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ORIGINAL CONTRIBUTION

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Effect of interfacial adhesion on the mechanical properties of poly(vinyl chloride) modified with cross-linked poly(methyl methacrylate) particles prepared by seeded emulsion polymerization

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Abstract The effect of interfacial adhesion on the mechanical properties of an incompatible polymer blend was investigated. For this purpose, the preparation of non-cross-linked and cross-linked poly(methyl methacrylate) particles having mean sizes of about 0.8 μm was completed by seeded emulsion polymerization, and the number and the distribution of cross-linked points in the particles were varied. The emulsion particles obtained were powdered by a freeze–dry method and dispersed into a poly(vinyl chloride) matrix by melt blending. The non-cross-linked particles were completely dissolved in the matrix because poly(methyl methacrylate) has good compatibility with poly(vinyl chloride). On the other hand, in the case of the cross-linked particles, the mutual diffusion of the polymer molecules was restricted within the particle/matrix interfacial regions owing to the cross-linked points. Additionally, interfacial structures with different concentration slope dependent upon the number and the distribution of inner cross-linked points were developed with the same domain size. Mechanical and fracture properties were measured. As a result, both yield stress and fracture toughness decreased with a decrease in the interfacial adhesion, and the decrease was found to occur as a result of interfacial debonding. When the interfacial adhesion was sufficient it was never observed that the level was lower than that of the components.

Key words Polymer blend · Compatibility · Interphase · Concentration slope · Emulsion polymerization

Introduction

Polymer composites with which inorganic filler particles are incorporated are widely utilized owing to their excellent performances, especially high specific modulus, thermal stability and low manufacturing cost. However, the yield stress of a ductile polymer such as poly(vinyl chloride) (PVC) is reduced with the incorporation of filler particles [1–5]. That is why some researchers [6–9] and we [4, 10] clarified the mechanism as follows. The particle/matrix interfacial debonding occurs at the yield point followed by the production of a matrix around the voids formed, i.e., the debonding stress becomes lower than the yield stress of the matrix polymer.

In our previous articles [5, 10, 11], it was confirmed that the decrease of yield stress could be depressed by the improvement of interfacial adhesion in the particle-filled PVC. The adhesion was developed by the surface-treatment of particles with a silane coupling agent having an amino group which reacts with PVC at the interfaces as mentioned by Arkles [12]. It was found that the occurrence of the debonding and the formation of the shear bands at the yield point were depressed and delayed by the improvement of the interfacial adhesion, from scanning electron microscope (SEM) observation of the surface of the specimen during the tensile test [10].

Incompatible polymer blends are also utilized in industrial applications. In general, there is poor interaction between the components. That is to say, this is the cause of the debonding at the dispersed domain/matrix interfaces [13, 14], and the yield stress becomes lower than that of the components. Therefore, the interfacial adhesion is essential, in terms of the improvement of the mechanical properties in these systems.

In this study, the effects of the interfacial adhesion on the mechanical and fracture properties were investigated. For this purpose, the preparation of non-cross-linked and cross-linked poly(methyl methacrylate) (PMMA) particles having almost the same particle sizes was completed by seeded emulsion polymerization. By varying the addition period and the concentration of the cross-linking monomer, the amount and the distribution of the cross-linked points in the particles [15] were controlled. These emulsions were dried and the powders obtained were dispersed into the PVC matrix by melt blending. Non-cross-linked PMMA particles can be completely compatible in the PVC matrix [16] because of the well known fact that PMMA has good compatibility with PVC. On the other hand, in the cases of the cross-linked PMMA particles, the cross-linked points restrict the mutual diffusion of the polymer molecules within the interfacial regions. As a result, it was expected that the interfacial structures with different "concentration slope" dependent upon both the amount and the distribution of inner cross-linked points would develop at the interfacial layer with the same domain size. The interfacial structure was characterized, and the investigation of the effects on the mechanical and fracture properties was carried out.

Experimental

Materials

Commercial grade MMA and ethylene glycol dimethacrylate (EGDMA) monomers were purified by distillation under reduced pressure in a nitrogen atmosphere and they were stored in a refrigerator. Analytical grade potassium peroxodisulfate and sodium lauryl sulfate (SLS) were used without further purification as initiator and surfactant, respectively. Commercial grade PVC (Geon 103 EP, Nippon Zeon Co., degree of polymerization: 1050) and lead stearate (Katayama Chemical Industries Co.) as a stabilizer for PVC were used.

