

Comparative Study on Rebound Resilience and Structures of Sodium Salts of Maleic Anhydride-Grafted Ethylene-co-ethyl Acrylates with Its Analogous Polymers

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SYNOPSIS

Sodium salts of ethylene-co-ethyl acrylate-*g*-maleic anhydride show high rebound resilience, the same as those of both saponified ethylene-co-ethyl acrylates and sodium salts of ethylene-co-methacrylic acids at low salt contents. The measurements of thermal and mechanical properties and dynamic viscoelastic behaviors indicate that the sodium salts of ethylene-co-ethyl acrylate-*g*-maleic anhydride behave like strong ionic bond cross-linkages close to covalent bond cross-linkages in the polymer, differing from the monocarboxylate salts of saponified ethylene-co-ethyl acrylate and the sodium salts of ethylene-methacrylic acid. It is concluded that the strong cross-linking of the dicarboxylate salts of the neutralized ethylene-co-ethyl acrylate-*g*-maleic anhydride causes the high rebound resilience. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It has been known that cross-linking of polymers through covalent bonds and ionic bonds provides to polymers higher rebound resilience properties. For example, neutralized ethylene-co-methacrylic acids with metal cations^{1,2} through ionic cross-linkages and poly(*cis*-1,4-butadiene) cross-linked with peroxides through covalent bond cross-linkages³⁻⁶ exhibit high rebound resilience.

Saponified ethylene-co-ethyl acrylate (Na-EEA) is also flexible and of high rebound resilience. The intermolecular ionic cross-linkages of sodium salts in Na-EEA cause high rebound resilience as well as do sodium salts of ethylene-co-methacrylic acids (Na-EMAA). The functional groups of Na-EEA are ethyl carboxylates and sodium carboxylates. If certain functional groups similar to sodium salts are possibly introduced into ethylene-co-ethyl acrylate (EEA) instead of saponifying⁷⁻¹¹ the EEA, it can be expected that a polymer almost equal to Na-EEA

in rebound resilience and other properties will be obtained. By using maleic anhydride (MAH) as the functional group, sodium carboxylates were introduced into EEA, i.e., MAH was grafted onto EEA in the presence of peroxides to give an ethylene-co-ethyl acrylate-*g*-maleic anhydride (EEA-*g*-MAH) that was rapidly neutralized with aq sodium hydroxide (NaOH) solution, as shown in Scheme 1.

The properties of the sodium salts of the neutralized EEA-*g*-MAH (Na-EEA-*g*-MAH) were evaluated, particularly the rebound resilience and the dynamic viscoelastic behavior, in comparison with those of Na-EEA and Na-EMAA.

EXPERIMENTAL

Materials

EEA (E 86.9 mol %, EA 13.1 mol %, MFR 25 dg/min) and EMMA (E 94.6 mol %, MAA 5.4 mol %, MFR 60 dg/min) were produced by DuPont-Mitsui Polychemical Co. MAH and NaOH are special grades of Kantho Chemical Co. Di-*tert*-butyl peroxide was obtained from Lucidol Yoshitomi Co. All reagents were used without further purification.

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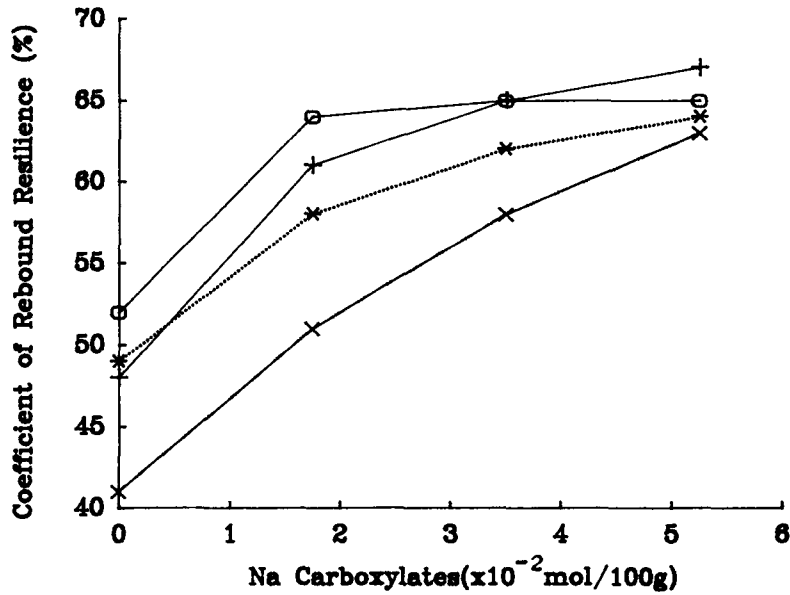


