DVB) is finely dispersed in the PVC phase. The copolymerizability of the first double bond of DVB with St is different from that of the second one, and this causes the heterogeneity of the polymer composition during the copolymerization.⁵ Thus, P(St-DVB)/PVC systems contain a multiphase morphology due to the incompatibility of the component polymers.

Furthermore, since the monomers used swell the PVC particles and are copolymerized to form a network structure, the P(St-DVB)/PVC systems supposedly have a semi-interpenetrating network. The interpenetrating structures

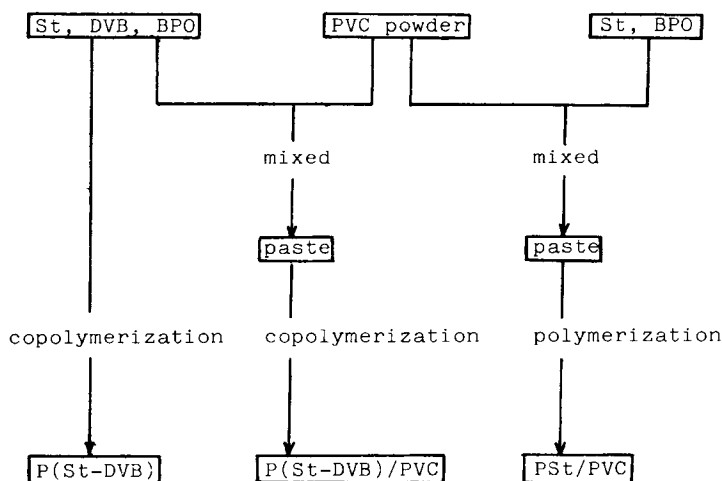


Fig. 1. Processes of sample preparations.

have been investigated in recent years, but little attention has been given to the P(St-DVB)/PVC systems. Recently, Djomo and co-workers⁶ have reported the mechanical properties of semi-interpenetrating networks composed of a PSt-PVC blend, in which PSt has a network structure by copolymerization with DVB. PSt network structure slightly enhances the tensile and impact strengths.

In order to throw light on the structure of the base membrane by the paste method, P(St-DVB)/PVC was prepared as a model of the base membrane without using any reinforcing material, and also characterized by infrared spectroscopy, transmission electron microscopy, and the dynamic mechanical test relating to microheterogeneity. Furthermore, the Takayanagi model⁷ was applied to investigate the dynamic mechanical behavior of the P(St-DVB)/PVC systems.

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, and distilled under nitrogen atmosphere. The DVB used is composed of *m*- and *p*-diethylbenzene (2.5%), *m*- and *p*-ethylvinylbenzene (42%), *m*- and *p*-DVB (55%), and 0.5% of other compounds. The fine PVC powder used was a commercial product by emulsion polymerization ($\bar{P}_n = 600$, particle diameter = 0.20–0.55 μ). The procedures to prepare the samples, P(St-DVB)/PVC, P(St-DVB), and PSt/PVC, are shown in Figure 1. A fine PVC powder was mixed with the monomer mixtures containing benzoyl peroxide (BPO) at room temperature with stirring. The paste obtained was then placed in an air-tight container, and the monomers were copolymerized at 80°C for 5 h.

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

| Sample | No. | St ^b | DVB ^b | PVC ^b |
|-----------------------|-------|-----------------|------------------|------------------|
| P(St-DVB)/PVC systems | A-1-2 | 9.5 | 0.5 | 5.0 |
| | A-2-2 | 9.0 | 1.0 | 5.0 |
| | A-3-2 | 8.0 | 2.0 | 5.0 |
| P(St-DVB) copolymers | M-0-2 | 9.0 | 1.0 | — |
| | M-1-2 | 8.0 | 2.0 | — |
| | M-2-2 | 7.4 | 2.6 | — |
| | M-3-2 | 8.7 | 1.3 | — |
| PSt/PVC composite | C-1-2 | 10.0 | — | 5.0 |

^a Polymerized at 80°C for 5 h in nitrogen atmosphere.

^b Compositions of St, DVB, and PVC are listed as weight parts.

Analysis of Polymers

P(St-DVB)/PVC, P(St-DVB), and PSt/PVC samples were crushed, and then extracted under nitrogen atmosphere with tetrahydrofuran (THF) for 20 h by using a Soxhlet extractor. The THF-extracted portion of the PSt/PVC composite was further extracted with benzene for 10 h. The compositions of each fraction were determined by IR spectroscopy. Molecular weight distributions of the benzene-extracted portion and the residue were determined at 23°C in a THF solution by gel permeation chromatography (GPC).

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 ($\tan \delta$) were measured between 20°C to 180°C with a heating rate of about 1°C/min. The sample dimensions were of the order of 0.2 × 0.8 × 8.0 cm.