Seeded emulsion polymerization

The recipes of seeded emulsion polymerizations are shown in Table 1. The concentration of surfactant (SLS) was lower than the critical micelle concentration. PMMA emulsion 1 was used as a common seed particle. EGDMA was used as a cross-linking monomer. Seeded emulsion polymerization with three stages was carried out to make the particle size larger. In the second and third stages, the monomer was added dropwise during the polymerization process. The PMMA particle obtained (no. 3) without EGDMA is called type A. In the preparation processes for emulsions 4–6, EGDMA was added in the third stage and the mole fraction was varied from 0.5 to 5% by in the final particle: they are called type B. EGDMA was added in the second stage for the no. 8 emulsion to obtain a mole fraction of 2.5%: the particle is called type C. The EGDMA content in the final particles is shown at the end of each type (e.g., type B-5). All the polymerizations were continued until the conversion was above 98%. The emulsions obtained were powdered by a freeze–dry method using a freeze-dryer (FDU-506, Tokyo Rikakikai Co.). The mean particle size determined using a SEM was about 0.8 μm for all the particles prepared.

Sample preparation

PVC, lead stearate (three parts per hundred parts of resin by weight, phr) and PMMA particles (10–50 phr) were mixed using a mixing roll at 200 ± 5 °C for 10 min. About 0.8-mm-thickness

Table 1 Recipe of seeded emulsion polymerization. Polymerization temperature: 70 °C. Atmosphere: N_2

Emulsion no.	1	2	3	4	5	6	7	8
Emulsion no. 1	–	62.70	–	–	–	–	63.15	–
Emulsion no. 2	–	–	10.27	10.30	10.20	10.10	–	–
Emulsion no. 7	–	–	–	–	–	–	–	11.38
Methyl methacrylate (g)	100.70	87.50	127.8	128.53	123.81	118.04	81.41	128.38
Ethylene glycol dimethacrylate (g)	–	–	–	1.40	6.37	12.34	6.19	–
Sodium lauryl sulfate (g)	0.40	–	0.40	0.40	0.40	0.40	–	0.40
Potassium peroxodisulfate (g)	0.40	0.35	0.50	0.50	0.50	0.50	0.35	0.50
Water (g)	400.2	350.0	512.0	510.7	512.5	510.0	350.1	498.7
Polymerization stage	lst	2nd	3rd	3rd	3rd	3rd	2nd	3rd
Methyl methacrylate/Ethylene glycol dimethacrylate A[a]			100/0	99.5/0.5	97.5/2.5	95/5		97.5/2.5
Concentration of cross-linked points[b]			No		Higher in the surface layer			Higher in the inner part
Code[c]			Type A	Type B-0.5	Type B-2.5	Type B-5		Type C-2.5

[a] Mol fraction in the particles finally obtained

[b] Expected from the stage of adding ethylene glycol dimethacrylate during seeded emulsion polymerization

[c] The mole fraction of ethylene glycol dimethacrylate is shown at the end of each type

sheets were prepared by compressing the mixed compounds at 200 °C under a pressure of 19.6 MPa for 2 min. The sheets so prepared were quenched using a cold press.

A conventional PVC/PMMA blend was also prepared to make a comparison with the particle-modified PVCs, and it is called "PMMA blended PVC" here. For this purpose, the PMMA was prepared from type A particles by dissolution in acetone and precipitation in water.

Dynamic mechanical analysis

The viscoelastic behavior was measured using a mechanical spectrometer (Rheolograph Solid S-1, Toyo Seiki Seisaku-Sho) with a frequency of 50 Hz, a constant heating rate of 1 °C/min and an initial tension of 150 g in the same way as previously [14]. The measured temperature range was from 30 to 130 °C.

Mechanical properties

A tensile test was carried out using a dumbbell-type specimen (Japanese Industrial Standard K6301-3 type) having about 0.8-mm thickness with a cross head rate of 5 mm/min and a chuck distance of 40 mm. The detailed conditions are given in previous articles [4, 17]. The yield stress and the elongation at break were measured. The fractured surface of the specimen was observed using a SEM (ABT-60 type, TOPCON Corp.) equipped with an electron probe microanalyzer (EPMA, DX-4 type, Philips Japan).