Figure 1 Coefficient of rebound resilience of (O) Na-EEA-g-MAH (α), (+) Na-EEA-g-MAH (β), (*) Na-EEA, and (x) Na-EMAA with concentrations of sodium carboxylates.

are shown in Figure 1. The rebound resiliences of Na-EEA-g-MAH (α) were unexpectedly as high as 64% and equaled those of Na-EEA and Na-EMAA. It is significant that the rebound resiliences of Na-EEA-g-MAH (α) were superior to those of the other polymers in a sodium carboxylate concentration

range lower than 5.25×10^{-2} mol/100 g, i.e., Na-EEA-g-MAH (α) at a slight sodium carboxylate concentration of 1.75×10^{-2} mol/100 g showed the same rebound resilience as those of Na-EEA and Na-EMAA at a 5.25×10^{-2} mol/100 g sodium carboxylate concentration.

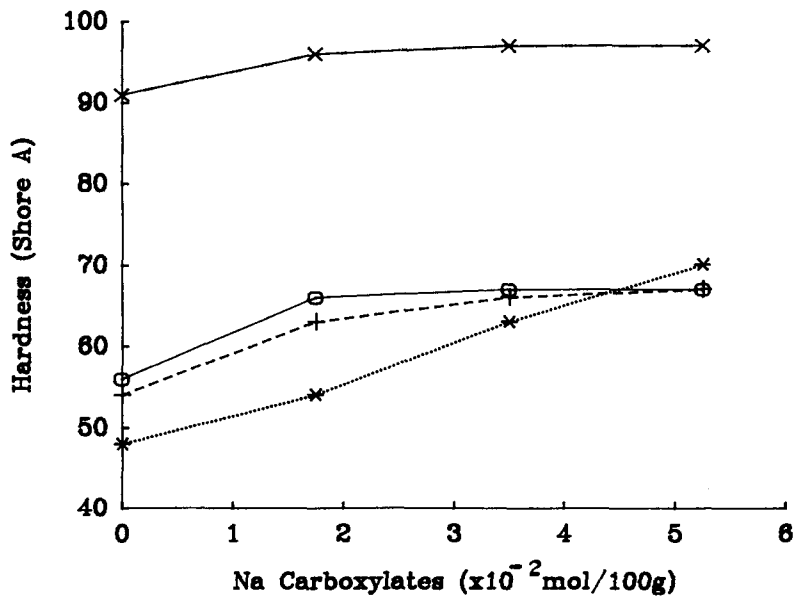


Figure 2 Hardness of (O) Na-EEA-g-MAH (α), (+) Na-EEA-g-MAH (β), (*) Na-EEA, and (x) Na-EMAA with concentrations of sodium carboxylates.