The morphological analyses of the PSt/PVC composite and P(St-DVB)/PVC systems were performed by a transmission electron microscopy (HU-12 from Hitachi Ltd.). Ultrathin sections about 1000 Å thick were prepared at room temperature by an ultramicrotome and stained by exposure to the vapor of aqueous osmium tetroxide solutions at room temperature for 2 days. Consequently, the electron micrographs show that the PVC phase is dark, and the PSt and P(St-DVB) phases are bright.

RESULTS AND DISCUSSION

Characterization

Table I shows the recipe of the prepared samples. The copolymerization conversions of all the samples were more than 95%. First, the samples were fractionated by the THF extraction.

(1) The P(St-DVB) copolymers were not extracted by THF.

(2) The extracted portions (33–34%) of the P(St-DVB)/PVC systems (samples A-1-2, A-2-2, A-3-2) consist of PSt and PVC, and the extraction residue contains P(St-DVB) copolymer and a very small amount of PVC, indicating that the

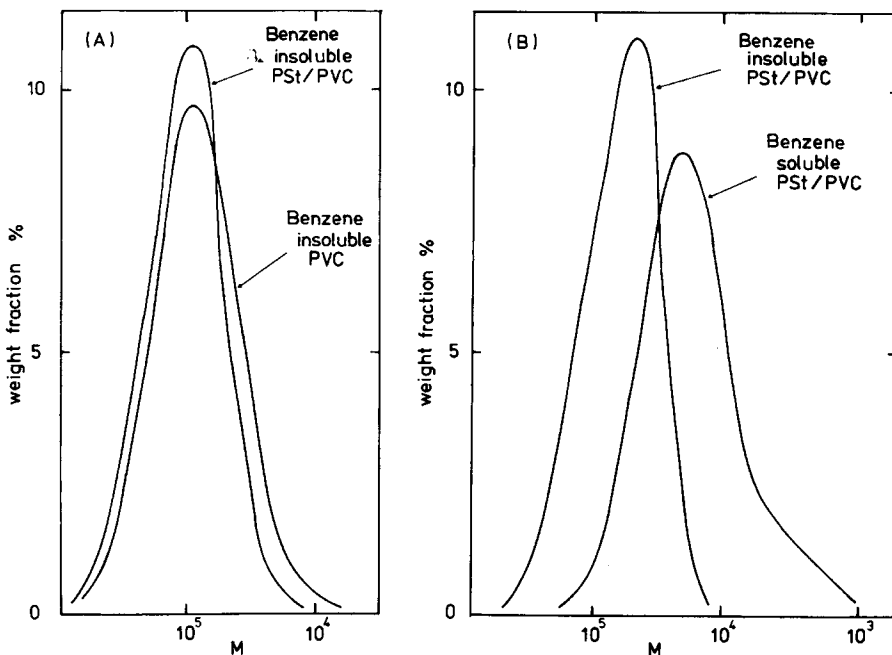


Fig. 2. GPC chromatograms of PSt/PVC composite: (A) differential refractometer; (B) UV absorption at 254 nm.

portions inextractable by THF of the P(St-DVB) copolymers and P(St-DVB)/PVC systems are composed of the crosslinked St-DVB copolymer.

(3) The PSt/PVC composite consists of only the THF-extracted portion, which subsequently was extracted by benzene. The THF-extracted portion of the PSt/PVC composite was successively extracted with benzene. The benzene-extracted portion (62%) consists of only PSt, and the extraction residue (35%) consists of PSt and PVC (PSt content = 14%). Figure 2 shows the GPC chromatograms of fractionated portions by the benzene extraction, elucidating that the GPC chromatogram of the benzene-insoluble fraction detected by differential refractometer shifts to the higher molecular weight side, compared with the chromatogram of the benzene-insoluble PVC. Further, the molecular weight of the PSt contained in the benzene-insoluble fraction is higher than that of the benzene-soluble fraction, supported by the fact that the peak of the former detected by UV absorption at 254 nm is observed at higher molecular weight side than that of the benzene-soluble fraction. These facts suggest that the PSt contained in the benzene-insoluble portion is the grafting PSt onto PVC (PSt-g-PVC), because of the restricted solubility of the backbone PVC.⁸

Assuming that the extraction residue is the graft copolymer, the degree of grafting and the grafting efficiency are estimated by the following equations:

$$\text{degree of grafting} = \frac{\text{wt grafting PSt}}{\text{wt PVC}} \times 100$$

$$\text{grafting efficiency} = \frac{\text{wt grafting PSt}}{\text{wt polymerized PSt}} \times 100$$

