Effect of Modifier Characteristics on Toughness of Poly(vinyl chloride)

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SYNOPSIS

The effects of the mechanical properties of an acrylic graft copolymer and a silicone/acrylic composite rubber graft copolymer on the toughening of poly(vinyl chloride) (PVC) are examined. In the experiment for improvement of impact resistance of PVC, toughness of the blend polymer of a silicone/acrylic composite rubber graft copolymer is improved remarkably. The effect is attributed to the suppression of stress concentration below the fibril strength of the polymer alloy effectively by releasing the constraint of strain resulting from easy void formation at low stress.

INTRODUCTION

It is well known that the method of employing an incompatible polymer alloy is effective in improving the toughness of polymer materials. Many possible toughening mechanisms by alloy have been proposed. Investigators have pointed out that brittle fracture of poly(vinyl chloride) (PVC) having a notch occurs when concentrated stress due to constraint of strain exceeds craze strength of this material.[1] A blend of acrylic graft copolymers improved its toughness remarkably. When load is applied, voids from the modifier, or crazes, are formed. Increased modifier content results in increased population of void, and strain constraint is released by Poisson's contraction between voids. As the result, the stress concentration is relaxed below the breaking strength of the material and the deformation is stabilized; consequently the toughness is improved. This mechanism was reported in our previous paper.[2]

Based on the above-mentioned mechanism of toughening by alloy, it is predicted that the condition of void formation, which depends on the mechanical properties of the modifier, closely affects the toughening. This prediction was validated by the study of toughness of polycarbonate blended with poly(acrylonitrile–butadiene–styrene) copolymer with different strength. In this study, it was suggested that the improvement of toughness was found to be very sensitive to the decrease of the cohesive strength of the modifier and was accomplished efficiently by a slight addition of a modifier of low cohesive strength.[3]

The purpose of this study is to examine the effect of the mechanical properties of various graft copolymers on the toughening of polymer alloys when two types of acrylic graft copolymer with different cohesions and recently developed silicone/acrylic composite rubber graft copolymer are blended as a modifier to PVC matrix resin.

EXPERIMENTAL

Procedures of compound of resins, preparation of specimens, evaluation of mechanical properties, and analysis of deformation process were carried out in the same manner as described previously.[2]

Strength Adjustment of Acrylic Rubber Graft Polymer

The modulus and strength of acrylic graft copolymers were adjusted by varying the quantity of allyl

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methacrylate (AMA) in the preparation of various graft polymers. Acrylic rubber was prepared by emulsion polymerization as previously reported.

Preparation of Silicone/Acrylic Composite Rubber Graft Polymer

A mixture of octamethyltetracyclosiloxane, tetraethoxysilane, and γ-methacryloxypropylmethyldimethoxysilane was added to an aqueous solution of dodecylbenzenesulfonic acid and emulsified using a homogenizer. The emulsion was heated to polymerization, followed by neutralization with caustic soda to obtain silicone latex. The silicone latex was mixed with n-butyl acrylate and a crosslinking agent, and n-butyl acrylate was polymerized with a redox polymerization initiator to form silicone/acrylic rubber graft polymer. Composition of modifiers are listed in Table I.

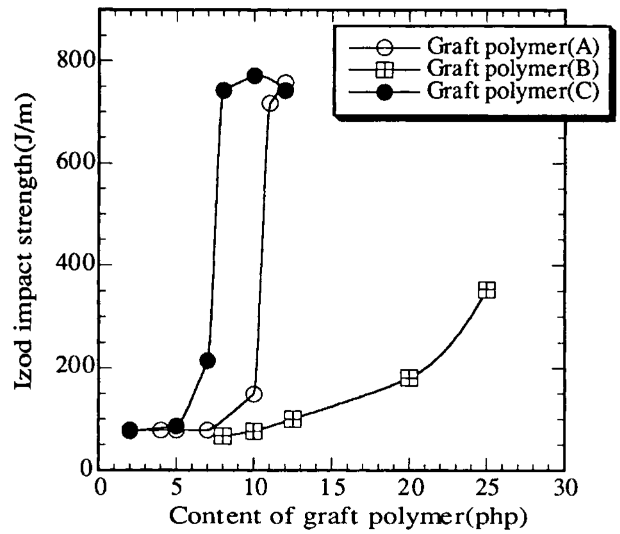

Figure 1 Effect of the amount of graft polymer on the Izod impact strength.