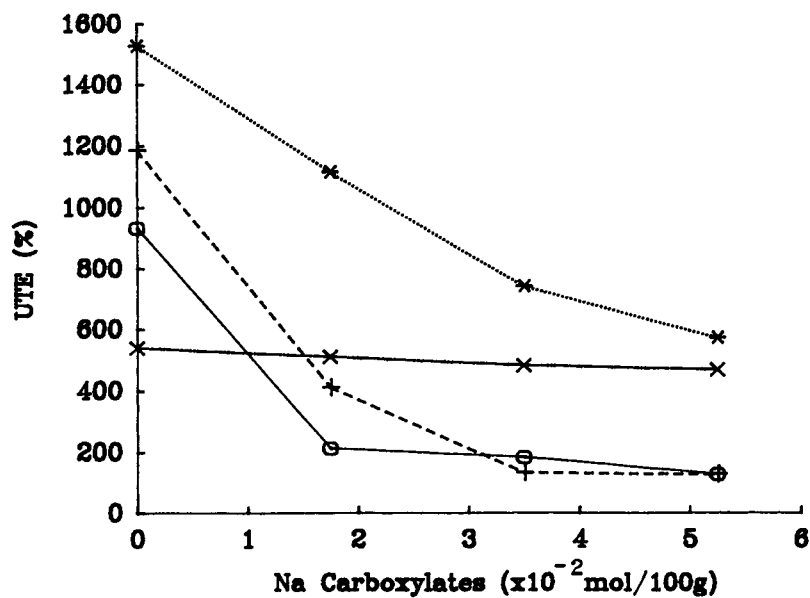


Figure 3 UTE of (O) Na-EEA-*g*-MAH (α), (+) Na-EEA-*g*-MAH (β), (*) Na-EEA, and (x) Na-EMAA with concentrations of sodium carboxylates.

Comparison of Na-EEA-*g*-MAH (α) with Na-EEA for Other Properties

Other properties except for the rebound resilience were compared between the polymers. The hardness,

the ultimate tensile elongation (UTE), and the ultimate tensile strength (UTS) vs. the concentration of sodium carboxylates in the polymers are shown in Figures 2, 3, and 4, respectively. As shown in Figures 2 and 3, Na-EEA-*g*-MAH (α) indicated higher

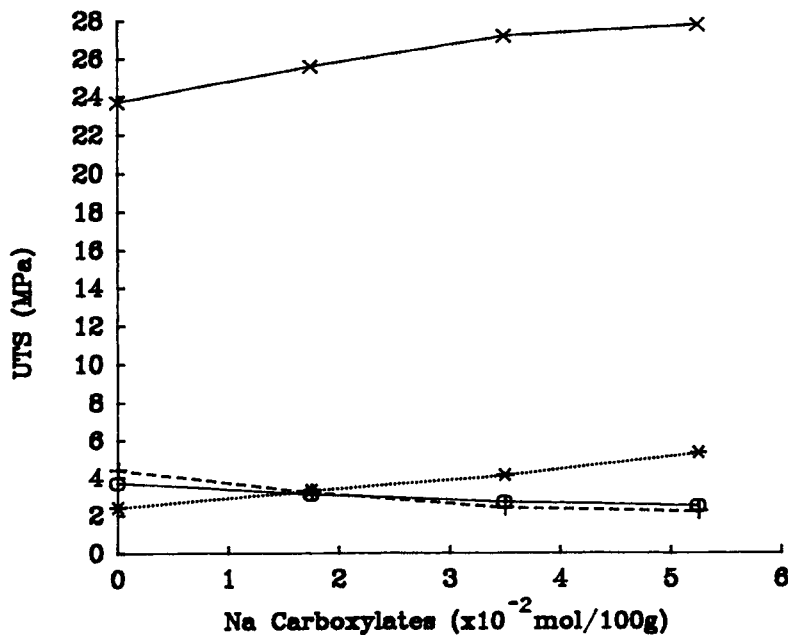


Figure 4 UTS of (O) Na-EEA-*g*-MAH (α), (+) Na-EEA-*g*-MAH (β), (*) Na-EEA, and (x) Na-EMAA with concentrations of sodium carboxylates.

hardness than that of Na-EEA at a sodium carboxylate concentration lower than 3.50×10^{-2} mol/100 g. For example, the hardness of Na-EEA-*g*-MAH (α) at a 1.75×10^{-2} mol/100 g sodium carboxylate concentration was Shore A 66 and that of Na-EEA was Shore A 54. The UTE of Na-EEA-*g*-MAH (α) remarkably decreased in comparison with that of Na-EEA. When increasing the concentration of the sodium carboxylates, the UTS of Na-EEA-*g*-MAH (α) showed a tendency to decrease in contrast to the increase of that of Na-EEA, as shown in Figure 4.