Fracture toughness

The fracture toughness for PVC was measured in accordance with the technique developed by Kim and Joe [18, 19] and applied by Nabi and Hashemi [20], Ha et al. [21] and others [22, 23] based on the nonlinear elastic fracture mechanics and the *J*-integral characterization. A single-edge notched (SEN) specimen having 100 -mm length, 10-mm width and about 0.8-mm thickness was prepared. A saw was used to make the slot, and a sharp initial crack was introduced using a new razor blade at the base of the slot. The total crack length varied in three levels of 3, 5 and 7 mm, approximately. The stress–displacement curve during the tensile test was recorded with a cross head rate of 5 mm/min and a chuck distance of 40 mm. The locus of crack initiation on the stress–displacement curve was determined, and the area enclosed by the curve, the locus line of the crack initiation point and the *x*-axis were measured as an energy for crack propagation (U_c). The linear relation between U_c/B and the crack length was plotted, in which B means the specimen thickness. From the slop of the relation, the essential fracture energy for a ductile polymer, J_c, was measured according to the following equation.

$$J_c = \frac{-1 \Delta U_c}{B \, \Delta a} \qquad (1)$$

Results and discussion

In this study, the cross-linked PMMA particles were prepared by seeded emulsion polymerization with three stages. The cross-linking monomer (EGDMA) was added in the third (final) stage for the type B particles, whereas it was added in the second stage for the type C particles as shown in Table 1. As a result, a different concentration slope of the cross-linked points was expected to be formed in the particle as follows:

1. Type A: no cross-linked points.
2. Type B: higher in the surface layer.
3. Type C: higher in the inner part.

In the type B particles, the number of cross-linked points in the particle should increase with an increase in the concentration of EGDMA added. Additionally, different interfacial structures with concentration slope with the same domain size should be formed in the PVCs modified with the type B and C particles.

The temperature dependence of the loss moduli (E'') measured by a dynamic mechanical analysis of PVC, PMMA and the particle-modified PVCs at a particle content of 50 phr is shown in Fig. 1. Only the temperature range including the E'' peaks corresponding to the α-transition temperatures are shown. The peaks for PVC and PMMA were observed at 102 and 125 °C, respectively. The type A particle-modified PVC showed a single peak between these peaks at about 117 °C. This means that PMMA has good compatibility with PVC and both components form a single phase [16]. A similar peak temperature was observed in the PVC blended with PMMA (the data is not shown in Fig. 1).

Next, to clarify the above point, the dynamic mechanical analysis for the type A particle-modified PVC with different PMMA content was carried out, and the E'' peak temperature and the storage modulus (E') in the glassy state (40 °C) are shown in Fig. 2. The closed circle shows the calculated E'' peak temperature (T_{calc}) using the following Fox equation [24, 25]:

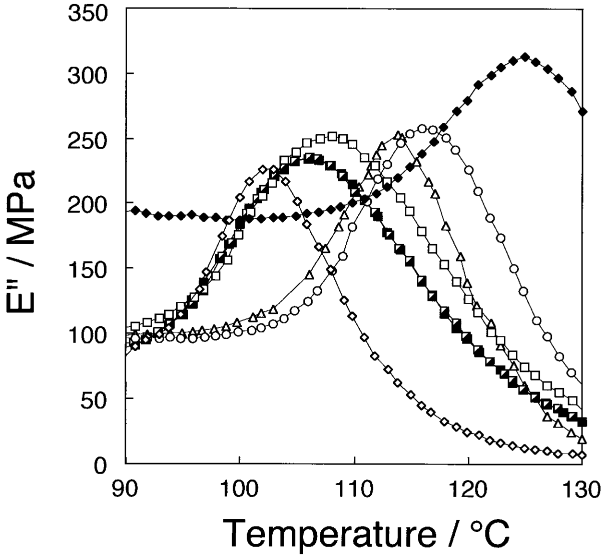


Fig. 1 Temperature dependence of loss moduli (E'') measured by a dynamic mechanical analysis of unmodified poly(vinyl chloride) *PVC* (◇) and poly(methyl methacrylate) (*PMMA*) (◆) and modified PVCs with non-cross-linked (○) and cross-linked (□, half-filled square, ■, △) PMMA particles. Modified particles: type A (○); type B-0.5 (□); type B-2.5 (half-filled square); type B-5 (■); type C-2.5 (△). Measurement frequency: 50 Hz. PMMA particle content: 50 phr