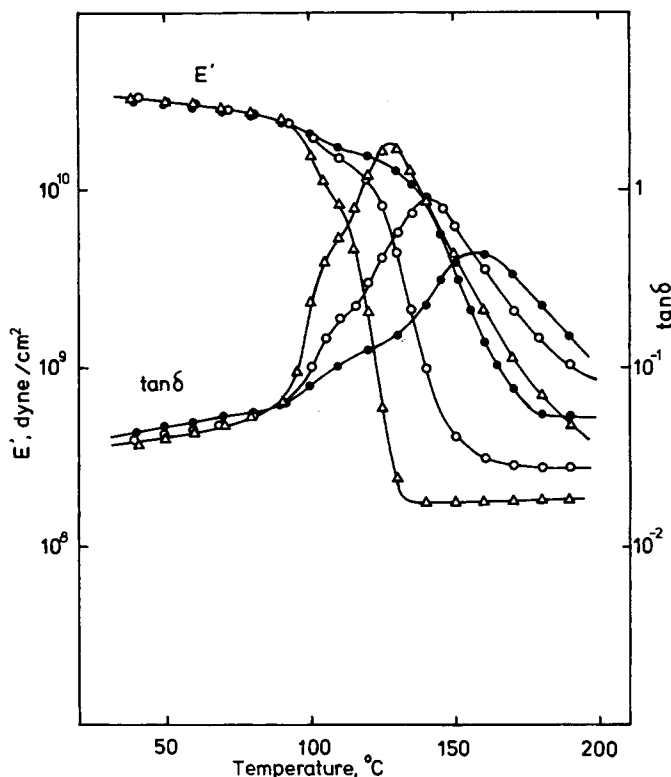


Fig. 3. Dynamic viscoelastic behaviors of P(St-DVB) copolymers: (Δ) sample M-0-2; (\circ) sample M-1-2; (\bullet) sample M-2-2.

The degree of grafting and the grafting efficiency of PSt/PVC composite were 15.8% and 7.2%, respectively, indicating that this polymerization method gives high grafting efficiency compared with the solution polymerization. These experimental facts suggest that P(St-DVB)/PVC should contain a similar amount of PSt-*g*-PVC or P(St-DVB)-*g*-PVC.

Dynamic Viscoelastic Behavior and Morphology

P(St-DVB) Copolymers

The dynamic mechanical test is a sensitive measurement of crosslinking or heterogeneity in the crosslinked structure at temperatures above the glass transition temperature (T_g). The crosslinked structure of P(St-DVB) copolymers were investigated by the value of storage modulus (E_r) at rubbery state and the peak temperature of $\tan \delta (T_\delta)$. Figure 3 shows the viscoelastic behaviors of P(St-DVB) copolymers. The peak of $\tan \delta$ becomes broader and shifts to a higher temperature with an increase in the DVB content, accompanied by an increase in the magnitude of the storage modulus at rubbery state, inherently due to the increase in the crosslinking density and the heterogeneity in the crosslinked structure. The values of crosslinking density (D_e), E_r , and T_δ are shown in Table II. (D_e is calculated from E_r by the equation $D_e = E_r/3dRT$, where d = density of polymer, R = gas constant, T = temperature).

TABLE II
Crosslinking Densities of P(St-DVB) Copolymers

| Sample | DVB ^a wt fraction | E_r^b (dyn/cm ²) | D_n^c (mol/g) | D_e^d (mol/g) | T_δ^e (°C) |
|--------|---------------------------------|-----------------------------------|-----------------------|-----------------------|----------------------|
| M-0-2 | 0.1 | 1.70×10^8 | 4.23×10^{-4} | 1.43×10^{-3} | 128 |
| M-1-2 | 0.2 | 2.65×10^8 | 8.46×10^{-4} | 2.28×10^{-3} | 141 |
| M-2-2 | 0.26 | 5.70×10^8 | 1.10×10^{-3} | 4.80×10^{-3} | 157 |
| M-3-2 | 0.13 | 2.30×10^8 | 5.50×10^{-4} | 1.94×10^{-3} | 136 |

^a DVB content of monomer mixture [DVB/(DVB + St)], listed as weight fraction.

^b Storage modulus at rubbery state.

^c Crosslinking density calculated from DVB content.

^d Crosslinking density calculated from E_r .

^e Peak temperature of $\tan \delta$.

