NOTES

Grafting Poly(ethylenimine) on Aluminum–Boron Double Oxide Whisker and Its Effects on Whisker–PVC Composites

Poly(ethylenimine) was grafted on aluminum–boron double oxide whisker. The graft polymer was characterized by scanning electron microscopy, diffuse reflectance infrared spectroscopy, and chemical analyses. The polymer-grafted whisker exhibited additional and specific reinforcements to poly(vinyl chloride) resin.

INTRODUCTION

Metal oxide gel coating has been applied to improve interfacial interactions between filler surface and polymer. An unsaturated carboxylate-containing titanium oxide gel served as a grafting substrate in a radical polymerization of styrene[1] or as a reinforcing coating for calcium carbonate filler for elastomers.[2] It has also been our interest that a grafting of an amino group-containing polymer on filler surface may afford an additional and specific reinforcement for the composite.

Aluminum–boron double oxide whisker (average length = 15.0 μm, average aspect ratio = 20)[3] exhibited fine reinforcements for thermosetting as well as did thermoplastic resins[4] without any surface modification. This short paper describes a methodology of organic–inorganic gel coating on the whisker and subsequent grafting of poly(ethylenimine) on the modified surface. Effects of this modification on physical properties of whisker–poly(vinyl chloride) (PVC) composites are also presented.

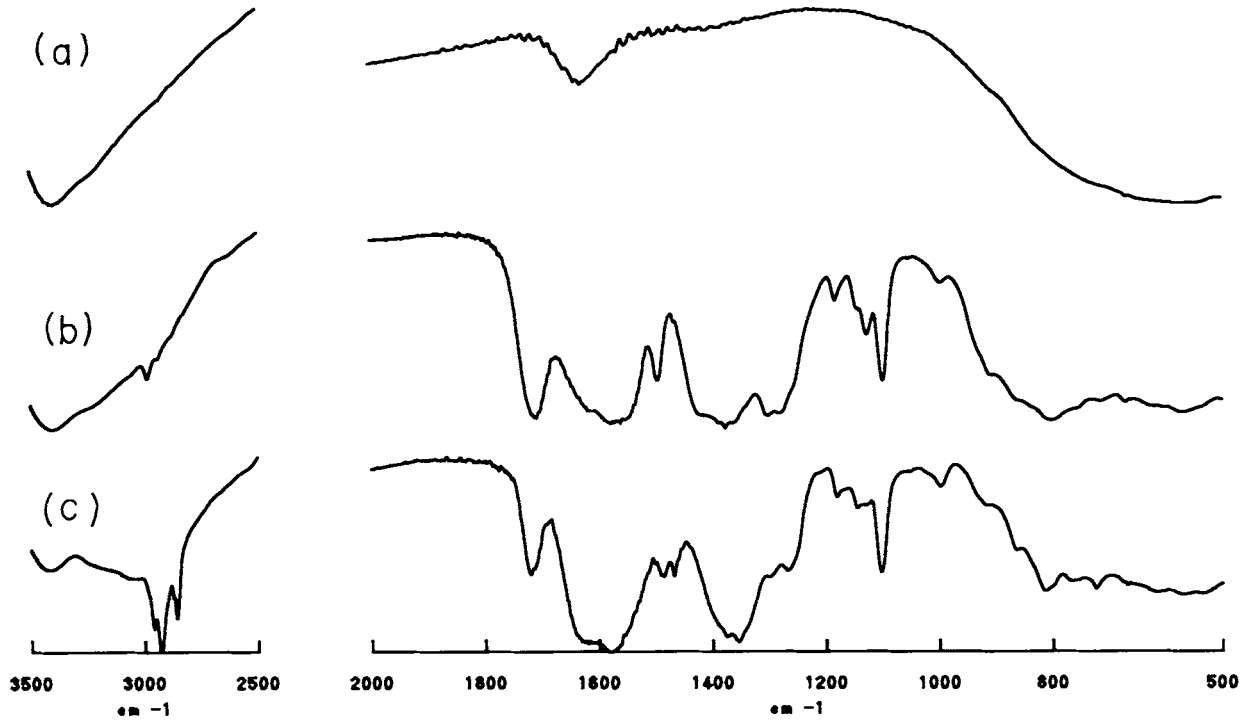

Figure 1 Diffuse reflectance FTIR spectra of (a) titanium oxide gel obtained by hydrolysis of titanium isopropoxide, (b) reaction product of titanium isopropoxide and pyromellitic anhydride (Gel-I), and (c) octylamine-treated gel (Gel-II) of Gel-I.