$$\frac{1}{T_{\mathrm{calc}}} = \frac{W_{\mathrm{PVC}}}{T_{\mathrm{PVC}}} + \frac{W_{\mathrm{PMMA}}}{T_{\mathrm{PMMA}}} \ , \qquad (2)$$

where W_{PVC} and W_{PMMA} are weight fractions and T_{PVC} and T_{PMMA} are E'' peak temperature for PVC and PMMA, respectively. The measured values are shown as open circles and they were higher than the calculated values. This indicated that the strong interaction, namely the dipole–dipole interaction between the H—C—Cl and C = O groups was formed in the system as Havriliak and Shortridge [26] reported. On the other hand, E' at 40 °C increased linearly with an increase in the PMMA content. This indicates that the interaction between PVC and PMMA molecules had a stronger affect on the α-transition temperature than on the modulus in the glassy state. The shift of the E'' peak seemed to correspond to the degree of mutual diffusion of PVC and PMMA molecules.

The E'' peak temperatures for types B-0.5 (□), B-2.5 (half-filled square), B-5 (■) and C (△) particle-modified PVCs are shown in Fig. 1 and were 108, 107, 106 and 114 °C, respectively. They were lower than the peak temperature for type A particle-modified PVC, and they decreased in the order type C-2.5 > B-0.5 > B-2.5 > B-5. In these cases, the mutual diffusion of PVC and PMMA is restricted within the interfacial regions owing to the cross-linked points. Therefore, the concentration slope at the interfacial layer was expected to be dependent upon the number and the distribution of cross-linked points in the particles, and the concentration slope is likely to fit the above order.

All the type B and C modified PVCs also showed single E'' peak as shown in Fig. 1, although they have a heterogeneous structure in which the cross-linked PMMA particles were dispersed in the PVC matrix. We presume the reason is as follows. The dispersed particle size was very small (about 0.8 μm) and this gives them a large interfacial area. As a result, the shape and

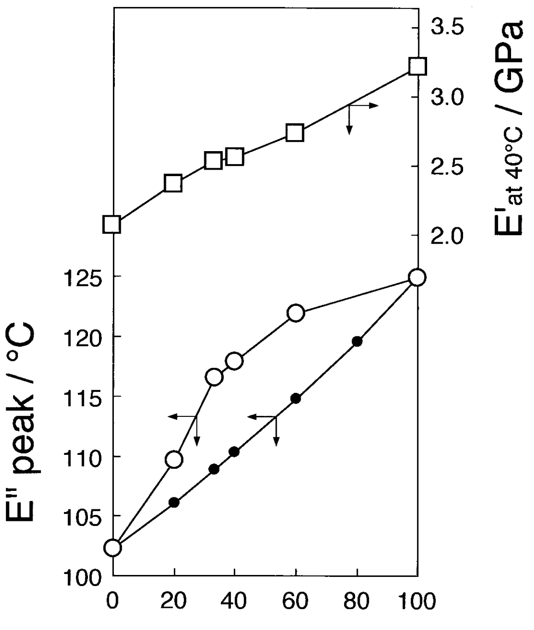


Fig. 2 Storage modulus (E') at 40 °C (□) and measured (○) and calculated (●) peak temperatures of E'' measured by a dynamic mechanical analysis of PVC modified with non-cross-linked PMMA particles (type A). Measurement frequency: 50 Hz