Figure 4 shows the relation between the crosslinking density (D_n) calculated from the DVB content and T_δ . The peak of $\tan \delta$ shifts to a higher temperature with the increase in the D_n value. The shoulder peak in the temperature range of 95–110°C corresponds to the glass transition region of PSt. These samples are not extracted by THF, and thus the copolymer networks of these samples are composed of a tightly crosslinked network and a loosely crosslinked structure. This two-phase structure, with the different crosslinking densities, is in agreement with the copolymerization kinetics reported by Kagiya et al.⁴ and Popov and Schwachula,⁹ who have deduced that DVB is more preferentially copoly-

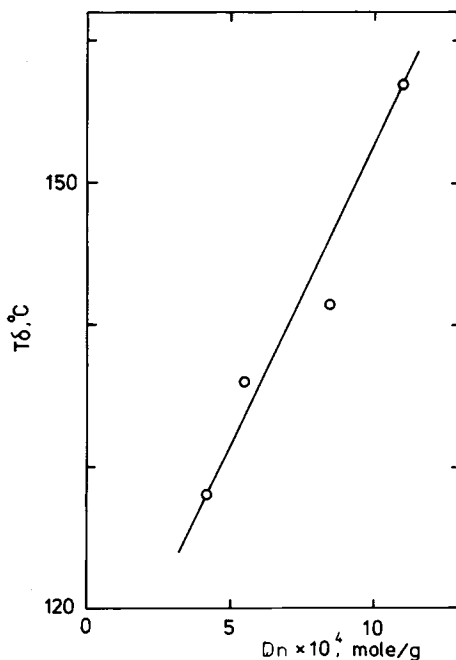


Fig. 4. Correlation of crosslinking density (D_n) of P(St-DVB) copolymers calculated from DVB content and peak temperatures of $\tan \delta$ (T_δ).

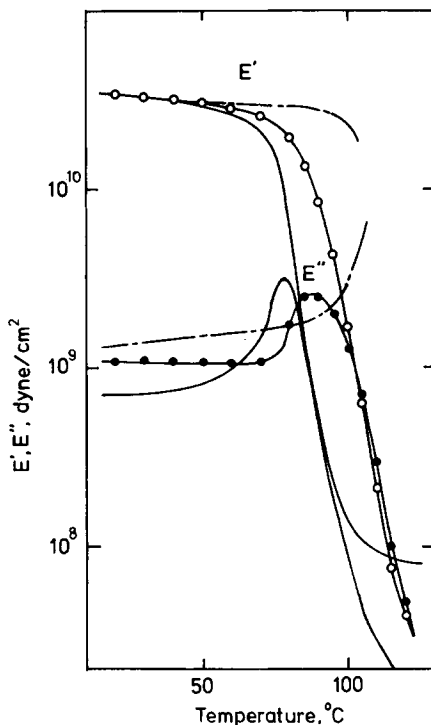


Fig. 5. Dynamic viscoelastic behavior of PSt/PVC composite: (○) E' ; (●) E'' ; (—) PVC; (---) PSt.

merized than St in the early stage of copolymerization and the loosely crosslinked copolymers are formed in the latter stage due to the decrease in the DVB concentration.

These results suggest that the copolymerization of St and DVB induces many tightly crosslinked copolymers in the early stage, and the crosslinking density of those is too much larger than that estimated from the DVB content in the recipe to be responsible for the large shift of $\tan \delta$ to higher temperature, as shown in Figure 4.

Table II also shows that D_e is three or four times larger than D_n . This fact is ascribed to physical crosslinks because the loosely crosslinked network superposes on the tightly crosslinked network to form physical crosslinks, similar to Shibayama and Suzuki's results¹⁰ on the multiple network of styrene-divinylbenzene copolymers.

PSt/PVC Composites

As Figure 5 shows, in the dynamic viscoelastic behaviors of the PVC, PSt, and PSt/PVC composite, only one broadened E'' peak of the PSt/PVC composite (C-1-2) is observed in the glass transition region. The blend of PSt-PVC exhibits two distinct peaks of E'' ,¹¹ somewhat shifted toward one another, as would be expected from each value of the solubility parameters (i.e., the solubility parameters of PSt and PVC calculated by Hoy's method¹² are 9.05 and 9.47, re-

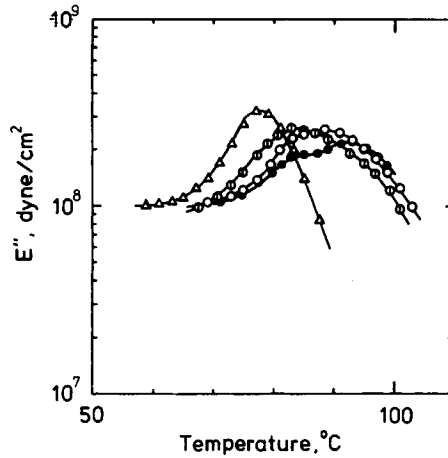


Fig. 6. Dynamic viscoelastic behavior of PSt/PVC composites at various St/PVC ratios in the recipe: (Δ) PVC; (\odot) St/PVC = 1.3; (\circ) St/PVC = 2.0; (\bullet) St/PVC = 4.0.

spectively). The peak temperature of E'' , as shown in Figure 6, shifts slightly to the higher temperature side with the increase in the PSt content, while the PSt/PVC composite with the composition ratio of St/PVC above 4.0 (weight ratio) has two peaks.

