

Interfacial and Mechanical Properties of γ -Fe₂O₃/Segmented Polyurethane/Poly(vinyl chloride) Composites

SUDARYANTO, TAKASHI NISHINO, MASAKI UENO, SEIJI ASAOKA, KATSUHIKO NAKAMAE

Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, Rokko, Nada, Kobe 657-8501, Japan

Received 27 October 2000; accepted 22 March 2001

ABSTRACT: Segmented polyurethane (SPU)/poly(vinyl chloride) (PVC) blends were particulated with γ -Fe₂O₃. Interfacial properties of the composite were studied through the adsorption behaviors of SPU and PVC and their blends on γ -Fe₂O₃ particles surface. Mechanical properties of the composite were measured with dynamic mechanical analysis and tensile test measurements. PVC with functional groups (FPVC), because of strong interactions, showed preferential adsorption on γ -Fe₂O₃ compared with SPU and PVC. Moreover, the γ -Fe₂O₃ particles were covered by FPVC in the γ -Fe₂O₃/SPU/FPVC composite. The adsorption layer of FPVC protected SPU from catalytic degradation by γ -Fe₂O₃, resulting in increasing hydrolytic stability for SPU. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3030–3035, 2001

Key words: segmented polyurethanes; poly(vinyl chloride) (PVC); polymer blends; interfacial properties; composites

INTRODUCTION

Recently, high-performance materials have been required in many important fields, but various demands in the fields could not always be fulfilled with materials consisting of only one kind of substance. Thus, materials with two or more kinds of substances, that is, composite materials, have been designed for complying with each demand. Nowadays, high-performance composite materials are available with a whole range of properties, and they are used in various applications, from aerospace to electronics to sports equipment. Because composites are manufactured by the combination of two or more kinds of substances, the characterization of interfacial properties is quite

important, and controlling these properties is one of the most important aspects in designing composites.

We investigated the interfacial interaction between a variety of polymers and inorganic particles and found that polymers with a proper amount of polar groups are available as binders for magnetic tapes, inks, paints, and so forth.^{1,2} In previous articles, we investigated the miscibilities of segmented polyurethane (SPU) and poly(vinyl chloride) (PVC).³ There, the chemical structure of SPU and the functional groups of PVC were found to affect the miscibilities and mechanical properties of the blends. The SPU/PVC blend system is the most common binder for magnetic recording tape, in which γ -Fe₂O₃ particles are particulated. However, the interfacial hydrolysis of SPU catalyzed by γ -Fe₂O₃ led to the degradation of the properties of the composites, limiting the durability of the SPU binder.⁴

Correspondence to: T. Nishino (tnishino@kobe-u.ac.jp).

Journal of Applied Polymer Science, Vol. 82, 3030–3035 (2001)
© 2001 John Wiley & Sons, Inc.