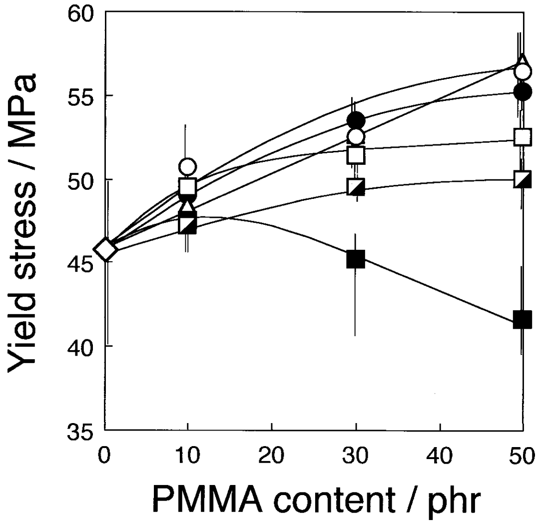


Fig. 3 Yield stress of PVC modified with non-cross-linked (○) and cross-linked (□, half-filled square, ■, △) PMMA particles and blended with PMMA (●). Modified particles: type A (○); type B-0.5 (□); type B-2.5 (half-filled square); type B-5 (■); type C-2.5 (△)

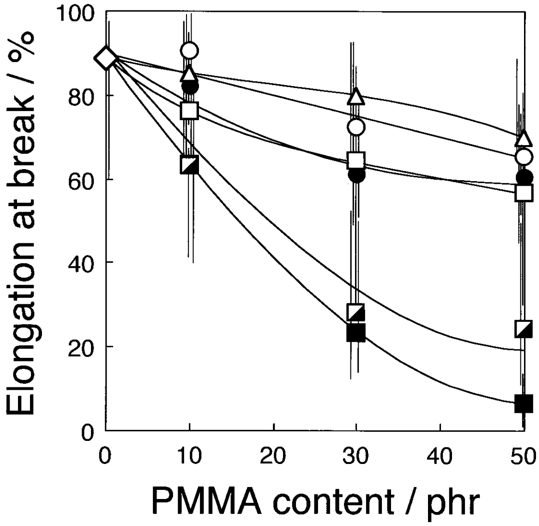


Fig. 4 Elongation at break of PVC modified with non-cross-linked (○) and cross-linked (□, half-filled square, ■, △) PMMA particles and blended with PMMA (●). Modified particles: type A (○); type B-0.5 (□); type B-2.5 (half-filled square); type B-5 (■); type C-2.5 (△)