Figure 7 shows two E'' peaks of the PSt/PVC composite polymerized at 65°C for 6 h and successively polymerized at 110°C for 2 h (the composition ratio of St/PVC is 2.0 by weight).

Figure 8(A) exhibits the electron microphotograph of the PSt/PVC composite,

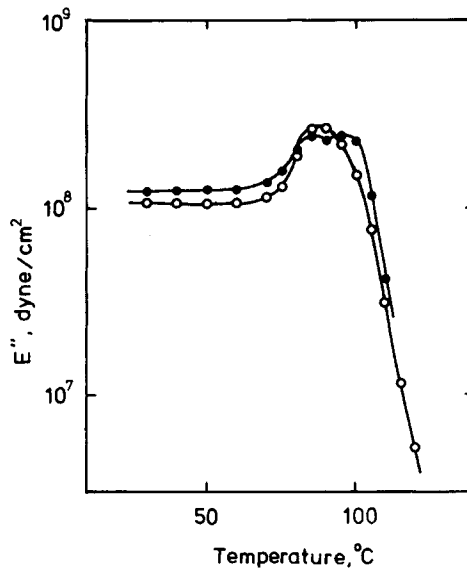


Fig. 7. Loss moduli of PSt/PVC composites: (\circ) polymerized at 80°C for 5 h; (\bullet) polymerized at 65°C for 6 h and successively polymerized at 110°C for 2 h.

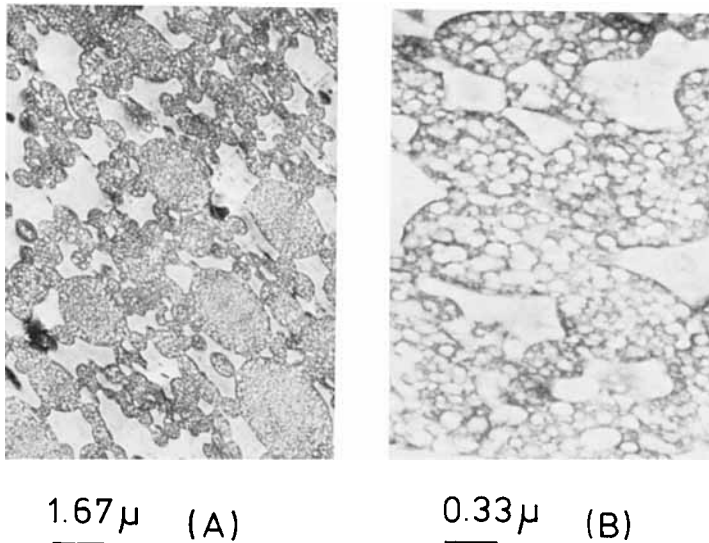


Fig. 8. Electron micrographs of PSt/PVC composites (C-1-2).

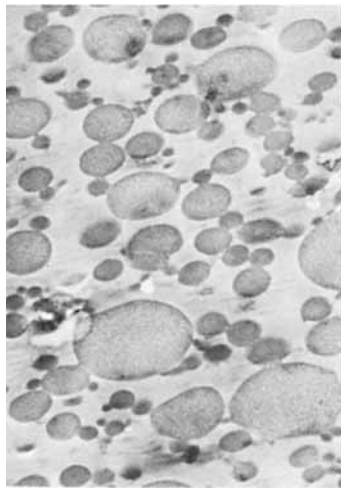
showing that the PVC phase is the dark portion and the PSt phase is the bright portion. Figure 8(B) shows that the size of the dispersed PSt in the PVC domain is 500–2000 Å.

In general, the dynamic mechanical data of the blend of compatible polymers, such as NBR and PVC,¹³ have only one peak of E'' . However, a single broadened peak is observed in the PSt/PVC composite, in spite of the two-phase nature, by electron microscopy. This result is a puzzle, but the authors deduce that the PSt/PVC composite contains not only PSt-*g*-PVC but also PSt finely dispersed in the PVC domain and that the glass transition temperatures of PSt and PVC are close to each other. When the composition of St/PVC is more than 4.0, two peaks are observed, as shown in Figure 6, owing to the fact that the PSt phase becomes much larger and forms the continuous phase.

