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AES와 폴리클로로프렌 및 폴리염화비닐 블렌드의 물성

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Properties of Blends Containing Polychloroprene or Poly(vinylchloride) with AES

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요 약 : 본 연구에서는 10-40 wt%의 폴리클로로프렌(CR) 및 폴리염화비닐(PVC)을 각각 THF에 녹여 아크릴로니트릴-EPDM-스티렌 공중합체(AES)와의 블렌드를 얻고 그 물성을 조사하였다. AES의 열적안정성, 내광성 및 난연성에 미치는 CR 및 PVC의 영향을 고찰하였다. AES/CR 블렌드에서는 CR의 함량이 증가할수록 열적 안정성과 난연성은 증가하였고 내광성은 감소하였다. AES/PVC블렌드에서는 PVC의 함량이 증가할수록 난연성은 증가하였으나 열적 안정성은 감소하고 블렌드의 내광성은 AES나 PVC보다 약간 나빴으나 ABS보다는 상당히 양호하였다. 형태학적 연구도 행하였는데 블렌드된 PVC는 CR보다 AES와 나은 상용성을 보였다.

Abstract : Blends of polychloroprene(CR) or poly(vinylchloride)(PVC) with acrylonitrile-EPDM-styrene copolymer(AES) were prepared by casting from tetrahydrofuran(THF). The contents of CR or PVC in the blends ranged from 10 to 40 wt.%. The effect of the blended CR or PVC was investigated on the thermal stability, light resistance, and flammability of AES. For AES/CR blends, the thermal stability and flame retardancy of AES increased but light resistance decreased as the contents of CR increased. For AES/PVC blends, the flame retardancy increased but the thermal stability decreased with increasing PVC contents. The light resistance of the AES/PVC blends was worse than AES or PVC but better than ABS. Morphological studies were also performed on the blends. It was found that the blended CR or PVC showed different effects on the properties of AES. PVC showed better compatibility with AES than CR at the same blend compositions.

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INTRODUCTION

Acrylonitrile(AN)-butadiene-styrene terpolymer (ABS) is one of the most commonly used engineering plastics but poor weatherability and flammability limit the outdoor use of the material and its blends.[1,2] Among the several attemps to improve the poor performance, substitutions of α-methylstyrene or ethylene-propylene-diene terpolymer (EPDM) for styrene or butadiene, respectively, have been widely investigated. A typical commercially available example is AN-EPDM-styrene terpolymer(AES)[3~7]. The poor performances of ABS have been improved also by alloying with other polymers such as polycarbonate and poly(vinyl chloride)(PVC) or by mixing additives like antimony oxide.[8~10]

Several works have been carried out in this laboratory to find a new ABS-grade engineering plastic, like AES resin, having enhanced thermal stability and light resistance without deterioriation of other mechanical properties by introducing specialty monomers or polymers such as EPDM, methylmethacrylate or vinylnaphthalenes.[11~14] The purpose of this work is to study the properties of blends containing polychloroprene(CR) or PVC with AES. CR or PVC was selected because of its chlorine content, which might be expected to give favourable flame retardancy to AES. Before synthesizing a new graft copolymer of AN and styrene onto CR or any chlorine-containing polymer in place of butadiene to obtain new materials having good flame retardancy, it would be of great importance to have information about the effects of blended CR or PVC on the general properties of the final material.

Thus, the aim of this paper is to blend CR or PVC with AES and to investigate the effect of content and kinds of the blended CR or PVC on the properties. The blends of AES with CR or PVC have been prepared by casting from tetrahydrofuran(THF). The portions of CR or PVC in the blends were 10, 20, 30 to 40% by weight. The properties of the AES/CR and AES/PVC blends were investigated by using thermogravimetric analyzer (TGA), fade-o-meter, and limiting oxygen index tester. Morphological studies were also carried out by scanning electron microscopy (SEM).

