

Mechanical and Fracture Properties of Methacrylic Particle-Modified PVC

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ABSTRACT

The effect of interfacial structure on the mechanical properties of an incompatible polymer blend have been investigated. For this purpose, uncrosslinked and crosslinked poly(methyl methacrylate) particles having the mean size of about 0.8 μm are prepared by a seeded emulsion polymerization, and then the amount and the distribution of crosslink points in the particles are varied. The obtained emulsion particles are powdered by a freeze dry method and dispersed into poly(vinyl chloride) matrix by a melt blending. The uncrosslinked particles are completely dissolved in the matrix due to a good compatibility of poly(methyl methacrylate) with poly(vinyl chloride). In the case of the crosslinked particles, the mutual diffusion of the polymer molecules is restricted within the particle/matrix interfacial regions by the crosslink points. The interfacial structures with different concentration slope dependent upon the amount and the distribution of inner crosslink points are developed with the same particle size. It is found that the yield stress decreases with a decrease in the interfacial adhesion. When the interfacial adhesion is sufficient, the yield stress was never lower than those of their components.

KEY WORDS

Poly(vinyl Chloride) / Compatibility/ Interphase/ Emulsion Polymerization / Poly(methyl Methacrylate)

INTRODUCTION

In this study, the effect of interfacial adhesion on the mechanical and fracture properties were investigated using a model system. For this purpose, uncrosslinked and crosslinked PMMA particles, which have the same particle size, were prepared by a seeded emulsion polymerization. The amount and the distribution of the crosslink points in the particles were controlled by varying the addition period and the concentration of the crosslinking monomer. These emulsions were dried, and the obtained powder was dispersed into the PVC matrix by melt blending. It is well known that PMMA has a good compatibility

with PVC. Thus, uncrosslinked PMMA particles can be compatible completely in the PVC matrix^{1,2}. On the other hand, in the cases of the crosslinked PMMA particles, the crosslink points restricted the mutual diffusion of the polymer molecules within the interfacial regions. As a result, it was expected that the interfacial structures with different "concentration gradient" dependent upon both the amount and the distribution of inner crosslink points would be developed at the interphase with the same particle size. The interfacial structure was characterized, and the investigation of the effects on the mechanical and fracture properties was carried out. And the effect of particle size was also investigated in the particle diameter range of 0.3 – 0.8 μm with the same interfacial adhesion level.

EXPERIMENTAL

Materials

Commercial grade methyl methacrylate (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 peroxydisulfate (KPS) and sodium lauryl sulfate (SLS) were used without further purification as initiator and surfactant, respectively. Commercial grade PVC (Geon 103 EP, Nippon Zeon Co., Ltd., polymerization degree: 1050) and lead stearate (Katayama Chemical Industries Co., Ltd.) as a stabilizer for PVC were used.

Table 1 Recipe of seeded emulsion polymerization^{a)}.

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
MMA ^{b)} (g)	100.70	87.50	127.8	128.53	123.81	118.04	81.41	128.38
EGDMA ^{c)} (g)	–	–	–	1.40	6.37	12.34	6.19	–
SLS ^{d)} (g)	0.40	–	0.40	0.40	0.40	0.40	–	0.40
KPS ^{e)} (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	1st	2nd	3rd	3rd	3rd	3rd	2nd	3rd
MMA/EGDMA ^{f)}			100/0	99.5/0.5	97.5/2.5	95/5		97.5/2.5
Concentration of crosslinked points ^{g)}			No		Higher in the surface layer			Higher in the inner part
Code ^{h)}			Type A	Type B-0.5	Type B-2.5	Type B-5		Type C-2.5

^{a)} Polymerization temperature: 70°C. Atmosphere: N₂.

^{b)} Methyl methacrylate.

^{c)} Ethylene glycol dimethacrylate.

^{d)} Sodium lauryl sulfate.

^{e)} Potassium peroxydisulfate.

^{f)} Mol fraction in the finally obtained particles.

^{g)} Expected from the added stage of EGDMA during seeded emulsion polymerization.

^{h)} Mol fraction of EGDMA was shown at the end of each Type.

Seeded Emulsion Polymerization

Table 1 shows the recipes of seeded emulsion polymerization. The concentration of surfactant (SLS) was lower than the critical micelle concentration. The No.1 PMMA emulsion was used as a common seed particle. EGDMA was used as a crosslinking monomer. The seeded emulsion polymerization with three stages was carried out to make the particle size larger. In the second and third stage, the monomer was added dropwise during the polymerization process. The obtained PMMA particle (No. 3) without EGDMA is called Type A. In the preparation processes for Nos. 4 – 6 emulsions, EGDMA was added

during the third stage, and then the amount was varied from 0.5 to 5 mol % in the final particle. They are called Type B. EGDMA was added in the second stage for the No. 8 emulsion at the content of 2.5 mol %. The particle is called Type C. The EGDMA content in the final obtained particles is shown at the end of each Type (ex. Type B-5). All polymerizations were continued until the conversion reached above 98 %. The obtained emulsions were powdered by a freeze-dry method using a freeze-dryer (FDU-506, Tokyo Rikakikai Co., Ltd.). The mean particle size was about 0.8 μm for all the samples described above, which was determined using scanning electron microscopy (SEM).