Figure 9 shows the electron microphotograph of the PSt/PVC composite polymerized at 65°C for 6 h and successively polymerized at 110°C for 2 h. PSt (bright portion) forms the continuous phase, and also PSt is finely dispersed in the PVC domain. The two peak temperatures of E'' are observed at 85°C and 95°C, as shown in Figure 7: the former corresponds to the glass transition of the dispersed phase, and the latter corresponds to that of the continuous phase. The amount of PSt dispersed in the PVC domain of this sample is smaller than that of sample C-1-2 polymerized at 80°C for 5 h due to the fact that the polymerization temperature in the first stage is below T_g of PVC, i.e., the diffusion of St into the PVC domain is more difficult, resulting in the two peaks of E'' .

These results suggest that the polymerization of St in the presence of PVC significantly improves the compatibility of PSt and PVC, incompatible components, but the heterogeneity of PSt/PVC depends on the polymerization temperature and the St/PVC ratio in the recipe.

Furthermore, Figures 5–7 show that the peak temperature of the phase-separated PSt phase of the PSt/PVC composite is 95°C though the peak tempera-



1.67 μ

Fig. 9. Electron micrograph of PSt/PVC composite polymerized at 65°C for 6 h and successively polymerized at 110°C for 2 h.

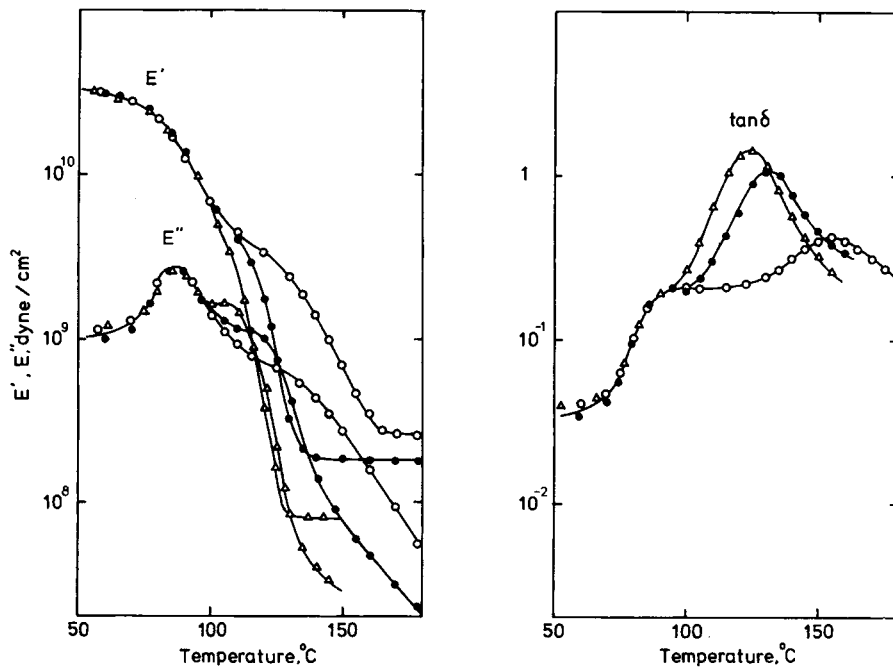


Fig. 10. Dynamic viscoelastic behaviors of P(St-DVB)/PVC systems: (Δ) sample A-1-2; (\bullet), sample A-2-2; (\circ) Sample A-3-2.

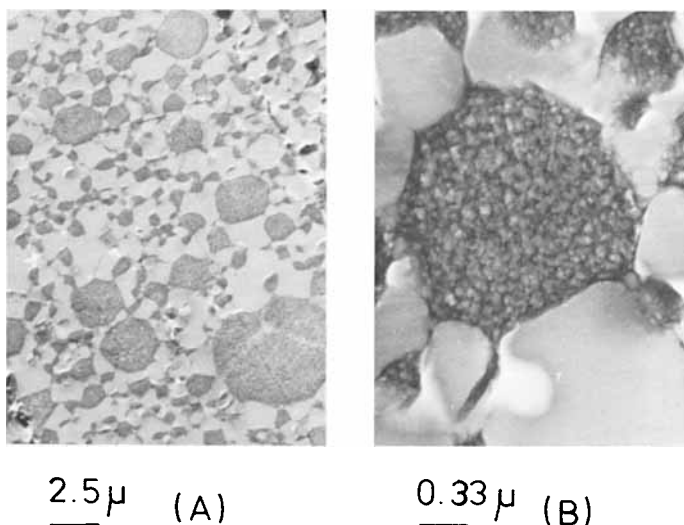


Fig. 11. Electron micrographs of P(St-DVB)/PVC system (sample A-3-2).

ture of the PSt homopolymer is more than 105°C . The reason is suggested as follows: PSt-*g*-PVC would enhance an interaction between PSt phase and the phase with PSt dispersed in the PVC domain.