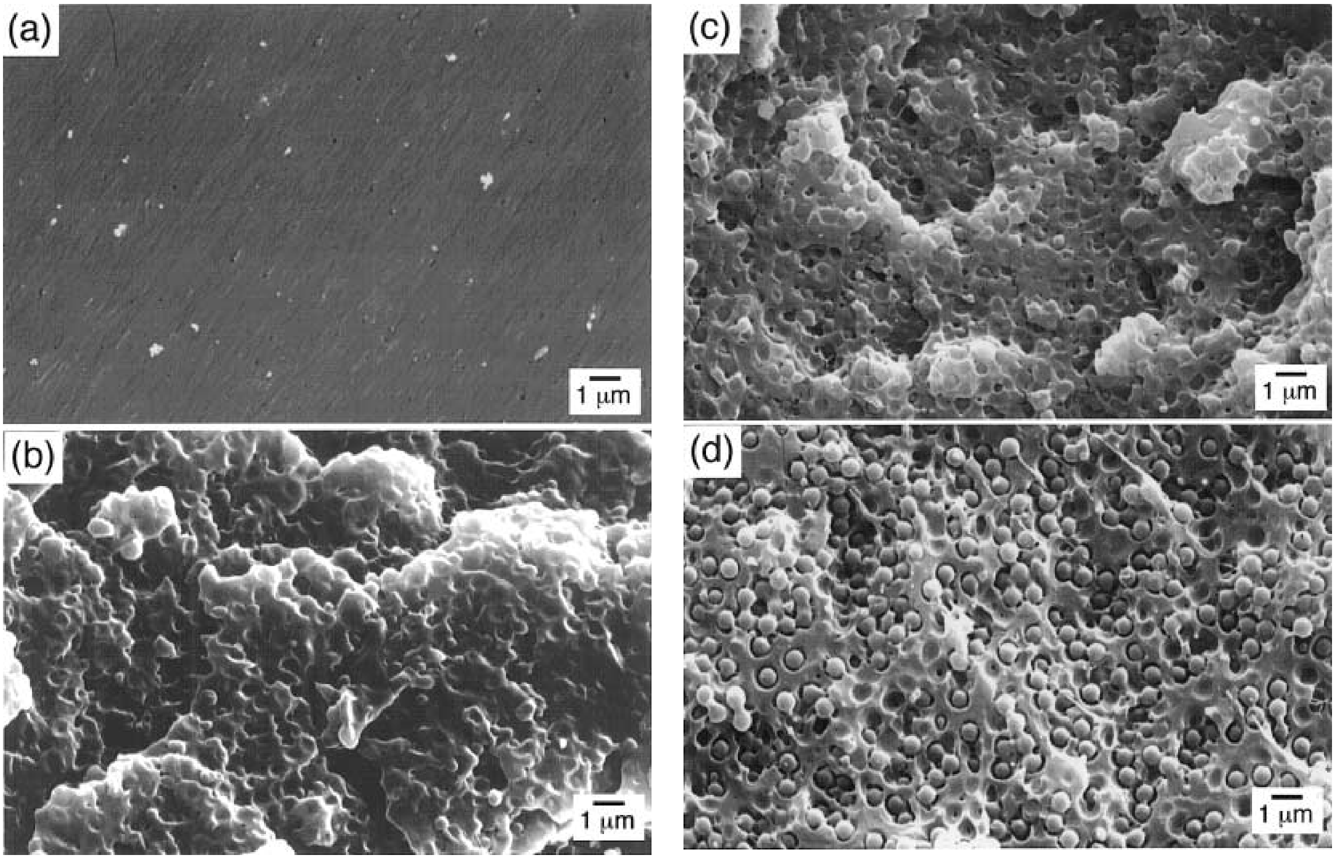


Fig. 5 Fractured surfaces after tensile test observed using a scanning electron microscope (*SEM*) of PVC modified with **a** non-cross-linked and **b**–**e** cross-linked PMMA particles at a particle content of 50 phr. Modified particles: **a** type A, **b** type B-0.5, **c** type B-2.5, **d** type B-5, **e** type C-2.5

the temperature of the E'' peak were affected by the interfacial area far more strongly than the inner domain.

The yield stress of particle-modified PVCs is shown in Fig. 3. The yield stress increased with an increase in the particle content in the type A particle-modified PVC. Similar tendencies were observed in the PMMA blended and the type C-2.5 particle-modified PVCs. In the type B particle-modified PVCs, the yield stress was lower than these values above 30 phr and it decreased more remarkably with an increase in the number of cross-linked points in the particles.

The elongation at break of the particle-modified PVCs is shown in Fig. 4. The elongation decreased gradually with an increase in the PMMA content for type A, B-0.5 and C-2.5 particle-modified PVCs and for the PMMA blended PVCs. However, it became clear that the elongation was far lower in the type B-2.5 and B-5 particle-modified PVCs than in the other PVCs.

From these results, it was clarified that the yield stress and the elongation at break were strongly affected by both the number and the distribution of cross-linked points in the particles. The mechanical properties

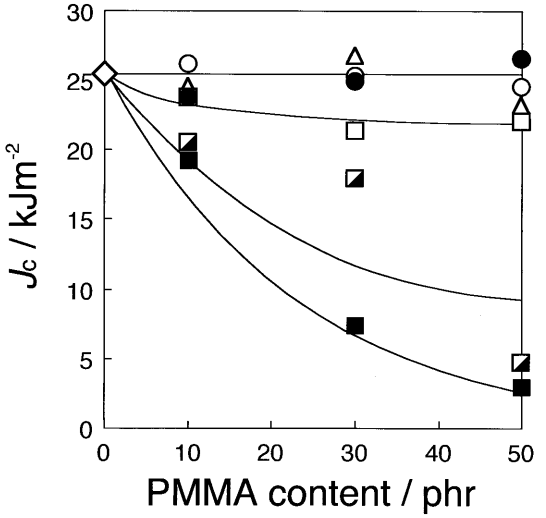


Fig. 6 Fracture energy, J_c, of PVC modified with non-cross-linked (○) and cross-linked (□, half-filled square, ■, △) PMMA particles and blended with PMMA (●). Modified particles: type A (○); type B-0.5 (□); type B-2.5 (half-filled square); type B-5 (■); type C-2.5 (△)

developed with a decrease in the number of cross-linked points within the type B particle-modified PVCs. Additionally, the better mechanical properties were obtained in the modified PVC with particles having the cross-linked points at the inner part (type C) than at the outer layer (type B).