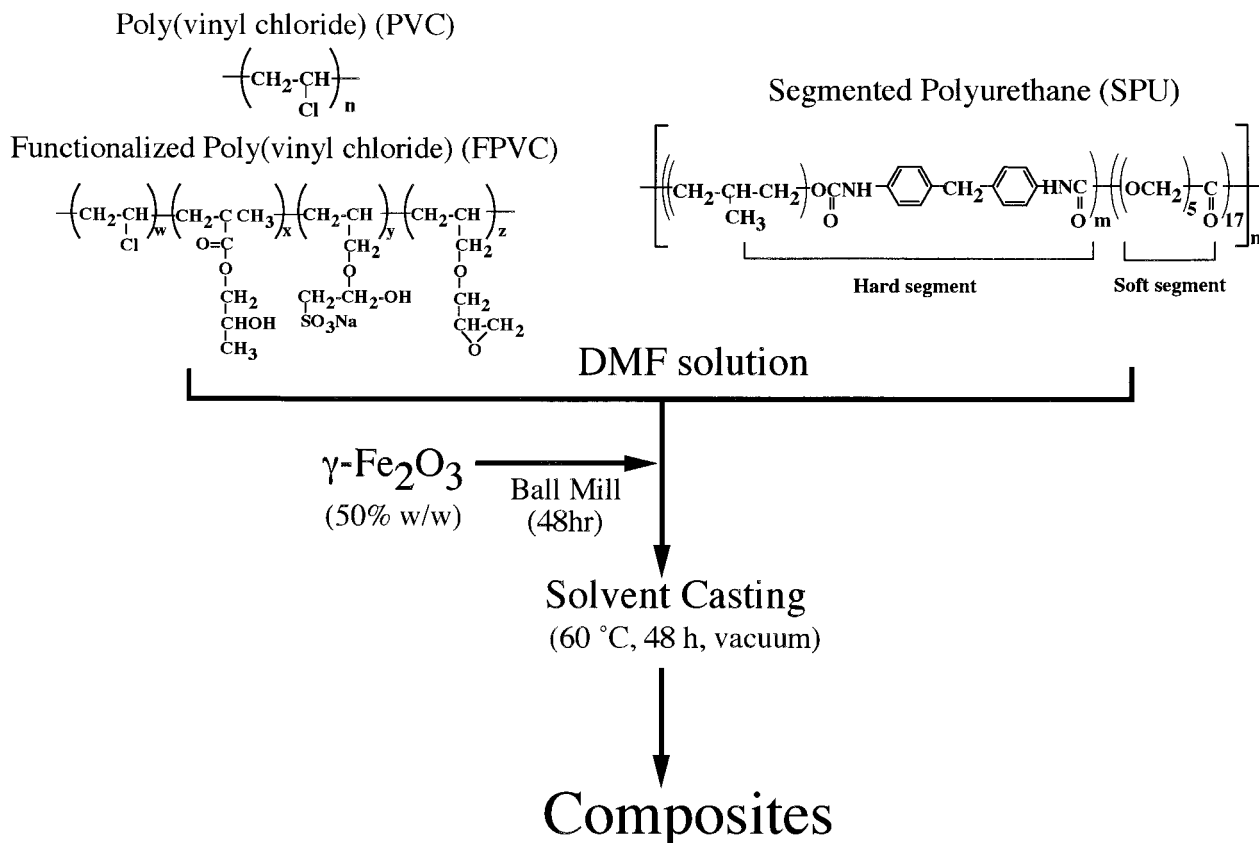


Figure 1 Preparation method of the γ -Fe₂O₃-filled composite based on SPU/PVC blends.

In this study, the interfacial and mechanical properties of composites made of SPU/PVC and γ -Fe₂O₃ were investigated, and a polymer blend system with reduced degradation is proposed.

EXPERIMENTAL

Materials

Polyurethane with a hard-segment content of 30 wt % was prepared with a conventional prepolymer preparation method as described in previous reports.^{4,5} PVC from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), with a number-average molecular weight (M_n) of 75,000, or functionalized PVC (FPVC) from Nippon Zeon Co., Ltd. (Kawasaki, Japan), with an M_n value of 38,000, was blended with SPU.

Figure 1 shows the blend processing and chemical structure of each component. SPU and PVC or FPVC (50/50 w/w) were codissolved in *N,N'*-dimethylformamide (DMF), a good solvent for

each polymer, a with total polymer concentration of 10 wt %. The solution was sufficiently stirred and kept for 24 h at room temperature. The sample was prepared by the casting of the solution under vacuum at 60°C for at least 48 h. The γ -Fe₂O₃-particulated films were also prepared by the addition of γ -Fe₂O₃ into the solution, which was then mixed with a ball mill for 48 h and cast under vacuum at 60°C for at least 48 h. γ -Fe₂O₃ (Pfizer Laboratories, Cambridge, MA) with a surface area of 19.3 m²/g was used as the filler, and its content was fixed at 50 wt %.