The Types B-2.5 and B-5 particles having the mean diameter of 0.6 μm were prepared by changing the amount of added monomers in the third stage. Those having the mean diameter of 0.3 μm were prepared by the seeded emulsion polymerization with two stages. That is, the MMA and EGDMA monomers were added to the common seed particles (No. 1) in the second (final) stage.

Sample Preparation

PVC, lead stearate (3 parts per hundred parts of resin by weight, phr) and PMMA particles (10 - 50 phr) were mixed using a mixing roll at $200 \pm 5^\circ\text{C}$ for 10 min. About 0.8 mm-thickness sheets were prepared by compressing the mixed compounds at 200°C under a pressure of 19.6 MPa for 2 min. The prepared sheets were quenched by a cold press.

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

Mechanical Properties and Fracture Toughness

Mechanical properties and J_c , as fracture toughness for ductile polymer were measured in the same way as the previous articles³⁻⁶.

RESULTS AND DISCUSSIONS

In this study, the crosslinked PMMA particles were prepared by the seeded emulsion polymerization with three stages. The crosslinking monomer (EGDMA) was added in the third (final) stage for the Type B particles, whereas in the second stage for the Type C particles as shown in Table 1. As a result, the different concentration gradient of the crosslink points is expected to be formed in the particle as follows:

Type A: No crosslink points.

Type B: Higher in the surface layer.

Type C: Higher in the inner part.

In the Type B particles, the amount of the crosslink points in the particle should be increased with an increase in the concentration of added EGDMA. And the different interfacial structures with concentration gradient with the same particle size should be formed in the PVCs modified with the Types B and C particles.

Firstly, the effect of interfacial structure on the mechanical properties was investigated. Figure 1 shows the yield stress of particle-modified PVCs. The yield stress increased with an increase in the particle content in the Type A particle-modified PVC. The similar tendencies were observed in the

PMMA blended and the Type C-2.5 particle-modified PVCs. In the Type B particle-modified PVCs, whereas the yield stress was lower than Type A above 30 phr in the order of Type B-0.5 > B-2.5 > B-5.

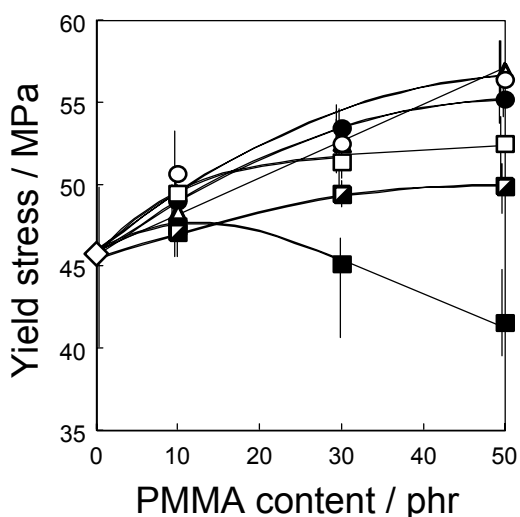


Figure 1 Yield stress of PVC modified with uncrosslinked (◇) and crosslinked PMMA particles and blended with PMMA (●). Modified particles: ○; Type A, □; Type B-0.5, ▣; Type B-2.5, ■; Type B-5, △; Type C-2.5.

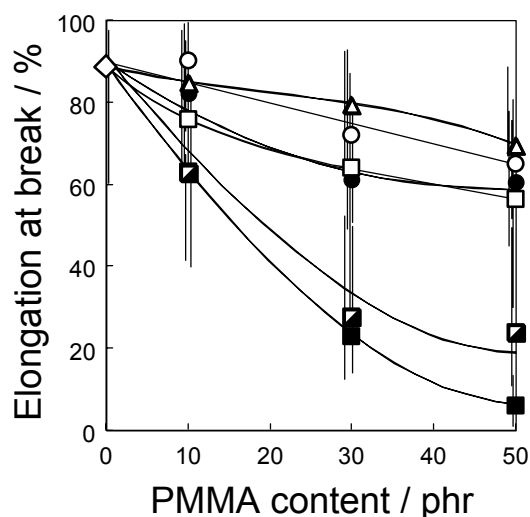


Figure 2 Elongation at break of PVC modified with uncrosslinked (◇) and crosslinked PMMA particles and blended with PMMA (●). Modified particles: ○; Type A, □; Type B-0.5, ▣; Type B-2.5, ■; Type B-5, △; Type C-2.5.