EXPERIMENTAL PROCEDURES

Materials

The characteristics of the polymers used in this study are summarized in Table 1. ABS was used for reference. ABS and AES(commercial grades) were purified to remove additives or stabilizers [14] ; ABS or AES was stirred in xylene at 100℃ for 24 hr. After this treatment the solid residue was filtered away from the hot xylene solution. The xylene-insoluble residue was refluxed in acetone for about 1 hr. The bulk of the acetone-insoluble fraction material was dried in vacuo to obtain purified ABS or AES. CR and PVC of reagent grades

Table 1. Polymer Materials

Sample Notation	Characteristics	Source
ABS	Sp.gr. : 1.03 M.F.I.[a] : 0.8 H.D.T.[b] : 86℃	JSR ABS #10 (Japan Synth. Rubber)
AES	Sp.gr. : 1.03 M.F.I.[a] : 0.8 H.D.T.[b] : 90℃	JSR AES #110 (Japan Synth. Rubber)
CR	ML : 40 d[c] : 1.23 $\overline{M}_n$[d] $= 2.9\times10^4$ $\overline{M}_w = 1.4\times10^5$	Chloroprene #502 (Scientific Polymer Products ; SP[2])
PVC	η_{inh} : 0.65[e] d[c] : 1.40 $\overline{M}_n$[d] $= 3.74\times10^4$ $\overline{M}_w = 8.35\times10^5$	Aldrich

[a] Melt flow index(measured at 180℃), units in g/10min.
[b] Heat deflection temperature.
[c] Density, units in g/cm³.
[d] Measured by GPC.
[e] Inherent viscosity(measured at 0.5 g/dl of THF solution at 28℃). units in dl/g.

were used as received.

Preparation of Blends

Blends were prepared by dissolving the component polymers in THF. The solutions were cast on a glass plate and most of the solvent was allowed to evaporate slowly in the air at room temperature. The resulting films were then completely dried in vacuo to constant weight. The compositions of the blends ranged were 10, 20, 30 and 40% of CR or PVC by weight. The sample notations are listed in Table 2.

Measurements

Molecular Weight : The molecular weights of the materials in Table 1 were determined by gel permeation chromatography(GPC)(Waters-Water 244). The measurements were conducted in THF. The appratus was calibrated with PS standards.

Thermal Stability : Thermal stabilities of polymers were examined with a Shimadzu DT30A Thermogravimetric analyzer(TGA) at a heating rate of 10℃/min. under N_2 atmosphere.

Light Resistance : The light resistances of samples were determined using a Fade-o-meter (Atlas) (at 60℃ and 65% R.H.) and a color difference meter (NO-101DP). The sample films were cast from a solution of 1.5g of polymer in 5ml of THF on a non-yellowing urethane-coated hiding paper. The films were dried slowly at room temperature and then under vacuum to constant weight. The areas of the films were $5\times10\ cm^2$ and the thickness was 35 μm. After the films had been exposed in the tester to u.v. for a given time (1 to 5 hr), the color difference(ΔE) of the sample was measured using the color difference meter.

Flammability : For flammability test, limiting oxygen index(LOI) was determined in a room corridor tester(Suga ON-1 type, Japan).[15] The oxygen indices of samples are the concentration of oxygen just supporting combustion under steady-state candle-like burning. A material is considered flammable at any temperature where the oxygen index is below 21.[16]

Morphology : Scanning Electron Microscopy (SEM) was carried out by DS-130C SEM. Samples were cryogenically fractured in liquid N_2 and etched with ethyl acetate/n-hexane mixture(1 : 1 v/v) or cyclohexanone at 50℃ to extract out CR or PVC, respectively, for 2 hr and dried for about 12 hr at 60℃ under vacuum, followed by platinum coating prior to placing in the SEM chamber.