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EXPERIMENTAL

An equimolar reaction of pyromellitic anhydride and titanium isopropoxide in dried THF was carried out at room temperature to give a gelled precipitate in a few minutes. The gelled product (Gel-I) was separated by evaporation of the solvent. One-half of the gel was further treated with octylamine at room temperature for 24 h. Filtration, washings with THF, and drying *in vacuo* gave an amine-incorporated gel (Gel-II).

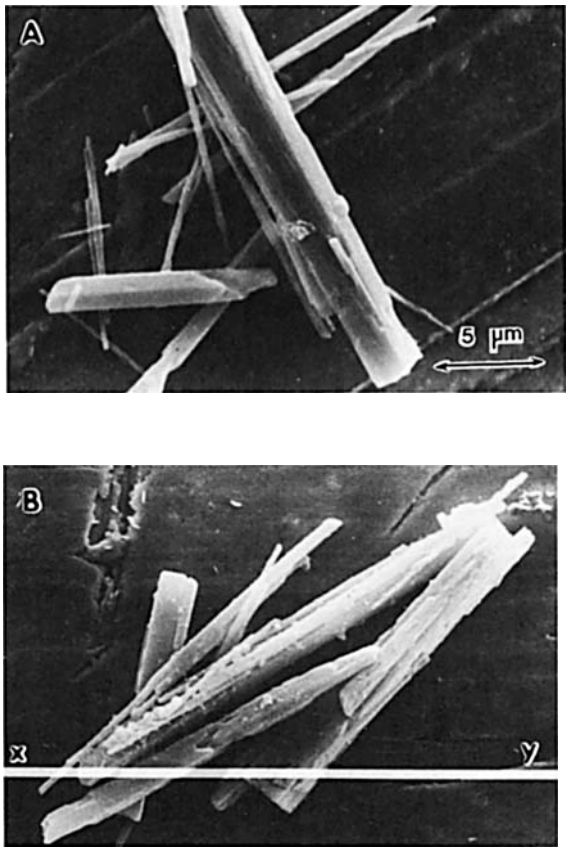

Figure 2 Scanning electron photomicrographs (SEM) of (a) original whisker and (b) poly(ethylenimine)–TiO_2 gel-coated whisker. (c) Line analysis of TiKα along x–y in the microphotograph of (b).

Table I Recipe and Formulation Conditions of Whisker-Loaded Poly(Vinyl Chloride)

Recipe	
PVC (Nippon Zeon 103EP)	100 phr
Dibutyltin maleate	3.0 phr
Polyethylene wax	0.5 phr
Whisker	0, 10, 25, 50 phr
Glycerol monostearate	1.8 wt % of whisker
Formulation conditions	
Whisker loading: on 8 in. roll, 165°C, 5 min	
Formulation: 175°C, 100 kg/cm^2, 15 min	

Poly(ethylenimine) (PEI) was grafted on the whisker ($9Al_2O_3 \cdot 2B_2O_3$) as follows: To the whisker suspended in 1500 mL tetrahydrofuran (THF) was added titanium tetrabutoxide (30 mL, 88 mmol) and trimellitic anhydride (8.4 g, 44 mmol), being dissolved in THF (100 mL). After the suspension was refluxed for 1 h in a rotary evaporator equipped with a reflux condenser, the THF was evaporated out under reduced pressure. A PEI solution ($\overline{M_w} = 7 \times 10^4$) in 230 mL water (4%) was introduced into the vessel, and a grafting reaction as well as hydrolytic gelation were simultaneously performed at 65°C for 2 h. The mixture stood still overnight, and the resulting whisker was filtered on a Buchner funnel, washed with water and methanol, and dried in an oven (107°C). Elemental analysis of the PEI–graft whisker was C: 2.38, H: 0.66, N: 0.75. Amount of the graft PEI was calculated on the nitrogen content to be 1.29 wt %.

RESULTS AND DISCUSSION

The Gel-I exhibited an infrared spectrum [Fig. 1(b)] having bands of the ester group (1710, 1301, and 1125 cm^{-1}) and the carboxylate group (1574 and 1380 cm^{-1}). By comparing the infrared spectra of the Gel-I and Gel-II [Fig. 1(c)], it is seen that the ester bands (1710, 1301, 1125 cm^{-1}) decrease and the alkyl peaks (2858–2957, 1467, 723 cm^{-1}) become more significant and an amide shoulder (1631 cm^{-1}) appears. IR spectrum of titanium oxide gel prepared by hydrolyzing titanium isopropoxide is also shown in Figure 1(a). These spectral results suggest the reaction scheme of gelation and amidation as follows: Titanium butoxide reacts with the anhydride to give ester-containing titanium carboxylate gel. The ester groups formed are successively transformed into amide.

