

금속 접착제 활용이 기대되는 클로로프렌과 무수말레인산 공중합체 연구

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(1992년 2월 14일 접수)

Poly(chloroprene-co-maleic anhydride) as a Potential Adhesive for Metals

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(Received February 14, 1992)

요약: 클로로프렌과 무수말레인산 공중합체를 자유라디칼중합으로 합성하였다. 이 공중합체는 무정형이었고 약 10°C의 유리전이온도를 가졌다. 내광성과 접착강도(lab shear stress)를 조사하였는데 이 공중합체는 폴리클로로프렌에 비해 자외선이나 열에 노출시켰을 때 우수한 내광성을 나타내었고 철-철 및 구리-구리에 대한 접착강도는 각각 6.86kg/cm², 4.76kg/cm²이었다.

Abstract: The copolymer of chloroprene(CP) and maleic anhydride(MAH) was prepared by radical polymerization. The copolymer was amorphous and had glass transition temperature of about 10°C. The light resistance and the lab shear strength of the copolymer were investigated. The copolymer showed fairly better light resistance under the environmental conditions both exposed to U. V. light and heat. The adhesion strength of the copolymer was determined in terms of lab shear strength as 6.86kg/cm² and 4.76kg/cm² for the adherend/substrate pairs of steel/steel and copper/copper, respectively.

INTRODUCTION

Polychloroprene(CR) is one of the most commonly used synthetic rubbers in adhesives and the automotive field or energy industries as the base

elastomer for a variety of components such as V- or conveyor belts and wire and cable because of its superior resistance to swelling in oil and its combination of polarity and crystallinity. A wide variety of types of CR is available to allow the users

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to formulate for their specific requirements. However, its poor heat resistance and weatherability limit the outdoor use of the material and its blends.^{1,2} Among the several attempts to improve the poor performances, the introduction of a second monomer into the CR backbone or the use of appropriate fillers for compounding has been widely investigated.^{3~7} The grafting of methyl methacrylate to CR is a typical example to enhance outdoor properties of CR adhesives.⁶

Recently we reported that the graft copolymer of acrylonitrile and methyl methacrylate onto CR exhibited improved weatherability and thermal stability of CR.⁷ In this work, we obtained a copolymer of chloroprene with maleic anhydride to have enhanced light resistance and adhesion. The maleic anhydride was selected as a second monomer because of its polar properties when ring-opened.

The copolymer was prepared by radical polymerization and characterized by IR and ¹H-NMR spectroscopies. The light resistance and the adhesive bond strength of the copolymer were investigated.

EXPERIMENTAL

Materials

Maleic anhydride, 1,4-dioxane and toluene, supplied by Junsei Chemical Co., were purified by the standard methods. 2,2'-azobisisobutyronitrile (AIBN) was purified by recrystallization in dehydrated ethanol. 3,4-dichloro-1-butene (DCB) and tetrahydrofurfuryl alcohol (THFA) (Aldrich Chemical Co.) were used as received without further purifications.

Chloroprene (2-chloro-1,3-butadiene) was prepared by reacting DCB in aqueous solution of sodium hydroxide in the presence of THFA at 55°C; 110 ml of THFA was added to 150 g of 30% aqueous NaOH solution in 500 ml of four-necked flask equipped with condenser, stirrer, separable funnel and gas inlet and outlet. The mixture was heated to 55°C. 108 ml of DCB was added dropwise to the mixture for 1 hr. 0.9 g of hydroquinone was then

added to inhibit any further thermal polymerization.

The product was filtered to remove sodium chloride and the supernatant was dried with CaCl₂ and distilled in argon under reduced pressure, the fraction collected at 25°C and 160mmHg was retained for copolymerization. The purity of chloroprene was confirmed to be 99.2% by gas chromatography (yield; 60%). Chloroprene was used as soon as possible after distillation because it was polymerized slowly during storage, even at low temperature.

The structure of chloroprene was identified by IR spectrophotometry (Perkin Elmer 1330) and ¹H-NMR spectroscopy (Bruker 300CW); The IR spectrum of chloroprene, as shown in Fig. 1, exhibited characteristic peaks of stretching vibration of vinyl C-H bond at 3020 and 3100 cm⁻¹ (b), whereas the characteristic peaks of DCB due to stretching vibration of aliphatic C-H bond were disappeared at 2950 and 2990 cm⁻¹ (a). In Fig. 2 the ¹H-NMR (CCl₄) spectrum of chloroprene showed =CH₂ and =CH- peaks at δ 5.2, 5.6, and 6.4 ppm (b) whereas the characteristic peaks of DCB was shown at δ 3.6 and 4.5 ppm due to -CH₂Cl and -CHCl, respectively (a).