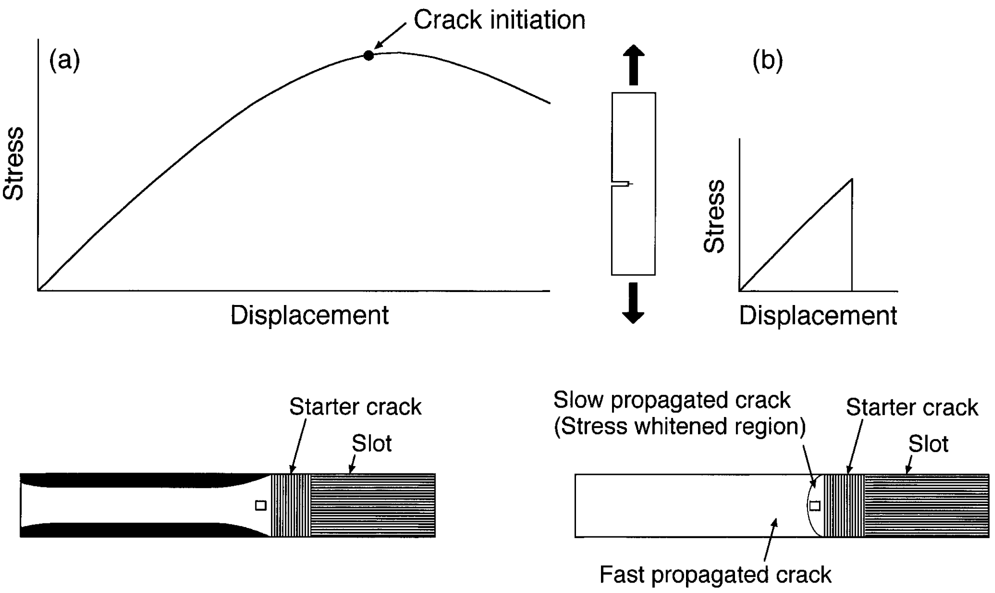
The fractured surfaces appearing after the tensile test observed using the SEM are shown in Fig. 5. In type A (Fig. 5a), no particles were observed on the surface. This indicated that the PMMA particles have good compatibility with the PVC matrix. A similar result was obtained in the PMMA-blended PVC (the data is not shown in Fig. 5).

On the other hand, in type B-5 (Fig. 5d), the mixed particles were clearly observed on the fractured surface and the interfaces were completely debonded. They had almost the same sizes as the modified type B-5 particles. The particles were also observed in types B-0.5 and B-2.5 (Fig. 5b, c); however, the interfaces became unclearer with a decrease in the number of cross-linked points. That is, it was found that the interfacial adhesion was larger in the order type B-0.5 > B-2.5 > B-5. In type C (Fig. 5e), no particles were observed on the surface and the surface was similar to that of type A (Fig. 5a). These results mean that the interfacial adhesion was stronger in type C-2.5 than in all the type B. These observations are in good accordance with the aspects obtained from the dynamic mechanical analysis shown in Figs. 1 and 2.

The J_c of particle-modified PVCs are shown in Fig. 6. There was no decrease in the J_c for the type A and C particle-modified PVCs and for the PMMA-blended PVCs with an increase in the PMMA content. The J_c values for the type B-0.5 particle-modified PVC were almost the same level as those of the PVCs described earlier. However, the J_c of the type B-5 and B-5 particle-modified PVCs decreased significantly with an increase in the particle content in the modified PVC and the number of cross-linked points in the particles.

The stress–displacement curves recorded during the fracture toughness test and schematic views for a fractured SEN specimen with an initial crack length of about 3 mm for the type B-0.5 (Fig. 7a) and B-5 (Fig. 7b) particle-modified PVCs at a particle content of 50 phr are shown in Fig. 7. In the type B-0.5 particle-modified PVC, a large and ellipsoidal whitened damage zone was formed at the crack tip region before crack initiation, and the crack initiated and propagated slowly

Fig. 7a, b Stress–displacement curves and schematic views for fractured surfaces of the fracture toughness test using a single-edge notched (*SEN*) specimen with about 3-mm initial crack length for PVC modified with cross-linked PMMA particles at a particle content of 50 phr. Modified particles: **a** type B-0.5, **b** type B-5. The region identified by a square mark on the surface of the fractured SEN specimen was the part observed using the SEM shown in Fig. 5