Interfacial Properties

The adsorption behavior of the polymers on γ -Fe₂O₃ was studied as follows. DMF solutions of the polymers were prepared in desired concentrations. A glass tube (25-cm³ capacity) containing 1.0 g of γ -Fe₂O₃ and 10 cm³ of the polymer solution was shaken for 24 h. Then, it was allowed to stand for another 48 h at 30°C for equilibration of the adsorption of the polymer onto the γ -Fe₂O₃

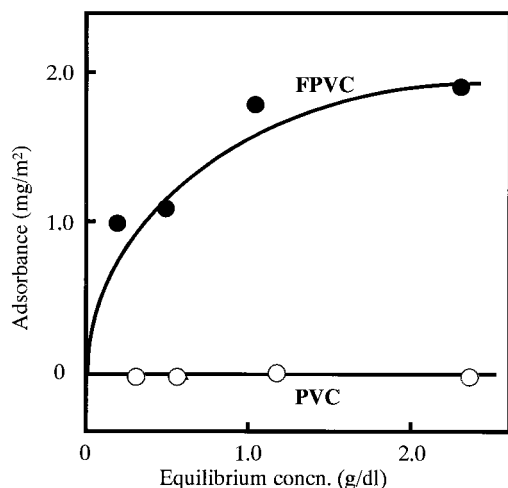


Figure 2 Adsorption isotherms of (○) PVC and (●) FPVC on $\gamma\text{-Fe}_2\text{O}_3$ from a DMF solution at 30°C.

surface. The polymer concentration after adsorption was determined through the measurement of the supernatant with gravimetry. The adsorbance of the polymer on $\gamma\text{-Fe}_2\text{O}_3$ was determined via calculation of the concentration change of the solutions before and after adsorption. The adsorbance was plotted with the equilibrium concentration of the solution after adsorption. The competitive adsorbance of each component in the blend system was determined through the measurement of the nitrogen content of the solutions before and after adsorption by elemental analysis (Sumigraph NCH-2, Sumika Chemical Analysis Service, Osaka, Japan).

The interfacial tension of the water/polymer solution in nitrobenzene was measured with a du Nöuy ring method.⁶ Nitrobenzene was used because it was a good solvent for each polymer and had a high interfacial tension at the water interface (27.6 mN/m). We carried out the measurements by pulling up the du Nöuy ring from the nitrobenzene phase (bottom) to the water phase (upper).

Mechanical Properties

A dynamic mechanical analyzer (ITK Co., DVA-200, Osaka, Japan) was used for characterizing the dynamic mechanical properties of the particulated composites. Rectangular samples (5 mm \times 10 mm \times 0.3 mm) were measured at 10 Hz in a stretching mode over a temperature range of -100 to 120°C at a heating rate of $6^\circ\text{C}/\text{min}$.

A tensile tester (Shimadzu, Autograph AGS-1kND, Kyoto, Japan) was also used for determin-

ing the mechanical properties of the composites. Samples, after being immersed in boiling water for 72 and 168 h, were also examined. Each sample was strained at 2 mm/min at room temperature with an initial length of 15 mm.

RESULTS AND DISCUSSION

Interfacial Properties

Figure 2 shows the adsorption isotherms of PVC and FPVC on $\gamma\text{-Fe}_2\text{O}_3$ from DMF solutions. The adsorbance of FPVC increased with the equilibrium concentration of the polymer and saturated at about 1.9 mg/m^2 . This isotherm obeyed the Langmuir type. However, no adsorption on $\gamma\text{-Fe}_2\text{O}_3$ was observed for PVC. We previously reported that the existence of a proper amount of polar groups in a polymer backbone brings higher adsorbance of the polymer to a metal oxide surface. In particular, a polymer containing strong acid, such as sulfonate groups or phosphate groups, adsorbs on $\gamma\text{-Fe}_2\text{O}_3$.^{7,8} Therefore, these results clearly show that the functional groups, especially sulfonate groups, in FPVC play an important role in the adsorption behavior of PVC on $\gamma\text{-Fe}_2\text{O}_3$.

Figure 3 shows the adsorption isotherms of FPVC and SPU from an SPU/FPVC blend (50/50 w/w) solution on $\gamma\text{-Fe}_2\text{O}_3$. Arrows indicate the saturated adsorbance of SPU and FPVC from each individual solution. SPU showed almost no