IR spectroscopic analysis of the PEI-modified whisker similarly indicates that an ester group formed on the surface was transformed into amide: A shoulder ascribable to amide was found at 1648 cm^{-1}. Bands of alkyl, ester, and carboxylate were observed at 2965; 2847, 1710, and 1576; and 1390 cm^{-1}, respectively.

A scanning electron photomicrograph of the PEI-grafted whisker is shown in Figure 2(b). Compared with the original whisker [Fig. 2(a)], scalelike precipitates ap-

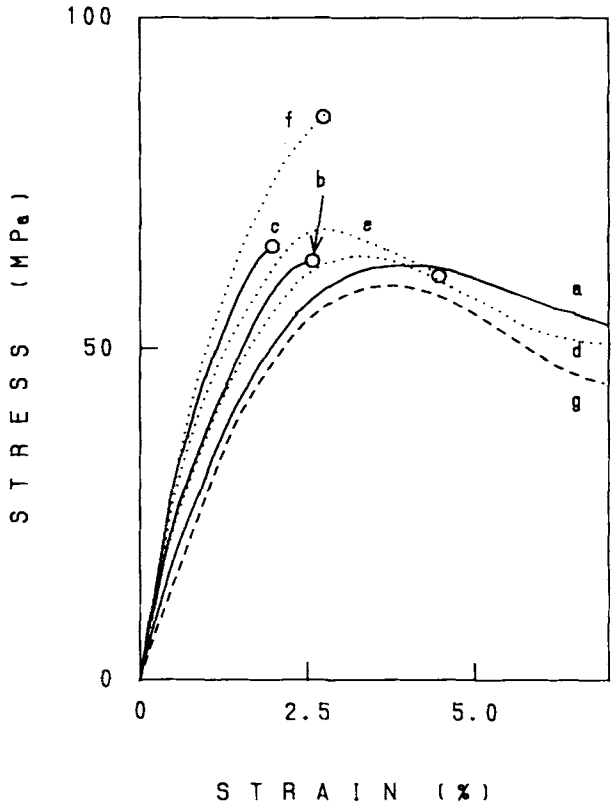

Figure 3 Stress–strain curves of original whisker-loaded PVC [whisker loading: (a) 10 phr; (b) 25 phr; (c) 50 phr); PEI-graft whisker-loaded PVC [(d) 10 phr; (e) 25 phr; (f) 50 phr]; and control PVC (g). The PEI was grafted by 1.29 wt %. Breakpoint is indicated by O.

pear to coat the whisker surface; however, the coating gel was not manifested [Fig. 2(b)]. To confirm the gel coating, line analysis of TiKα along the x–y line in Figure 2(b) was undertaken and TiKα was significantly detected at the whisker surface [Fig. 2(c)].

Whether the graft PEI has a reactivity of amine was briefly examined. When sodium nitroprusside–actaldehyde reagent[5] was treated in an alkaline solution at room temperature, the white PEI–graft whisker turned blue-violet. Accordingly, a high reactivity of the graft PEI was expected in polymer resins.

Whisker–PVC composite was formulated on an 8 in. roll by a standard method. The recipe and formulation conditions are summarized in Table I. Stress–strain curves about the whisker-filled PVC were measured and are shown in Figure 3, where it is seen that tensile strength and ultimate elongation of the composite are significantly improved by the PEI grafting. Under highly strained conditions, stress of the matrix should be effectively transferred from whisker to whisker via the PVC and PEI layer at the interface.[6]

Young's moduli of the PEI-graft whisker-filled composite were, however, slightly lower in general than were those of original whisker-containing composite. This may be explainable by the soft flexible PEI graft polymer.[7] Charpy impact strength was also improved from 0.25 to 0.34 kJ/m^2 by 50 phr PEI-grafted whisker loading. This improvement is also accounted for by the flexible interface layer of the PEI.

CONCLUSION

The graft poly(ethylenimine) improved the interfacial interaction between the whisker and PVC matrix. Additional and specific reinforcement ascribable to the graft polymer was observed in the PVC composites.

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