RESULTS

Mechanical Properties of Graft Polymers

Moduli of three graft polymers used in this experiment are compared in Table I. Acrylic grafted copolymer [Graft polymer(A)], which contains AMA crosslinking agent in the largest quantity, exhibits the highest modulus, whereas silicone/acrylic composite rubber graft copolymer [Graft polymer(C)] exhibits the lowest modulus among the graft polymers used.

Impact Strength and Toughness

Two types of acrylic graft copolymers with different moduli and silicone/acrylic composite rubber graft copolymer were blended in PVC. Figure 1 shows the change of Izod impact strength with change in content of modifier. The improvement effect is different depending on the type of modifier, though impact strength is improved with increased modifier content. The content of modifier at which impact strength is critically improved depends on the type of modifier. The critical content is approximately 7 parts by weight for silicone/acrylic composite rubber graft polymer (graft polymer C), 10 parts by weight for acrylic graft copolymer (graft polymer A) with lower modulus, and 25 parts by weight for acrylic graft copolymer with higher modulus (graft polymer B). Figure 2 shows the change of toughness with change in content of modifier. This toughness was evaluated using bending moment–displacement curve obtained by the three-point bending test on a U-notched specimen under a loading speed condition as high as 125 mm/s. Results of the acrylic graft copolymer (graft polymer A) were reported previously[2]; results of new two cases of acrylic graft copolymer (graft polymer B) and silicone/acrylic composite rubber graft polymer (graft polymer C) are shown in Figure 2. For both modifiers, it is obvious from the figure that deformation mode changes from brittle fracture to ductile deformation, which involves general yielding with increasing modifier

Table I Characteristics of Used Modifier

Polymer	Composition (wt %) Silicone/Acryl/AMA/MMA	Tensile Modulus (MPa)	Tensile Strength (MPa)
Graft polymer A	0.0/84.1/0.9/15.0	10.9	1.50
Graft polymer B	0.0/83.4/1.8/15.0	14.8	1.65
Graft polymer C	21.3/62.5/1.2/15.0	4.9	0.78

Acryl, butyl acrylate; AMA, allyl methacrylate; MMA, methyl methacrylate.

content. The modifier content at brittle-to-ductile transition is nearly identical with the critical modifier content in the Izod impact test. In the previous paper, the correspondence of Izod impact strength and high-speed three-point bending test on a U-notched specimen under a loading speed of 125 mm/s was examined for PVC modified with acrylic graft copolymer with low modulus; in addition, the results of this study show that the correspondence is applicable to other modifiers.

Yield Stress and Strength in Uniaxial Tensile Test

Figure 3 shows the change of shear yield stress and tensile strength of an oriented specimen, obtained by uniaxial tensile test with change in modifier content. In the uniaxial tensile test, after yielding, the orientation hardening occurs at the strain of 1.0–1.2, and the oriented specimen is fractured at the strain of 1.5–2.0. Samples of low modifier content clearly form unstable necking in the extension process, but samples of high modifier content tend to deform uniformly and stably. Both shear yield stress and strength decrease with increasing modifier content. Addition of modifier of low modulus results in the decreasing of strength and yield stress, though the difference between modifiers is small. When the deformation mode is ductile at high content of modifier, as shown in Figure 2, the decrease in the moment of general yielding is caused by the decrease of yield stress with increasing content of modifier.

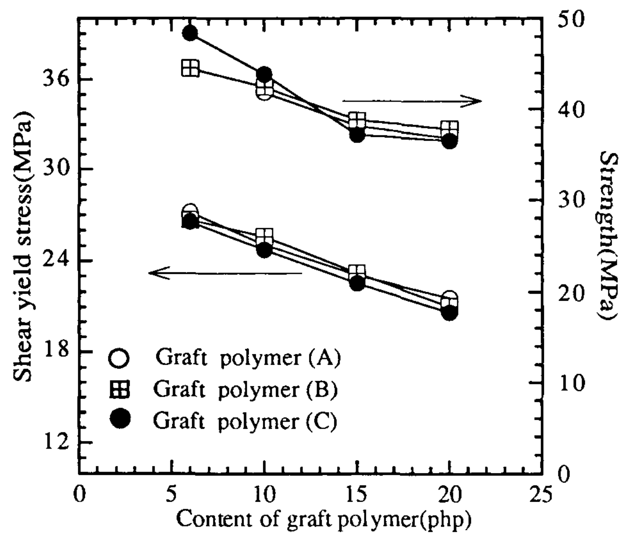

Figure 3 Effect of the amount of graft polymer on the yield stress and strength of fibril.