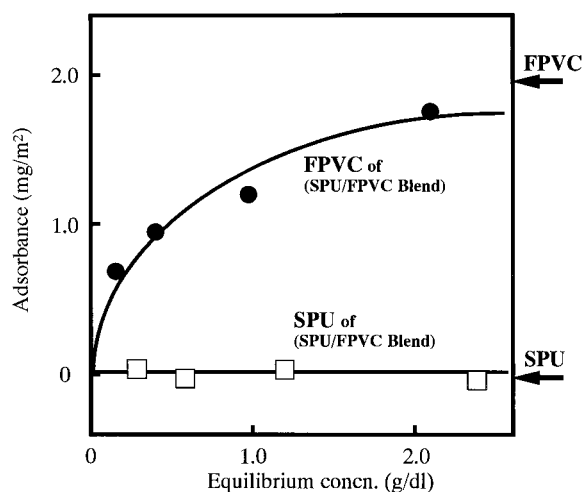


Figure 3 Adsorption isotherms of (●) FPVC and (□) SPU from an SPU/FPVC blend solution on $\gamma\text{-Fe}_2\text{O}_3$. Arrows indicate the saturated adsorbance of FPVC and SPU from each separated solution.

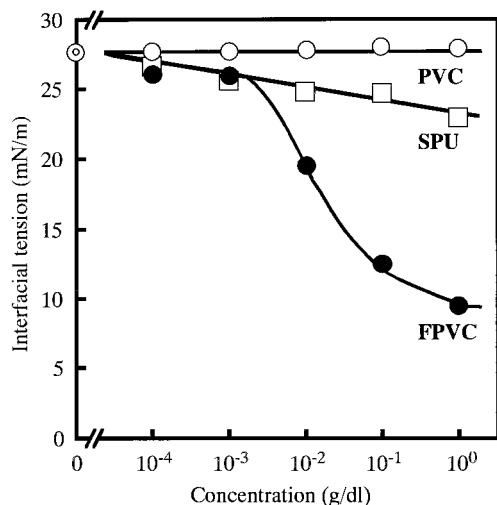


Figure 4 Relationship between the polymer concentration and the interfacial tension in a water/nitrobenzene solution of (□) SPU, (○) PVC, and (●) FPVC.

adsorption on γ -Fe₂O₃. However, the adsorbance of FPVC in the blend system increased with the equilibrium concentration of the polymer and saturated at about 1.7 mg/m². This isotherm was almost equal to that in Figure 2. This indicates that the interaction of FPVC with γ -Fe₂O₃ is stronger than that of SPU, and the existence of SPU in the blend system does not disturb the adsorption behavior of FPVC on the surface of γ -Fe₂O₃.

The surface of γ -Fe₂O₃ particles possesses chemically or physically adsorbed water. Thus, the surface of γ -Fe₂O₃ particles can be expressed with the water phase qualitatively; that is, the adsorption behavior of polymers at the liquid/solid interface could be interpreted on the basis of the interfacial tension at the water/polymer solution interface and the contact angle of water on the polymer film.⁸

Figure 4 shows the relationship between the polymer concentration in a solution and the interfacial tension in a water/nitrobenzene solution of SPU, PVC, and FPVC. The interfacial tension for PVC was independent of the concentration, whereas that of SPU slightly decreased and that of FPVC abruptly decreased with increasing polymer concentration. It is well known that the polymer with a stronger interaction with metal oxide gives a lower interfacial tension for the water/polymer solution than a polymer with a weaker interaction with metal oxide. Accordingly, the decrement of the interfacial properties should be due to an orientation of the polymer at the inter-

face, and FPVC acts as a surfactant.⁹ These results corresponded to the result in Figures 2 and 3, in which PVC and SPU did not adsorb but FPVC strongly adsorbed on the γ -Fe₂O₃ surface.

Figure 5 shows the relationship between the concentration of FPVC and the interfacial tension between water and FPVC and SPU/FPVC blend solutions. The interfacial tensions for both the FPVC and SPU/FPVC blend systems decreased with increasing FPVC concentration. This indicates that the adsorption behavior of FPVC was not hindered by the existence of SPU in the SPU/FPVC blend system. These results evidently showed that FPVC preferentially adsorbed on γ -Fe₂O₃ particles, as shown in Figure 3, in which the functional groups play a great role.