P(St-DVB)/PVC Systems

The dynamic mechanical properties and morphologies of P(St-DVB) copolymers and PSt/PVC composites offer the available information for the characterization of the structure of P(St-DVB)/PVC systems. Typical dynamic viscoelastic behavior of P(St-DVB)/PVC systems are shown in Figure 10. There exist two $\tan \delta$ peaks in all the samples. The first peak at a lower temperature remains unaffected both in magnitude and position, whereas the second peak at a higher temperature decreases in magnitude and shifts toward the temperature side higher than would be expected by the P(St-DVB) copolymer with the same composition of DVB/(St + DVB). In addition to the change of the peak position, Figure 10 shows that the second peak of $\tan \delta$ is greatly broadened with increasing the DVB content. If there were no distribution in the length of chains between crosslinks, the transition region would remain fairly sharp as it does in a linear polymer. The position of the first $\tan \delta$ peak is consistent with that of PSt/PVC composite independent of DVB content, and the peak position of E'' remains constant and is the same as that of the peak of PSt/PVC composite in the position and magnitude.

These experimental facts indicate that P(St-DVB)/PVC systems consist of two phases: one is composed of PSt and PVC likely for the microstructure of the PSt/PVC composite (PSt-PVC phase), and the other phase is attributed to the crosslinked P(St-DVB) component with phase continuity, suggested by the storage modulus of more than 10^8 dyn/cm² at rubbery state.

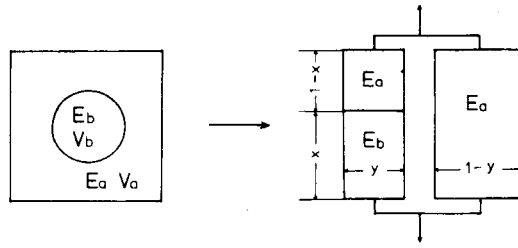


Fig. 12. Morphological and mechanical models of P(St-DVB)/PVC systems. E_a : elastic modulus of P(St-DVB) phase; E_b : elastic modulus of PSt-PVC phase; V_a : Volume fraction of P(St-DVB) phase; V_b : Volume fraction of PSt-PVC phase.

Electron microscopy on these samples, as shown in Figure 11(A), confirms the viscoelastic behaviors and explicitly shows the microheterogeneity of the system and the phase domain size. The bright portion is the continuous P(St-DVB) phase and the dark portion is the PSt-PVC phase of $0.5\text{--}2.0\ \mu$ in diameter, as shown in Figure 11(B), in which PSt is finely dispersed in the PVC domain; and perhaps there exists P(St-DVB)-*g*-PVC in the interfacial zone of two phases.

The volume fractions of the PSt-PVC phase and the P(St-DVB) phase ob-

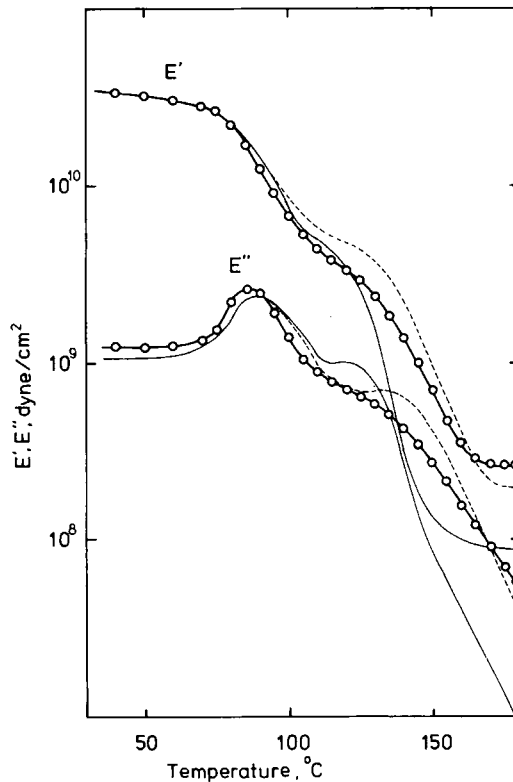


Fig. 13. Temperature dependences of E' , E'' of P(St-DVB)/PVC system (sample A-3-2) calculated by Takayanagi's equation: (O) observed; (—) sample M-1-2 [P(St-DVB) copolymer] as a continuous phase; (---) sample M-2-2 [P(St-DVB) copolymer] as a continuous phase.