Figure 2 shows the elongation at break of particle-modified PVCs. The elongation decreased gradually with the increase in the PMMA content for the Types A, B-0.5 and C-2.5 particle-modified and the PMMA blended PVCs. However, it became clear that the elongation was far lower in the Types B-2.5 and B-5 particle-modified than in the other PVCs.

From the results above, it was clarified that the yield stress and the elongation at break were strongly affected by both the amount and the distribution of crosslink points in the particles. And, the mechanical properties developed with a decrease in the amount of crosslink points within the Type B particle-modified PVCs. And then, the better mechanical properties were obtained in the modified PVC with particles having the crosslink points at the inner part (Type C) than those at the outer layer (Type B).

Figure 3 shows the tensile fractured surfaces observed by SEM. In the Type A (a), no particles were observed on the surface. This indicated that the PMMA was dissolved in the PVC matrix, because PMMA have a good compatibility with PVC. The similar result was obtained in the PMMA blended PVC (The data does not appear in Figure 3).

On the other hand, in the Type B-5 (c), the mixed particles were clearly observed on the fractured surface, and the interfaces were completely debonded. They had almost the same sizes of the modified Type B-5 particles. The particles were also observed in the Type B-0.5 (b); however, the interfaces became more unclear. The interface of Type B-2.5 was intermediate between Types B-0.5 (b) and B-5 (c). That is, it was found that the interfacial adhesion was stronger in the order of Type B-0.5 > B-2.5 > B-5. In the Type C (d), no particles were observed on the surface, and the surface was similar to that of Type A (a). These results show that the interfacial adhesion was stronger in the Type C-2.5 than in the all Type B.

From the results above, the concentration gradient of both polymers at the interfacial layer is expected to be higher in the order of Type B-5 > B-2.5 > B-0.5 > C-2.5. The similar aspects of above observations were also obtained from the dynamic mechanical analysis.

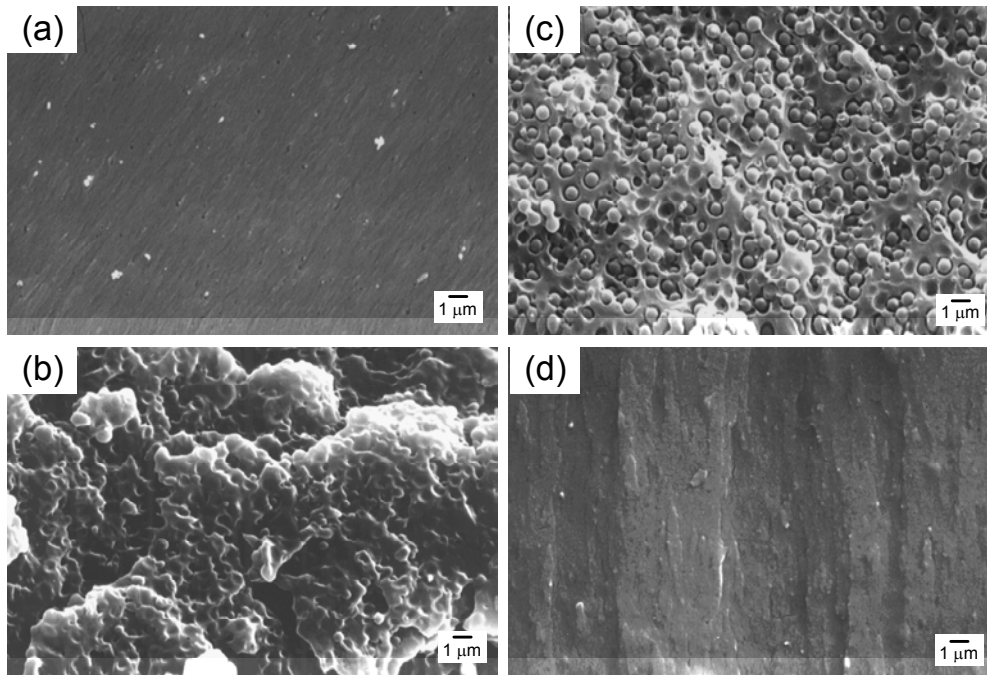


Figure 3 Fractured surfaces after tensile test observed by SEM of PVC modified with uncrosslinked (a) and crosslinked (b-d) PMMA particles at a particle content of 50 phr. Modified particles: (a) Type A, (b) Type B-0.5, (c) Type B-5, (d) Type C-2.5.