Mechanical Properties

Figure 6 shows the temperature dependence of mechanical $\tan \delta$ for the SPU/FPVC blend and γ -Fe₂O₃/SPU/FPVC composite. Both samples had a single $\tan \delta$ peak regardless of the existence of γ -Fe₂O₃; this showed the high miscibility of this blend.¹⁰ The peak top temperature of $\tan \delta$ increased with the incorporation of γ -Fe₂O₃. The intensity of the $\tan \delta$ peak of the γ -Fe₂O₃/SPU/FPVC composite was lower than that of the SPU/FPVC blend. This is undoubtedly due to the existence of γ -Fe₂O₃ as fillers.¹¹⁻¹⁵ Previously, we reported that the interaction between poly(methyl methacrylate) and γ -Fe₂O₃ as fillers led the shifting of the $\tan \delta$ peak to a higher temperature.¹¹ A

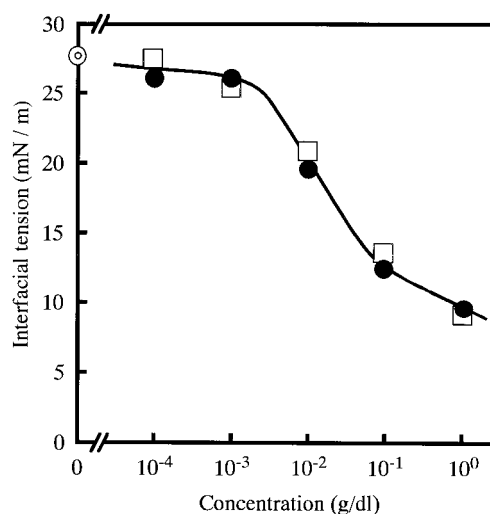


Figure 5 Relationship between the concentration of FPVC and the interfacial tension in a water/nitrobenzene solution of (●) FPVC and (□) an SPU/FPVC blend.

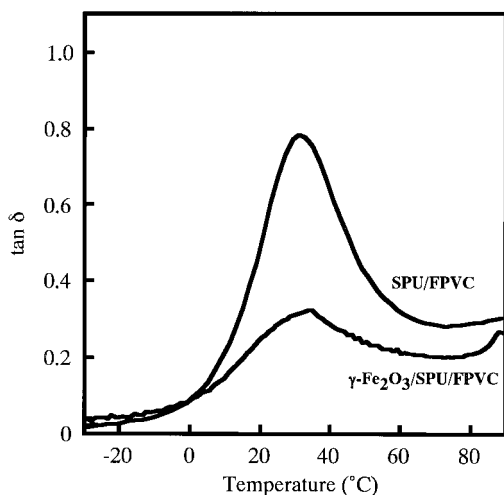


Figure 6 Temperature dependence of the mechanical $\tan \delta$ value for an SPU/FPVC blend and a $\gamma\text{-Fe}_2\text{O}_3$ /SPU/FPVC composite.

similar result was also reported by Yim et al.¹² for a silica-filled polymer composite. The effect of the interfacial interaction on the $\tan \delta$ peak intensity was also discussed in detail by several researchers, who observed that the lower the $\tan \delta$ peak intensity was, the stronger the interaction was between the polymer and the metallic particle as a filler.^{13,14} In a more recent study, Cuillery et al.¹⁵ reported the influence of the metal/polymer interaction on the $\tan \delta$ peak of a laminated material. There is no doubt that the incorporated filler interfered with the molecular motion of the matrix at the interface, resulting in the increment of the peak top temperature and the decrement of the peak intensity of $\tan \delta$. Thus, the degree of the decrement in the intensity of the $\tan \delta$ peak can be a criterion of the interfacial interaction. The value of $r_{\tan \delta}$, the intensity ratio of the $\tan \delta$ peak of a sample with a filler to that without a filler, was determined as follows:

$$r_{\tan \delta} = \frac{\tan \delta \text{ peak intensity with } \gamma\text{-Fe}_2\text{O}_3}{\tan \delta \text{ peak intensity without } \gamma\text{-Fe}_2\text{O}_3}$$

Table I shows the $r_{\tan \delta}$ values of composites with different components. The $\gamma\text{-Fe}_2\text{O}_3$ content of each composite was 50 wt %. The $r_{\tan \delta}$ value for $\gamma\text{-Fe}_2\text{O}_3$ /SPU is higher than unity. It is thought that the filler might disturb the formation of the hard domain of SPU; this results in the increase in the molecular motion. Small interfacial interaction between the polymer and filler could also