Mode of Plastic Deformation and Fracture

Figure 4 is a micrograph which illustrates the deformation process of PVC containing 4 parts by weight of silicone/acrylic composite rubber graft copolymer (graft polymer C). The loading speed is as moderately high as 12.5 mm/s. The deformation process is similar to that of the sample containing acrylic graft copolymer modifier. First, plastic deformation accompanying the formation of shear band similar to PVC starts at the tip of a notch.

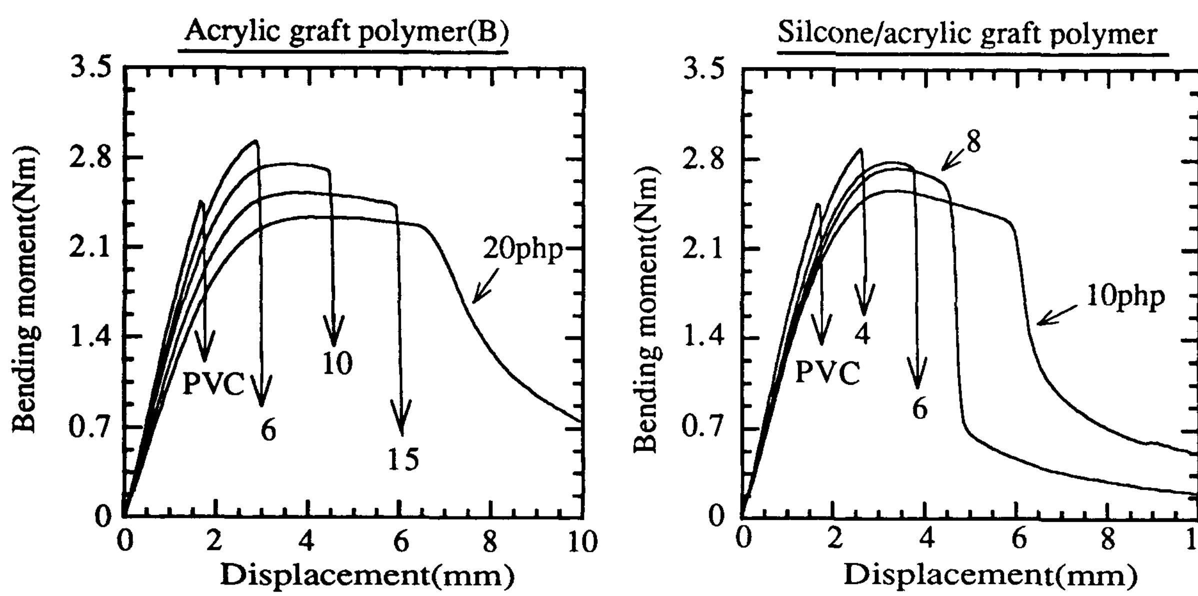

Figure 2 Effect of the amount of graft polymer on the bending moment–displacement curves of U-notched samples.

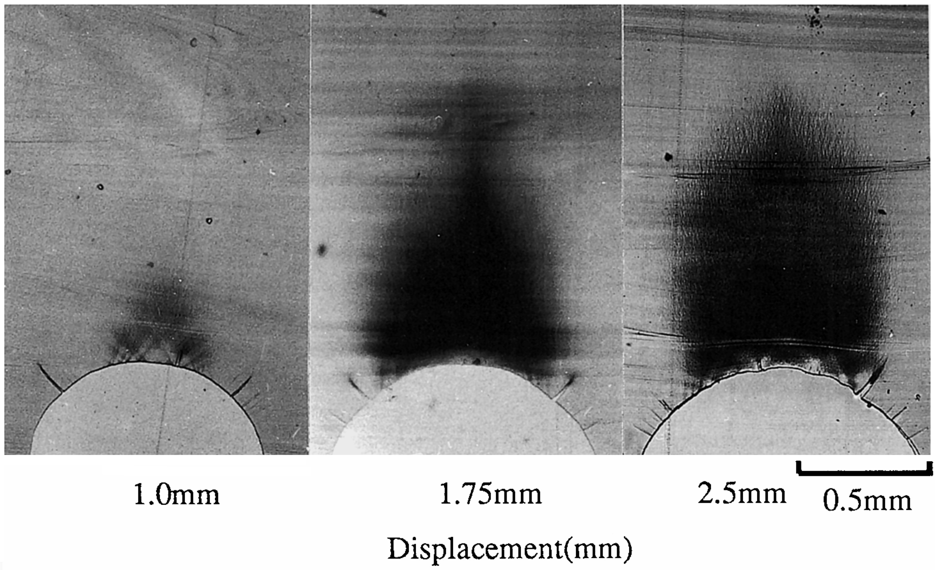

Figure 4 Deformation process of PVC blended with 4 php of silicone/acrylic graft polymer.