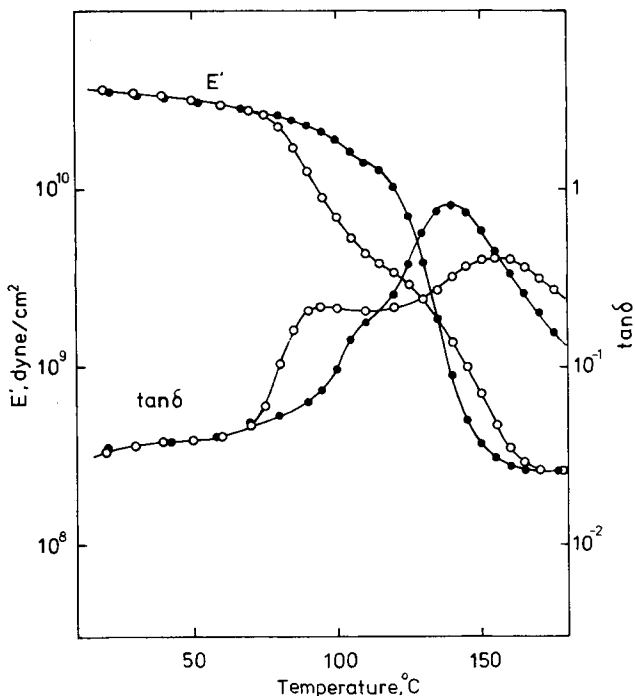


Fig. 14. Dynamic viscoelastic behavior of P(St-DVB)/PVC system and P(St-DVB) copolymer: (O) P(St-DVB)/PVC system (sample A-3-2); (●) P(St-DVB) copolymer (sample M-1-2).

tained from the electron micrograph shown in Figure 11(A) were 0.44 and 0.56, respectively. Assuming that the dispersed phase composed of PSt and PVC contains little P(St-DVB) copolymer because the position of the second peak of $\tan \delta$ (or the peak of E'') is independent of the DVB content, we proposed the model structure of P(St-DVB)/PVC as shown in Figure 12. This model conflicts with the morphology of the "paste method" cation-exchange membranes by treatment with hydrogen peroxide, proposed by Mizutani et al.,^{2,3} i.e., in the base membrane for the cation exchange membrane, the styrene-divinylbenzene copolymer is the dispersed phase and the PVC is the continuous one. However, the cation-exchange membrane contains the reinforcing material (PVC cloth), which is swollen with St and DVB in the process of paste coating and thermal polymerization. Thus the dominant factor is the difference of the compositions of PVC/(St + DVB) between our samples and the cation exchange membranes, which is responsible for the phase transition.

Based on this model structure, we calculated the storage and loss moduli of P(St-DVB)/PVC system (A-3-2) from those values of PSt/PVC composite (C-1-2) and P(St-DVB) copolymer (M-1-2) at various temperatures from 20°C to 180°C by using Takayanagi's equation as follows:

$$E^* = \left(\frac{y}{(1-x)E_a^* + xE_b^*} + \frac{1-y}{E_a^*} \right)^{-1}$$

where $x = (2 + 3V_a)/5$, $y = 5V_b/(2 + 3V_a)$, V_a = volume fraction of P(St-DVB) phase, and V_b = volume fraction of PSt-PVC phase. This calculation was per-

formed assuming that the dispersed PSt-PVC phases are spheres, and the results are shown in Figure 13. These calculated values agree with the experimental results in the temperature range from 20°C to 110°C, but the calculated values deviate from the experimental results at temperatures above 110°C.

Figure 14 shows the viscoelastic behaviors of the P(St-DVB)/PVC system (A-3-2) and the P(St-DVB) copolymer (M-1-2). In spite of the same DVB/(St + DVB) ratio in the recipe, the peak positions of $\tan \delta$ [P(St-DVB)/PVC system] and of $\tan \delta$ (PSt/PVC composite) are, respectively, 155°C and 130°C. This peak position of $\tan \delta$ of P(St-DVB)/PVC is nearly equal to that of the P(St-DVB) copolymer (M-2-2) as shown in Table II, and the crosslinking density of the P(St-DVB)/PVC system (A-3-2) is as large as that of the P(St-DVB) copolymer (M-2-2 [St/DVB = 7.4/2.6]). Thus the crosslinking density of the P(St-DVB) phase in the P(St-DVB)/PVC system should increase more than the value that would be estimated from the DVB/(St + DVB) ratio.

On the basis of the above consideration, the storage and loss moduli of the P(St-DVB)/PVC system (A-3-2), as shown in Figure 13, were calculated according to Takayanagi's equation, assuming that the P(St-DVB) copolymer (M-2-2) is the continuous phase. The calculated curves are in good agreement with the observed data. Thus, the crosslinking density of the continuous P(St-DVB) phase is assumed to be much higher than that estimated from the DVB/(St + DVB) ratio in the recipe, and the PSt-PVC dispersed phase contains a small amount of the DVB unit, the reason for which is probably ascribed to the difference of the diffusion constants of St and DVB into the PVC particles on the paste formation and polymerization process. A detailed investigation of the diffusion of monomers into PVC particles will be dealt with in a subsequent paper.

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