Table I $r_{\tan \delta}$ Values of $\gamma\text{-Fe}_2\text{O}_3$ /SPU, $\gamma\text{-Fe}_2\text{O}_3$ /SPU/PVC, and $\gamma\text{-Fe}_2\text{O}_3$ /SPU/FPVC Composites

Composite	$r_{\tan \delta}$
$\gamma\text{-Fe}_2\text{O}_3$ /SPU	1.2
$\gamma\text{-Fe}_2\text{O}_3$ /SPU/PVC	0.8
$\gamma\text{-Fe}_2\text{O}_3$ /SPU/FPVC	0.4

be a reason for the increasing $\tan \delta$ peak reported by Tario et al.¹³ The $r_{\tan \delta}$ value of the $\gamma\text{-Fe}_2\text{O}_3$ /SPU/FPVC composite was smaller than that of the $\gamma\text{-Fe}_2\text{O}_3$ /SPU/PVC composite. This suggests a stronger interaction between FPVC and $\gamma\text{-Fe}_2\text{O}_3$ than between PVC and $\gamma\text{-Fe}_2\text{O}_3$.

Figure 7 shows the relative elongation at break and relative tensile strength of $\gamma\text{-Fe}_2\text{O}_3$ /SPU, $\gamma\text{-Fe}_2\text{O}_3$ /SPU/PVC, and $\gamma\text{-Fe}_2\text{O}_3$ /SPU/FPVC composites after immersion in boiling water for 72 and 168 h. The elongation at break and tensile strength before immersion were taken to be 100%. The elongation at break of $\gamma\text{-Fe}_2\text{O}_3$ /SPU greatly decreased after immersion. However, for composites based on the blend systems, especially the SPU/FPVC blend, the decrease in the elongation could be reduced. It is obvious, therefore, that PVC and FPVC increased the hydrolytic stability of SPU. A similar tendency was also observed for

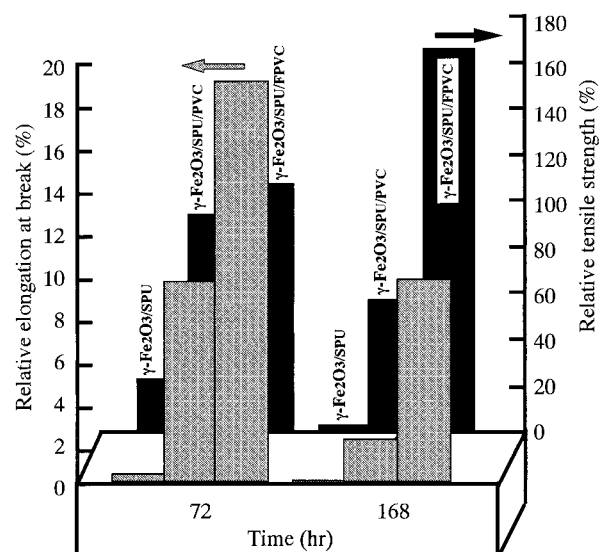


Figure 7 Histograms of the relative elongation at break (front, gray) and the relative tensile strength (back, black) of $\gamma\text{-Fe}_2\text{O}_3$ /SPU, $\gamma\text{-Fe}_2\text{O}_3$ /SPU/PVC, and $\gamma\text{-Fe}_2\text{O}_3$ /SPU/FPVC composites (left to right) after immersion in boiling water. The values before the immersion were taken to be 100%.