Because the stress distribution in the plastic zone formed around the tip of a notch has its maximum at the tip due to plastic constraint, when this plastic zone spreads to a certain critical size with increasing loaded strain, voids from the modifier and fine and stable microcrazes are generated at the tip of the plastic zone. These voids and microcrazes are observed by scanning electron micrograph, as shown in Figure 5. The size of plastic zone at the start of void formation is smaller than that of a specimen containing acrylic graft copolymer modifier, which means that void due to modifier is generated more easily at lower stress than that of a specimen containing acrylic graft copolymer modifier. With further increase in load, the plastic zone containing the voids and microcrazes spreads. When displacement exceeds about 3 mm in the three-point bending test, deformation at the tip of the plastic zone becomes unstable, causing both local concentration of strain and cracks, and a fracture begins. Figure 6 shows a fractured surface of PVC blended with 4 php of silicone/acrylic graft polymer. A fracture nuclei which indicates the starting point of fracture is found at the position distant from the tip of the notch. Microphotographs of the plastic zone are shown in Figure 7 for each modifier. The modifier content is 8

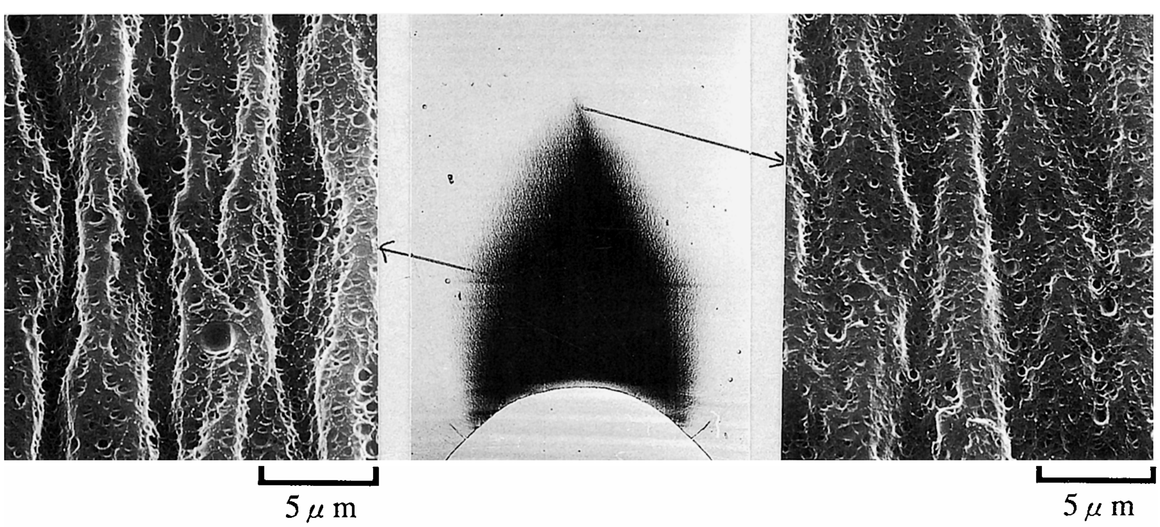

Figure 5 Scanning electron micrographs of the microcraze of PVC samples blended with 8 php of silicone/acrylic graft polymer. Deformation rate: 125 mm/sec.

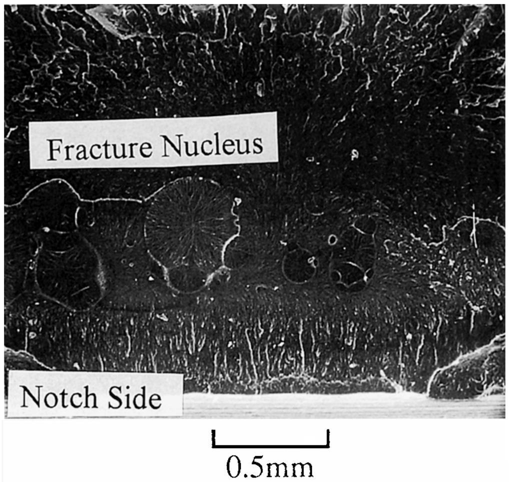

Figure 6 Scanning electron micrographs of the fracture surface of PVC blended with 4 php of silicone/acrylic graft polymer.