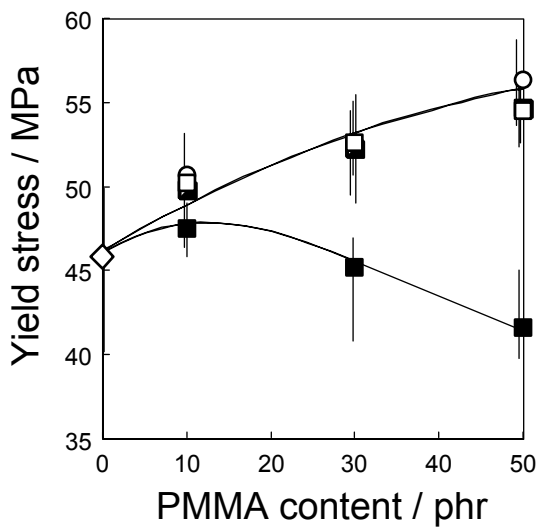


Figure 4 Yield stress of PVC modified with uncrosslinked (\circ , Type-A) and crosslinked PMMA particles. Mean particle size \circ ; 0.8 μm , \square ; 0.3 μm , \blacksquare ; 0.6 μm , \blacksquare ; 0.8 μm .

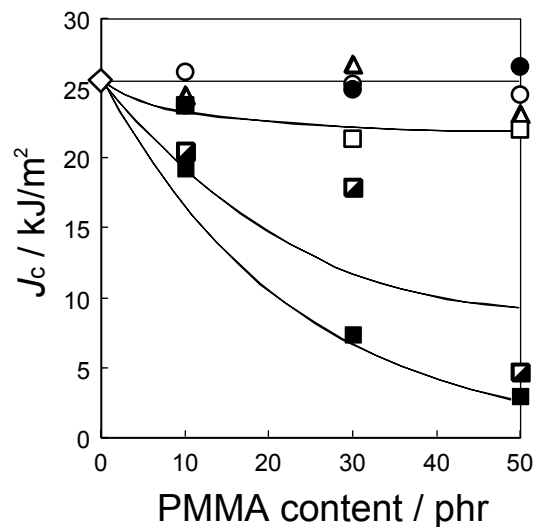


Figure 5 Fracture energy J_c of PVC modified with uncrosslinked (\circ) and crosslinked PMMA particle and blended with PMMA (\bullet). Modified particles: \circ ; Type A, \square ; Type B-0.5, \blacksquare ; Type B-2.5, \blacksquare ; Type B-5, \triangle ; Type C-2.5.

Secondly, the effect of particle size on the mechanical properties was investigated in the particle diameter range of 0.3 – 0.8 μm in the Type B-5 particle-modified PVC having the weakest interfacial adhesion. The results of their yield stress is shown in Figure 4. The decrease of yield stress was never observed when the particle size was 0.6 μm and below in both modified PVCs. The following facts were confirmed; (i) the particles were well dispersed in the PVC matrix; and (ii) there was no influence of particle size on the interfacial adhesion from the SEM observation for the fractured surfaces and the AFM observation for the polished stress-whitened surfaces of the tensile specimen after test. As Figure 4 indicates, it is clear that the yield stress never decreased when the particle size is effectively small, despite having weaker interfacial adhesion.

Figure 5 shows the J_c of particle-modified PVCs with the same particle size (0.8 μm). There was no decrease in the J_c for the Types A and C particle-modified and the PMMA blended PVCs with an increase in the PMMA content. The J_c values for the Type B-0.5 particle-modified was almost the same level as those of above PVCs. On the other hand, the J_c of the Types B-2.5 and B-5 particle-modified PVCs were different and decreased significantly with an increase in the particle content in the modified PVC and the amount of crosslink points in the particles.

From the results above, it seems reasonable to suppose that the interfacial gradience would bring the effective blend or particle-filled composite without sacrificing anything in their mechanical and fracture properties.

CONCLUSIONS

It was an investigation of the effects of interfacial adhesion and particle size on the mechanical properties and fracture toughness in the PVC modified with crosslinked PMMA particles prepared by a seeded emulsion polymerization having different amount and distribution of crosslink points. Following results were obtained.

- i) The interfacial structures with different concentration gradience which is dependent upon the amount and the distribution of inner crosslink points seemed to be developed.
- ii) The yield stress and the fracture toughness decreased with a decrease in the interfacial adhesion, namely an increase in the concentration gradience.
- iii) The decreasing of particle size with a weaker interfacial adhesion has the effect on the improvement of the yield stress.
- iv) When the interfacial adhesion is sufficient, it never occurred that the level was lower than those of their components in the mechanical properties and the fracture toughness.

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