Comparison of Na-EEA-*g*-MAH (α) with Na-EMAA for Other Properties

Na-EMAA exhibits the same tendency of increasing hardness with higher concentration of sodium carboxylates as that of Na-EEA-*g*-MAH (α), as shown in Figure 2. However, the absolute values of the hardness of the former were much higher than those of the latter because the low hardness of the latter is due to the ester groups being contained in the polymer. The UTE of Na-EMAA was less changed than that of Na-EEA-*g*-MAH (α) with increase of the concentration of the sodium carboxylates, as

indicated in Figure 3, and the UTS of the former had the same tendency to increase in comparison with the decrease of that of the latter, as shown in Figure 4.

Comparison of Dynamic Viscoelastic Behaviors of Na-MAH-*g*-EEA (α) with the Other Polymers

The relations between the concentration of sodium carboxylates and their dynamic viscoelastic behaviors are shown in Figures 5-7. Na-EEA-*g*-MAH (α) does not show a large change of either the storage modulus (E') or $\tan \delta$ at the rebound resilience-measuring temperature of 23°C with the concentration of the sodium carboxylates of more than 1.75×10^{-2} mol/100 g, but Na-EEA and Na-EMAA showed an increase of E' and a decrease of $\tan \delta$ at the same conditions. This tendency was in accord with the changes of the rebound resiliences of the polymers with higher concentration of sodium carboxylates. A tendency of the rebound resilience to increase with both the higher storage modulus E' and the lower $\tan \delta$ was observed.

As mentioned above, the behaviors of Na-EEA-*g*-MAH (α) are different from those of Na-EEA and