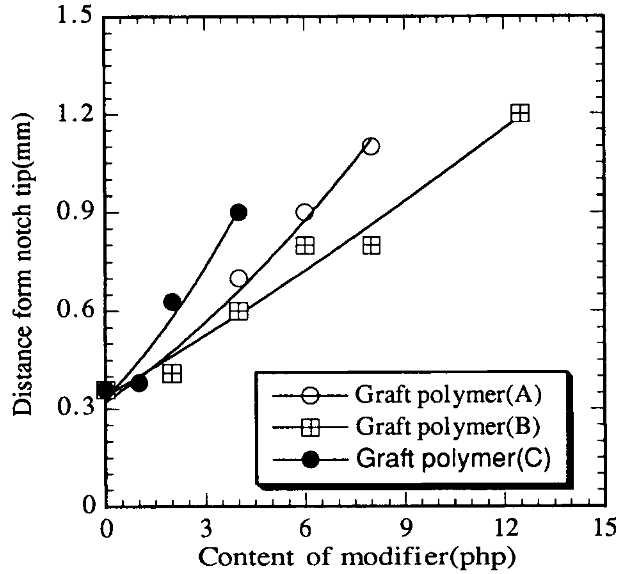

Figure 8 Distance from the notch tip to the fracture nucleus of toughened PVC.

parts by weight, and bending speed is 125 mm/s. The deformation was fixed at a specific point for observation. The specified deformation for silicone/acrylic composite rubber graft copolymer modifier is at the start of general yielding, and is just before fracture for acrylic graft copolymer. Therefore, naturally, the size of plastic zone of high-modulus acrylic graft copolymer (graft polymer B) is the smallest, low-modulus acrylic graft copolymer (graft polymer A) is the medium, and silicone/acrylic composite rubber graft copolymer (graft polymer C) is the largest. The size of plastic zone which spreads at the tip of a notch until voids are formed is in reverse order. Figure 8 shows a relationship between modifier content and distance from the tip of a notch to fracture nuclei, determined by observing the fracture surface in the three-point bending test. The distance corresponds with the size of plastic zone

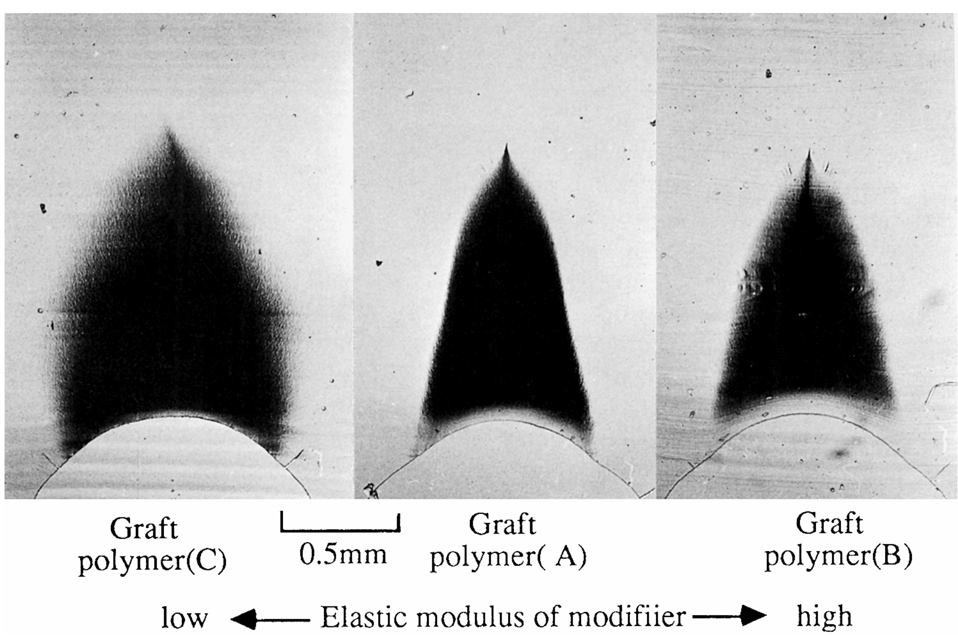

Figure 7 Effect of the strength of graft polymer on the deformation mode of PVC blended with 8 php of modifier. Deformation rate: 125 mm/sec.

having spread until cracks are formed at the tip. The change in size of plastic zone having spread to crack formation (spread plastic zone size) with change in modifier content depends significantly on the mechanical properties of the modifier. The spread plastic zone length increases with increase in modifier content in general; the gradient is largest for silicone/acrylic composite rubber graft copolymer modifier, which has the smallest modulus, and the gradient decreases with increase of modifier modulus. The change of Izod impact strength with a change in modifier content corresponds well with the change in fracture nuclei position estimated from the U-notched specimen with a change in modifier content.