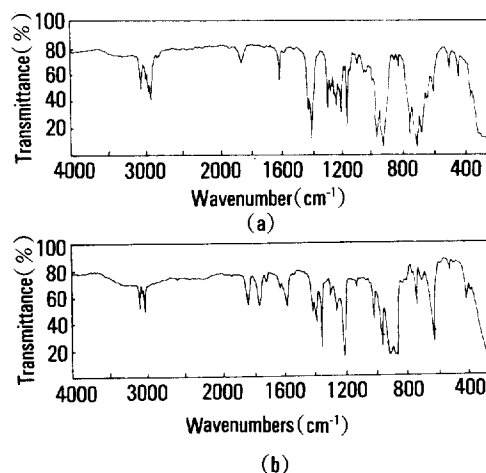


Fig. 1. IR spectra of (a) 3,4-dichloro-1-butene and (b) 2-chloro-1,3-butadiene (KBr liquid cell).

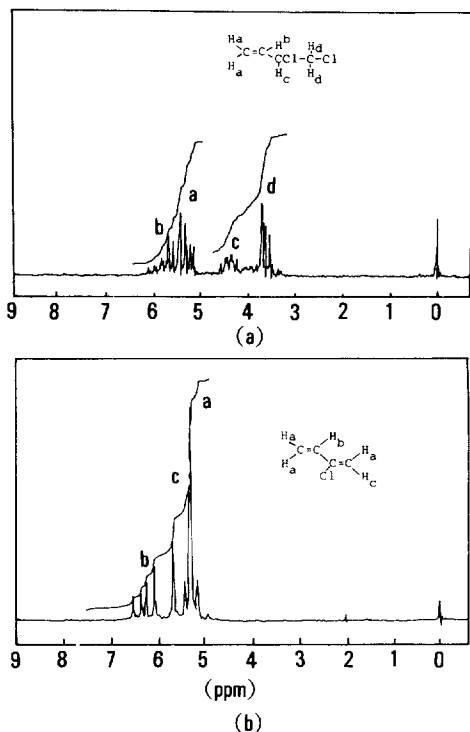


Fig. 2. ¹H-NMR spectra of (a) 3,4-dichloro-1-butene and (b) 2-chloro-1,3-butadiene (Carbon tetrachloride).

Synthesis of Poly(chloroprene)

Polychloroprene (CR) was prepared in a glass ampoule. 1,4-dioxane was used as diluent for the polymerization. 0.25 mole of chloroprene was radically polymerized with 0.25 mole % AIBN as an initiator at $60 \pm 0.05^\circ\text{C}$ in 100 ml of 1,4-dioxane. After 50 min, the reaction mixture was poured into a large amount of toluene. The product CR recovered from toluene was dried under vacuum at ambient temperature to remove all volatiles.

Synthesis of Poly(chloroprene-co-maleic anhydride) [Poly (CP-co-MAH)]

The copolymer of chloroprene and maleic anhydride was obtained by the same method as described for CR; 0.25 mole of chloroprene and 0.25 mole of maleic anhydride were radically copolymerized with 0.25 mole % AIBN as an initiator at $60 \pm 0.05^\circ\text{C}$ in 100 ml of 1,4-dioxane. After 50 min, the reaction mixture was poured into a large amount of toluene. The product poly (CP-co-MAH)

recovered from toluene was dried under vacuum at ambient temperature to remove all volatiles. The composition ratio of this poly (CP-co-MAH) was determined as $[\text{MAH}]/[\text{CP}] = 0.775$ by using ¹H-NMR (Bruker 300CW) spectrophotometer.⁸ The poly (CP-co-MAH) was used for characterization and property measurements, unless specifically noted. However, for adhesive bonding tests, two other copolymers with different mole ratios in feed were also prepared; the monomer mole ratios of [CP] to [MAH] in feed were 0.66 and 1.5, respectively.