Table 2. Sample Notation

Sample notation	Composition(wt.%)		
	AES	CR	PVC
E100	100	–	–
E90CR10	90	10	–
E80CR20	80	20	–
E70CR30	70	30	–
E60CR40	60	40	–
E90PVC10	90	–	10
E80PVC20	80	–	20
E70PVC30	70	–	30
E60PVC40	60	–	40

RESULTS AND DISCUSSION

Thermal Stabilitites

Figure 1 shows typical TGA thermograms of AES/CR blends. The final decomposition temperature increased with increasing CR content. This result means that the incorporation of CR enhanced the thermal stability of AES because of the flame retardant effect of the chlorine content in CR. It should be noted that AES and its blends with CR showed better thermal stabilities than ABS. The higher thermal stability of AES is ascribed to the presence of EPDM having good heat resistance. The effects of the content of PVC on the thermal stabilities of AES/PVC blends are illustrated in Fig. 2. In contrast to the AES/CR blends, the thermal stabilities of the blends decreased with rising content of PVC.

Another interesting feature is that the thermal degradation of ABS or AES follows simple inverse-sigmoidal kinetics but both the AES/CR and AES/PVC blends show two-stage degradation kinetics around 350~500℃. The second-stage degradations, as indicated by arrows in Figs. 1 and 2,

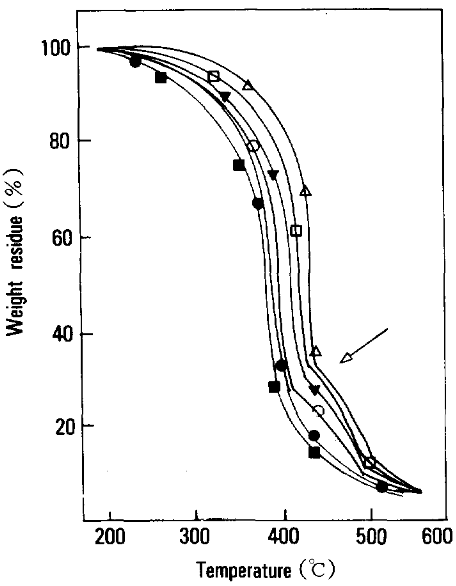


Fig. 1. Effects of the CR content on the TGA thermograms for AES/CR blends : ■ ABS, ● E100, ○ E90CR 10, ▼ E80CR20, □ E70CR30, △ E60CR40.

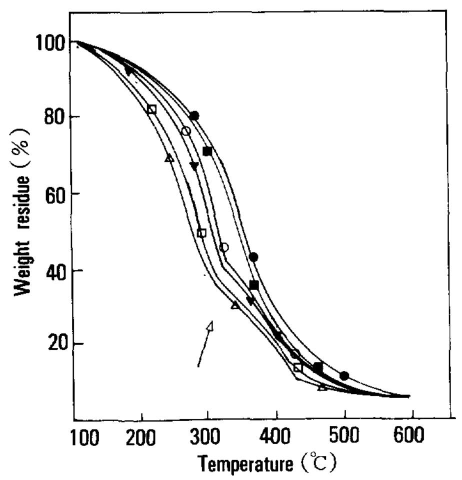


Fig. 2. Effects of the PVC content on the TGA thermograms for AES/PVC blends : ■ ABS, ● E100, ○ E90 PVC10, ▼ E80PVC20, □ E70PVC30, △ E60PVC40.

are ascribed to the typical decomposition behaviour of CR or PVC giving residues followed by dehydrochlorination.[17] The exact comparison of the decom-position behavior of CR with that of PVC in the blends of AES was not easy, as already pointed

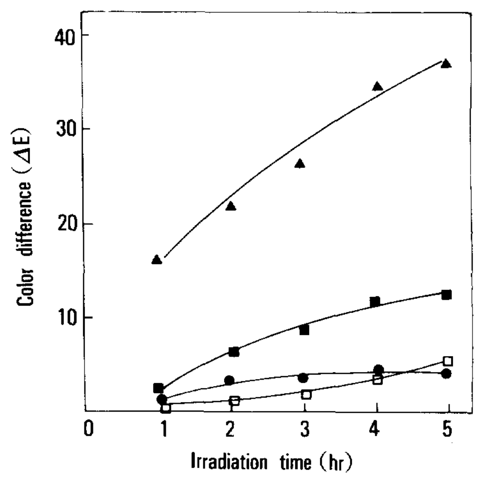


Fig. 3. Plot of color difference vs irradiation time for various samples : ■ ABS, ● E100, ▲ CR, □ PVC.