DISCUSSION

It is well known that improved toughness of polymer alloy is attributed to the absorption of loaded energy capability involving plastic deformation due to shearing deformation or formation of crazes. The toughening mechanism of brittle polymer material comprised of a single component by addition of modifier, that is, how the polymer is provided with energy absorption by plastic deformation, has been discussed from various standpoints.[4-6] For example, Wu suggested that at a certain critical distance between interfacial surfaces of modifier particles, shearing deformation between particles becomes dominant.[7,8] One investigator suggested that the dispersion structure of dispersed particles affects the toughness substantially, and image analysis technique was applied to examine the mechanism.

The present authors suggested that brittle fracture of PVC occurs when stress concentration due to plastic constraint exceeds the fibril strength of the material.[1] Based on this fracture mechanism, improvement of fibril strength or suppression of stress concentration due to plastic constraint below the fibril strength could be the way to prevent the fracture.[9] The development of many voids at modifier leads to the release of the constraint of strain which is the origin of the stress concentration. Therefore, the brittle–ductile transition takes place when the stress ahead of the local plastic zone developed from the notch tip became less than the strength of craze due to the release of the constraint of strain. Consequently, it has been suggested by investigators of PVC polymer alloy[2] and also by other studies[3,10] that the deformation is stabilized and finally the toughness is improved.

Based on the above-mentioned toughening mechanism for polymer alloy, it is easily derived that the void formation at low stress by addition of modifier of low strength (voids that are formed from dispersed particles to release the constraint of strain) and small decreases of craze strength are essentially important for effective improvement of toughness. The strength of a specimen oriented by necking predicted from uniaxial tensile test decreases with increasing content of modifier in the same manner as yield stress, and is independent of type of modifier. This result suggests that the craze strength is also similar for different modifiers. It is known that the modulus of elastomer depends on crosslinked network concentration or the structure of crosslinking, and that the strength depends on modulus.[11] It is predicted from the modulus of graft polymer used in this experiment that acrylic rubber with large AMA content exhibits the highest strength and silicone/acrylic composite rubber exhibits the smallest strength. The prediction is validated by the coincidence with the order of void-forming stress estimated from the starting position of whitening observed on the micrograph of a specimen. These studies suggest that a graft polymer with lower strength used as a modifier to improve PVC impact strength can result in effective improvement of toughness regardless of the graft polymer composition.

For generation of voids due to modifier, either the internal of the modifier or the interface between modifier and matrix resin is considered as the starting point. The dispersion structure depends on the type of selected compatibilizer and the method of processing. In this study, methyl methacrylate grafted rubber served as a compatibilizer. The quantity is equal independent of type of rubber, as shown in Table I. The modifier is dispersed in crazes formed in polymer alloy, as shown in Figure 5. If compatibility between modifier and PVC is insufficient, the strength of interface between modifier and matrix resin in the fibrils which constitute crazes decreases, and consequently the toughness decreases. On the other hand, when compatibility is sufficient, the modifier disperses homogeneously and the interface is sufficiently strong; consequently the void formation depends on the strength of modifier, as suggested in this study. Because the cohesion of silicone rubber is smaller than other rubbers, it is presumed that silicone rubber easily results in void formation. This study used silicone/acrylic composite rubber graft copolymer, which is incorporated with such silicone rubber; the remarkable effect of incorporation is found, the result is attractive, and further studies will be conducted in future.

From the viewpoint described above, it is important for improvement of the toughness of polymer alloy that the high-compatibility combination between dispersed particles and matrix resin is used, the interfacial strength is increased to suppress the strength reduction of fibrils, the strength of dispersed particles is maintained at a lower level, and thus the constraint of strain is effectively released, involving void formation.

CONCLUSION

We found that in the experiment for improvement of impact resistance of PVC by blending various graft polymers with different strengths as modifier, the blend of silicone/acrylic composite rubber graft copolymer with the lowest strength among modifiers used in this experiment results in the greatest effect.

We concluded that the greatest effect is attributed to the suppression of stress concentration below the fibril strength of the polymer alloy effectively by releasing the constraint of strain resulting from easy void formation at low stress when a modifier of low strength is used.

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