Characterization

CR and poly (CP-co-MAH) were characterized by Infrared spectroscopy (Perkin Elmer 1330) and ¹H-NMR (Bruker 300CW) spectrophotometer. The molecular weight of the copolymer was determined by gel permeation chromatography (GPC) (Waters 244) with Ultrastaygel 500 Å linear columns. The measurement was conducted in THF at 28°C . The apparatus was calibrated with PS standards.

The glass transition temperatures of polymers were measured by using differential scanning calorimetry (DSC; DuPont 990). Thermal analyses were performed under nitrogen gas at a heating rate of $10^\circ\text{C}/\text{min}$.

Measurement

Light resistance: The light resistance was studied with a Q panel UV B313 weathering Tester at 40°C using a U. V. lamp with a 315-280 nm wavelength, according to ASTM G53. The samples were prepared as follows. The films were cast from a solution of 1.5 g of polymer in 5 ml of THF on a nonyellowing urethane-coated hiding paper. The films were dried slowly at room temperature and then kept under vacuum until they reached a constant weight. The size of the films was $3 \times 5 \text{ cm}^2$ and the thickness was $35 \mu\text{m}$.

The light resistance of the films was measured under two different conditions; For one condition, the films had been exposed directly to U. V. light in the Tester for a given time (up to 3 hrs) without any pre-heat treatment. For another condition, the

films had been exposed to heat at 100°C for 24 hrs in a thermal aging oven before placing into the Tester chamber. The color difference(ΔE) of the samples exposed to U. V. or heat was calculated using the Hunter-Schofield equation.^{9,10} For measurements of the color difference, a color difference meter(ND-101 DP, Japan) was used.

Lab shear strength : The adhesive bond strength of CR and copolymer adhesives was measured by using lab shear strength according to ASTM D10 02-72. The bond plane is 25.4 mm wide and a 12.7 mm overlap. Adherend thickness was 1.63 mm. The adhesive was prepared from a solution of 1.5 g of CR or copolymer in 5 ml of THF. Carbon steel (mild), copper and aluminum were used as adherends after degreasing with trichloroethylene. The same substrate was used for each adherend. The lab shear strength was measured in unit of maximum load per cross section area of the bond plane (kg/cm^2) when fractured.

RESULTS AND DISCUSSION

Characterization

The structure of copolymer was identified by IR spectrophotometer. The IR spectrum of CR, as shown in Fig. 3(a), exhibited characteristic peaks at 3020 (stretching vibration of vinyl C-H bond), 2926 and 2853(stretching vibration of aliphatic C-H bond), 1650($\text{C}=\text{C}$ double bond), 1465 cm^{-1} (scissoring of CH_2), 600 and 670 cm^{-1} (C-Cl bond). The IR spectrum of poly(CP-co-MAH), as shown in Fig. 3(b), exhibited characteristic peaks at 3020 (stretching vibration of vinyl C-H bond), 2930 and 2960(stretching vibration of aliphatic C-H bond),

1855 and 1775 cm^{-1} (anhydride group), and 1660 cm^{-1} ($\text{C}=\text{C}$ double bond).

The molecular weight of CR was determined as $\bar{M}_n=23,000$, $\bar{M}_w=55,000$ and that of poly(CP-co-MAH) was determined as $\bar{M}_n=8,000$ and $\bar{M}_w=12,500$. In this case, the poly(CP-co-MAH) having composition ratio of $[\text{MAH}]/[\text{CP}]=0.775$ was measured, as mentioned in the experimental section. The copolymer is well dissolved in tetrahydrofuran(THF), acetone and methyl ethyl ketone. For reference, Table 1 lists the solubility of CR and the copolymer in various organic solvents.

Glass Transition Temperature

Fig. 4 shows DSC thermograms of CR and poly(CP-co-MAH). The copolymer has glass transition temperature of around 10°C, which is higher by about 40°C than that of polychloroprene. The result may be due to the bulky and rigid property of ma-

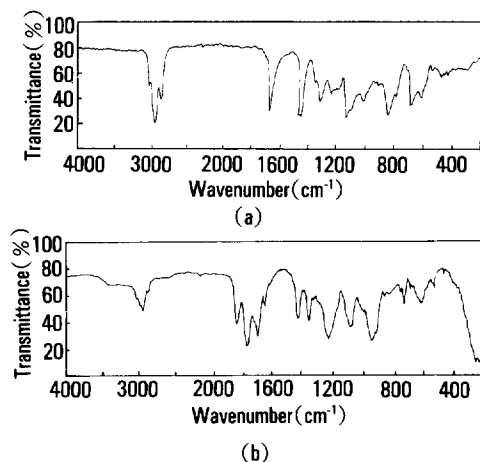


Fig. 3. IR spectra of (a) CR and (b) poly(chloroprene-co-maleic anhydride)(KBr film).