out by Gardner and McNeill.[17]

Light Resistance

The light resistances of samples were semi-quantitatively expressed in terms of color difference (ΔE) with National Bureau of Standards Unit.[18~21] The color difference theories imply that the smaller ΔE means better light resistance and weatherability.[12,18] The samples were exposed in the Fade-o-meter for measurements of light resistance for 1, 2, 3, 4 and 5 hr.

Figure 3 shows the light resistances of various homopolymer samples. The ΔE data follow the order PVC<AES<ABS<CR. The superior light resistance of AES is due to the excellent outdoor properties of EPDM in AES. It is interesting that PVC showed better light resistance than AES, even though the differences are not large. The bad light resistance of CR is due to the inherent yellowing properties associated with allylic chlorines for u.v. or visible light.

Figure 4 shows the effect of CR contents on the light resistances of AES/CR blends. As expected, the light resistances decreased with increasing CR contents.

Figure 5 shows the effects of PVC content on the light resistances of AES/PVC blends. Strange enough, ΔE of the blends were higher than those

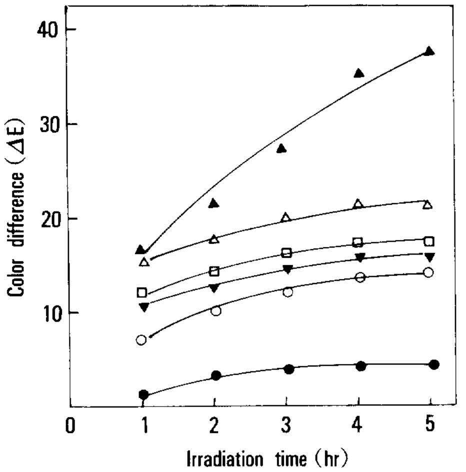


Fig. 4. Plot of color difference vs irradiation time for AES/CR blends : ● E100, ○ E90CR10, ▼ E80CR20, □ E70CR30, △ E60CR40, ▲ CR.

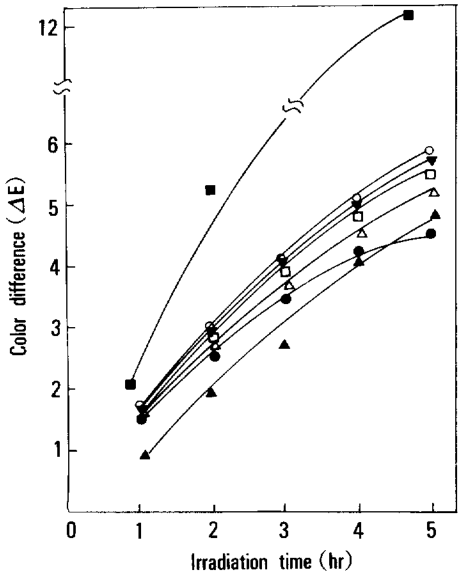
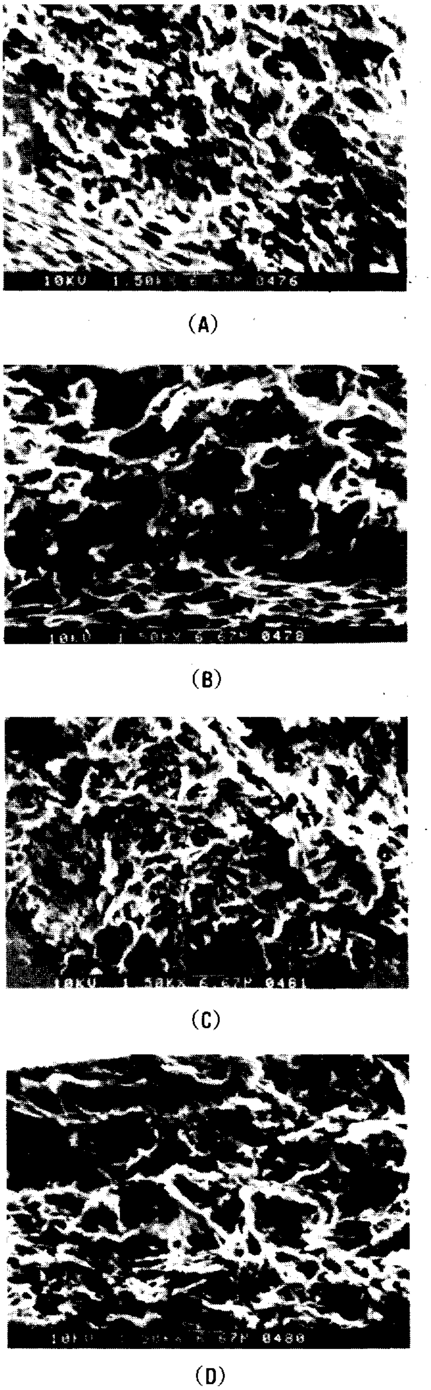