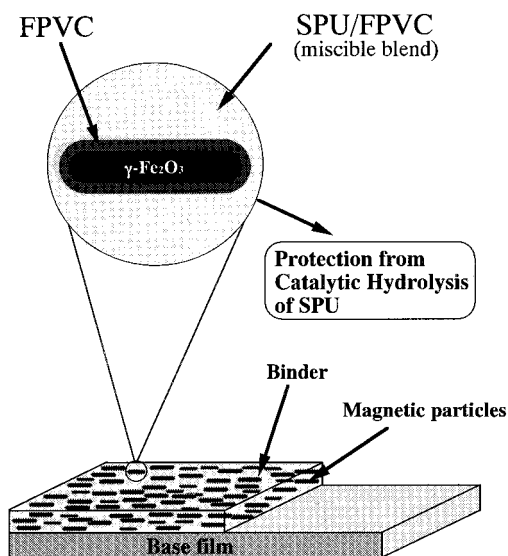


Figure 8 Schematic representation of the γ -Fe₂O₃/SPU/FPVC composite.

the tensile strength. The tensile strength of the γ -Fe₂O₃/SPU composite decreased after immersion in boiling water. This might have been caused by degradation through the interfacial hydrolysis of SPU catalyzed by γ -Fe₂O₃. However, the tensile strength of the composite based on SPU/FPVC increased after immersion. This might have been caused by the progression of the epoxy moiety during immersion in boiling water.

Figure 8 shows a schematic representation of the γ -Fe₂O₃/SPU/FPVC composite. The results of this study show that the γ -Fe₂O₃ particle could be covered by the FPVC component. Thus, the catalytic hydrolysis effect of γ -Fe₂O₃ particles on the degradation of SPU can be reduced by FPVC preferentially adsorbed on γ -Fe₂O₃.

CONCLUSIONS

The interfacial and mechanical properties of a γ -Fe₂O₃ particulated composite based on the SPU/PVC blend system were investigated. The

interaction of FPVC with γ -Fe₂O₃ was stronger than the interactions of SPU and PVC with γ -Fe₂O₃. That is the reason FPVC showed preferential adsorption on γ -Fe₂O₃ particles. Moreover, SPU in the SPU/FPVC blend system did not interfere with the adsorption behavior of FPVC. On the basis of these results, we concluded that the γ -Fe₂O₃ particles were covered by FPVC in the SPU/FPVC blend system. The FPVC layer protected SPU from catalytic degradation by γ -Fe₂O₃; this resulted in increased hydrolytic stability of the SPU matrix.

REFERENCES

1. Nakamae, K.; Sumiya, K.; Matsumoto, T. *Prog Org Coat* 1984, 12, 143.
2. Matsumoto, T.; Nakamae, K. In *Adhesion and Adsorption of Polymer*; Lee, L. H., Ed.; Plenum: New York, 1980; Part B, p 707.
3. Sudaryanto; Nishino, T.; Ueno, M.; Asaoka, S.; Nakamae, K. *J Appl Polym Sci* 2001, 82, 3022.
4. Stivala, S. S.; Kimura, J.; Gabbay, S. M. In *Degradation and Stabilization of Polyolefins*; Allen, N. S., Ed.; Elsevier: London, 1983; p 63.
5. Nakamae, K.; Nishino, T.; Asaoka, S.; Sudaryanto. *Int J Adhes Adhes* 1996, 16, 233.
6. Adamson, A. W. *Physical Chemistry of Surface*, 2nd ed.; Interscience: New York, 1967.
7. Nakamae, K.; Tanigawa, S.; Nakano, S.; Sumiya, K. *Colloids Surf* 1989, 37, 379.
8. Nakamae, K.; Tanigawa, S.; Sumiya, K.; Matsumoto, T. *Colloid Polym Sci* 1988, 266, 1014.
9. Matsumoto, T.; Nakamae, K.; Nonaka, K. *Kobunshi Ronbunshu* 1974, 31, 7.
10. Yang, W.; Shen, J.; Zhu S.; Chan, C. *J Appl Polym Sci* 1998, 67, 2035.
11. Nakamae, K.; Sumiya, K.; Imai, M.; Matsumoto, T. *J Adhes Soc Jpn* 1980, 16, 4.
12. Yim, A.; Chahel, R. S.; St. Pierre, L. E. *J Colloid Interface Sci* 1973, 43, 583.
13. Tario, M.; et al. *Chem Eng Commun* 1991, 105, 11.
14. Lipatov, Y. S. *Adv Polym Sci* 1977, 22, 1.
15. Cuillery, P.; Tatibouet, J.; Mantel, M. *J Adhes Sci Technol* 1998, 12, 271.