Table 1. Solubility of CR and Poly(CP-co-MAH) in Various Solvents

Polymers	Solvents*									
	Tol	THF	CCl_4	DCE	Acetone	Cycl	EA	DMF	MEK	Dioxane
CR	++**	++	++	+	-	-	-	-	+/-	+/-
Poly(CP-co-MAH)	-	++	-	-	++	+	+	+/-	++	+

*Tol ; Toluene, THF ; Tetrahydrofuran, CCl_4 ; Carbon tetrachloride, DCE ; 1,2-Dichloroethane, Cycl ; Cyclohexanone, EA ; Ethyl acetate, DMF ; Dimethyl formamide, MEK ; Methyl ethyl ketone

**++ ; good soluble, + ; soluble, +/- ; swelling, - ; insoluble

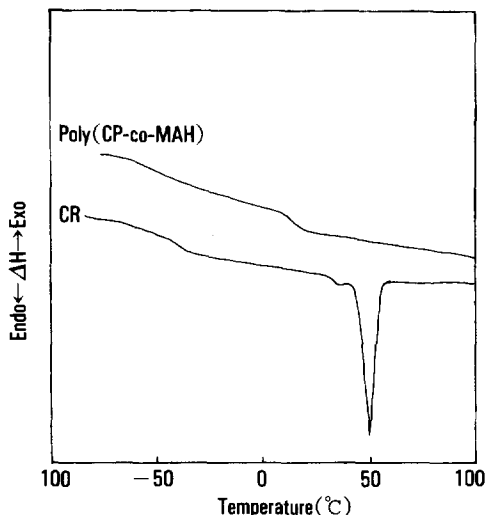


Fig. 4. DSC curves of CR and poly(CP-co-MAH) at 10 °C/min heating rate in the stream of nitrogen.

leic anhydride. The CR exhibited a melting peak around at 50°C but the copolymer does not show any melting peak, meaning that the CR has some degree of crystallinity whereas the copolymer is amorphous.

Light Resistance

The light resistance of samples was semi-quantitatively expressed in terms of color difference (ΔE) with National Beureau of Standards Units. The color difference theories imply that the smaller ΔE means better light resistance and weatherability.¹⁰⁻¹² The samples were exposed in the Weathering Tester for 30 through 180 minuits.

Fig. 5 shows light resistances of CR and poly (CP-co-MAH) after exposure to UV light. It can be shown that the light resistance of the copolymer was much improved compared to that of CR due to the introduction of maleic anhydride, while CR possess inherently yellowing property in outdoor uses because of its allylic chlorine content. ΔE is almost constant as a function of time up to 3 hrs for the copolymer. The fact implies that the copolymer might be stabilized to U.V. light because there remains little allylic chlorine content due to the presence of maleic anhydride in the polymer chain.

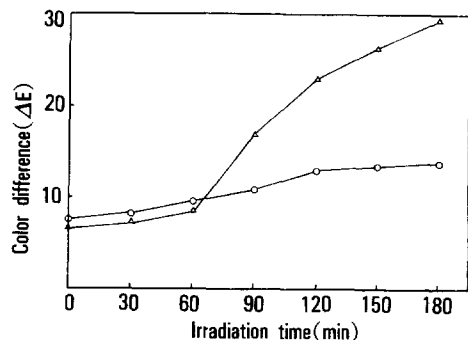


Fig. 5. Color difference change against irradiation time for two different samples without heat pretreatment, \triangle : CR, \circ : poly(CP-co-MAH).

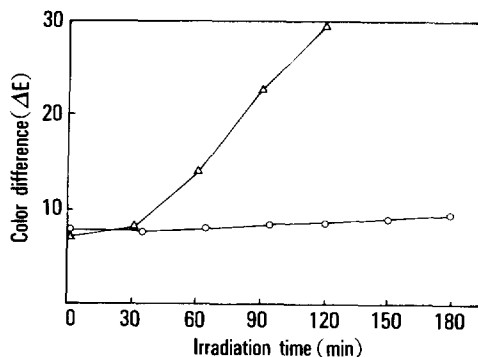


Fig. 6. Color difference change against irradiation time for two different samples after exposure to heat (100°C) in thermal aging oven for 24hrs, \triangle : CR, \circ : poly(CP-co-MAH).