Fig. 5. Effects of the CR content on the light resistance for AES/PVC blends : ■ ABS, ● E100, ○ E90 PVC10, ▼ E80PVC20, □ E70PVC30, △ E60PVC40, ▲ PVC.

of AES or PVC single component, regardless of the PVC content, meaning that the light resistances became worse as PVC was introduced. However, it is important to note that the absolute values of



(A)

(B)

(C)

(D)

Fig. 6. SEM micrographs of AES/CR and AES/PVC blends : (a) E90CR10, (b) E60CR40, (c) E90PVC10, (d) E60PVC40.

ΔE are smaller than that of ABS.

Morphology

The morphologies of AES/CR and AES/PVC blends were analyzed by SEM. Figure 6 shows both blends are incompatible and their phases are grossly separated, when the contents of CR or PVC are 10 and 40 wt.%. The SEM micrographs show that CR or PVC domains are distributed in the AES matrix, where the dark portions represent the CR or PVC phase extracted out by solvent. It is interesting that the blends show two-phase structure over the experimental composition range but the phase separation between two components is more evident in AES/CR blends than in AES/PVC blends(compare Fig. 6-b and 6-d).

The different TGA or light resistance behaviour in the two blends may be related to the difference in compatibility of CR or PVC with AES. Further studies, however, should be made to investigate more thoroughly interactions between CR or PVC and AES.

Flammability

Table 3 shows the LOI of ABS, AES, AES/CR and AES/PVC blends. The highest LOI was observed when 40 wt.% PVC was blended with AES. It is seen that ABS and AES are flammable since the LOI values are below 21.[16] Although the LOI values increased with increasing CR or PVC contents for both AES/CR or AES/PVC blends because of greater chlorine contents leading to flame retardancy, Table 3 implies that AES is "not flammable" on the basis of LOI only when more than 40 wt.% of CR are blended or more than 20 wt.% of PVC are blended. It is clearly shown that PVC improves the flame retardancy of AES more prominently than CR.

Table 3. LOI of AES/CR or AES/PVC Blends

Sample notation	LOI
ABS	18
E100	18.5
E90CR10	18.5
E80CR20	19.5
E70CR30	20.5
E60CR40	21.5
E90PVC10	19.5
E80PVC20	22.0
E70PVC30	23.5
E60PVC40	24.5

CONCLUSIONS

Blends of CR or PVC with AES were prepared and the effects of blended CR or PVC on the several properties of AES were studied. The conclusions follow.

1. The thermal stabilities of AES increased with CR contents but decreased with PVC contents.
2. The light resistance of AES decreased with increasing content of CR in AES/CR blends whereas that of AES became worse as PVC was included regardless of the PVC contents in AES/PVC blends.
3. PVC showed better compatibility with AES than CR, from morphological observations.
4. The flame retardancy of AES was improved by the blended CR or PVC and the effect was more prominent in AES/PVC blends.

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