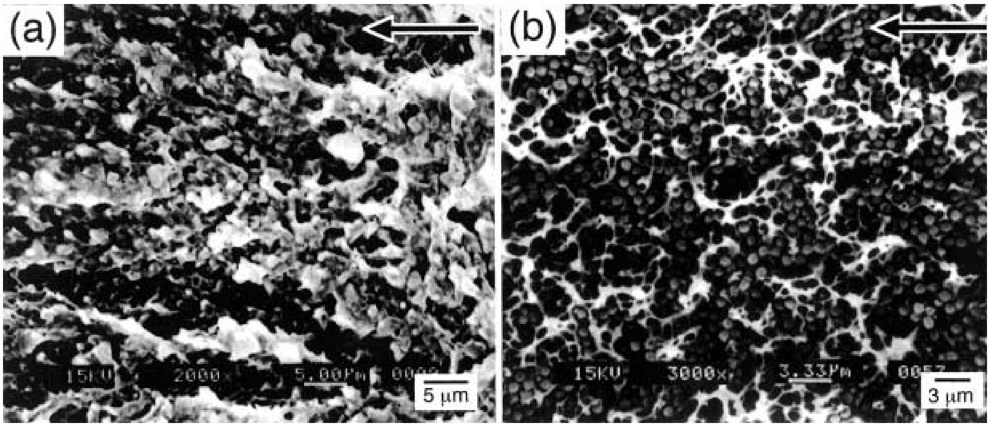


Fig. 8a, b Slowly propagating crack regions of the surface of the fractured SEN specimen observed using a SEM for PVC modified with cross-linked PMMA particles at a particle content of 50 phr. Modified particles: **a** type B-0.5, **b** type B-5. The *arrow* indicates the direction of crack propagation

at the marked point with a closed circle without specimen break. On the fractured surface, a large-scale shrinkage appeared in the direction of the specimen thickness. These are typical features of ductile fracture, and similar features were also observed in type A and C particle-modified PVCs, PMMA-blended PVCs and the blank PVC.

In the type B-5 particle-modified PVC the damage zone never formed before crack initiation, the crack initiated at the lower stress level and the specimen break occurred immediately. On the fractured surface, the shrinkage was appeared, but a small amount of the stress-whitened region, i.e., a slowly propagating crack region, was observed. These are typical features of brittle fracture.

The slowly propagating crack regions of the surfaces of fractured SEN specimens observed using a SEM are shown in Fig. 8 for type B-0.5 and B-5 particle-modified PVCs at a particle content of 50 phr. The observed parts were identified by the square marks on the schemes of the surfaces of the fractured SEN specimens in Fig. 8. In the type B-0.5 particle-modified PVC (Fig. 8a), the surface was extremely rough and torn; therefore, the feature was clear evidence of shear failure. The particle/matrix interfacial debonding was rarely observed. In the type B-5 particle-modified PVC (Fig. 8b) the surface was not very rough. The particle/matrix interfaces were completely debonded and only the matrix parts between particles were torn. That is, the specimen seemed to be fractured without sufficient deformation as observed in type B-0.5 (Fig. 8a); therefore, it showed brittle fracture, although it has a ductile matrix. It was found that a blend or a composite with a ductile continuous phase undergoes a ductile/brittle transition with an increase in the interfacial area having insufficient adhesion.

From these results, the sufficient interfacial adhesion seems to create the effective blend or particle-filled composite without sacrificing anything in the mechanical and fracture properties.

Conclusions

We performed an investigation of the effect of interfacial adhesion on the mechanical properties and fracture toughness in PVC modified with cross-linked PMMA particles prepared by seeded emulsion polymerization having different numbers and distributions of cross-linked points. The following results were obtained.

1. From the dynamic mechanical analysis and the SEM observation of the fractured surfaces it seemed that interfacial structures with different concentration slope dependent upon the numbers and the distribution of inner cross-linked points were developed.
2. The yield stress and the fracture toughness decreased with a decrease in the interfacial adhesion, namely an increase in the concentration slope.
3. The decrease was found to occur owing to interfacial debonding.
4. When the interfacial adhesion is sufficient, in the mechanical properties and the fracture toughness, it was never observed that the level was lower than those of the components.

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