The light resistance of CR and the copolymer after exposure to heat(100°C) is illustrated in Fig. 6. It is also shown that the light resistance of copolymer under the thermal aging condition is also superior to that of CR due to the stabilizing role of maleic anhydride to heat. Careful examination of the two figures reveal that the yellowing property of CR adhesive is more severe for the samples exposed to heat than for those non heat-treated ones whereas the copolymer shows considerable anti-yellowing property under even severe environmental condition.

Lab Shear Strength

Table 2 shows the lab shear strengths of the CR or copolymer adhesives for steel , aluminum and

Table 2. Lab Shear Strength of CR and Copolymer Adhesives

Adherend/Substrate	Lab shear strength (kg/cm ²)	
	CR	Poly (CP-co-MAH)
Steel/Steel	3.74	6.86
Copper/Copper	3.54	4.76
Al/Al	8.61	5.71

copper adherends. It was found that the lab shear strength of copolymer adhesive is given as 6.86 kg/cm² for steel to steel adhesion, which is almost double as that of CR adhesive for the same adherend-to-substrate pair; CR adhesive showed the lab shear strength of only 3.74 kg/cm². The adhesive strength of the copolymer for copper to copper adhesion is 4.76 kg/cm², whereas that of CR adhesive is 3.54 kg/cm². The result may be ascribed to the fact that the interaction between the metal adherends or substrates and the copolymer adhesive is stronger than that between metals and CR adhesive due to the polarity of maleic anhydride.

For aluminum adherend and aluminum substrate, however, the copolymer adhesive shows weaker adhesion (5.71 kg/cm²) than CR adhesive (8.61 kg/cm²). The result may be caused by the different interaction of aluminum with chlorine in CR and oxygen in maleic anhydride. The results in Table 2 imply that aluminum has weak interaction with oxygen while it has strong interaction with chlorine and/or the presence of oxygen may weaken the interaction between aluminum and chlorine. The adhesion strength may become weaker especially upon exposure to moisture, even though all-out efforts were made to treat samples for adhesion tests under dry conditions. For copper or steel adhesion, the introduction of oxygen may enhance synergistically the interaction between chlorine atom and steel or copper. The decrease of bond strength was reported in the aluminum-epoxy joint during moisture aging¹³ because of the conversion of epoxide to boehmite, AlOOH. However, more detailed works should be made to interpret those results accurately.

Table 3. Effect of MAH Contents on the Lab Shear Strength of Copolymer Adhesives

Adherend/Substrate	Lab Shear Strength (kg/cm ²)		
	(MAH/CP = 0.66)	(MAH/CP = 1.0)	(MAH/CP = 1.5)*
Steel/Steel	4.88	6.86	7.93
Copper/Copper	2.73	4.76	5.80
Al/Al	5.64	5.71	6.49

* in monomer feed ratio

In order to investigate the effect of maleic anhydride contents on the adhesion, we also prepared two more copolymers having different copolymer compositions. Table 3 also shows the results. The adhesion strength increased as the composition of maleic anhydride increased in the copolymer regardless of the kinds of adherends. The lab shear strength of copolymer adhesive is 7.93 kg/cm² for steel to steel adhesion and the adhesive strength for copper to copper adhesion is 5.80 kg/cm², when the mole ratio of [CP] to [MAH] is 1.5. The result seems to prove the speculation that the interaction between metal adherend or substrate and the copolymer adhesive is related to the polarity of maleic anhydride.

CONCLUSIONS

In this work, a copolymer of chloroprene and maleic anhydride was prepared by radical polymerization. It was found that the copolymer was amorphous and had glass transition temperature of about 10°C. The copolymer showed fairly better light resistance when exposed both to U.V. light and heat at 100°C. It was observed that the lab shear strength of copolymer adhesive was given as 6.86 kg/cm² and 4.76 kg/cm² for steel to steel and copper to copper adhesion, respectively, which are almost double as that of CR adhesive for the same adherend to substrate pairs. The poly(CP-co-MAH) is, however, not suitable adhesive for the adherend/substrate pair of aluminum/aluminum.

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