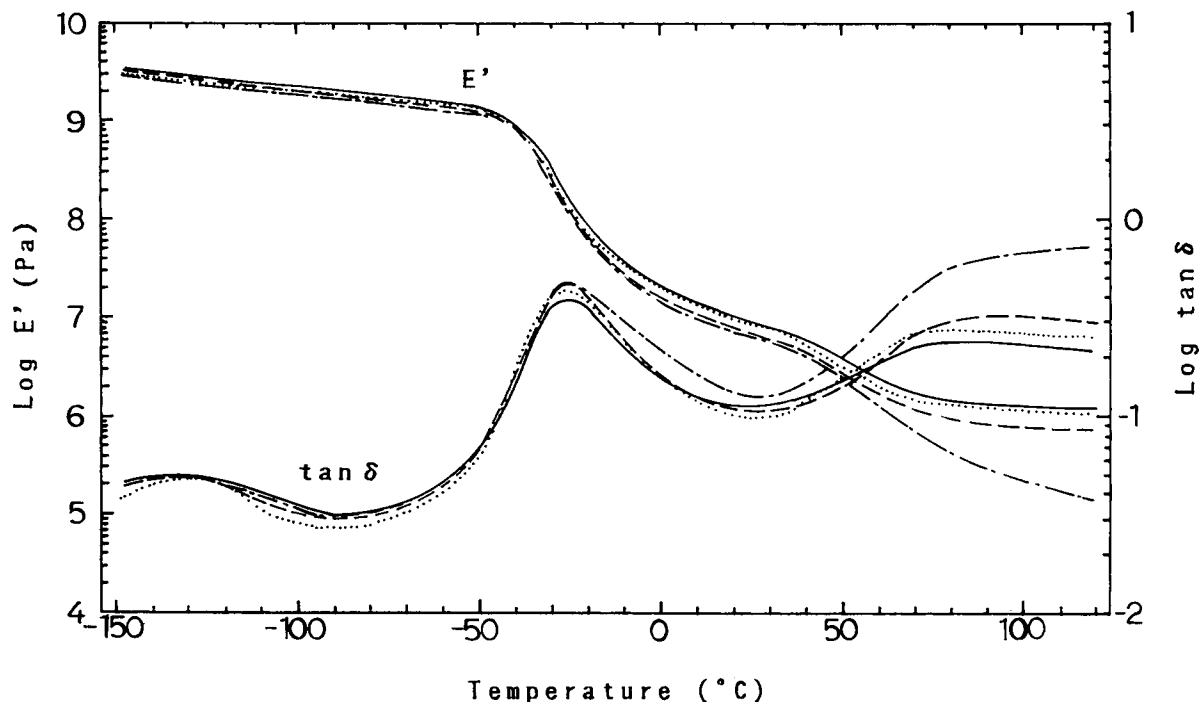


Figure 5 Dynamic viscoelastic behaviors of Na-EEA-*g*-MAH (α) with sodium carboxylates of (· · · ·) 0, (---) 1.75, (- · - · -) 3.50, and (—) 5.25×10^{-2} mol/100 g. E' = storage modulus.

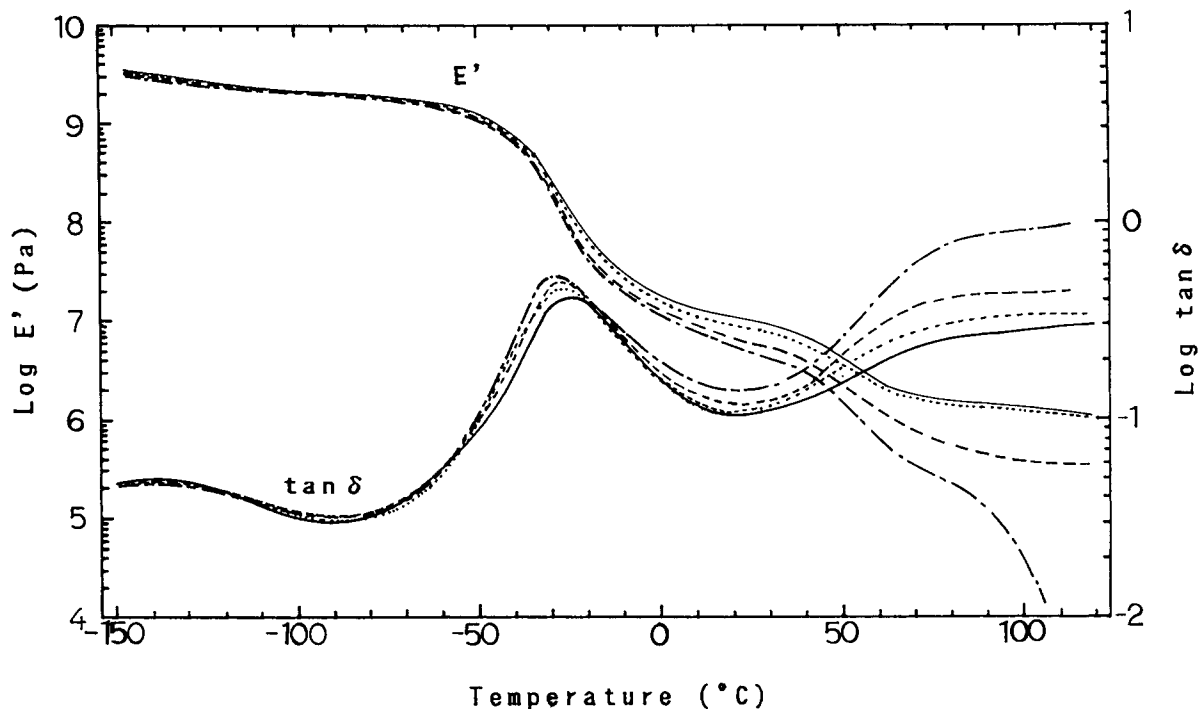


Figure 6 Dynamic viscoelastic behaviors of Na-EEA with sodium carboxylates of (· · · · ·) 0, (---) 1.75, (· · · · ·) 3.50, and (—) 5.25×10^{-2} mol/100 g. E' = storage modulus.

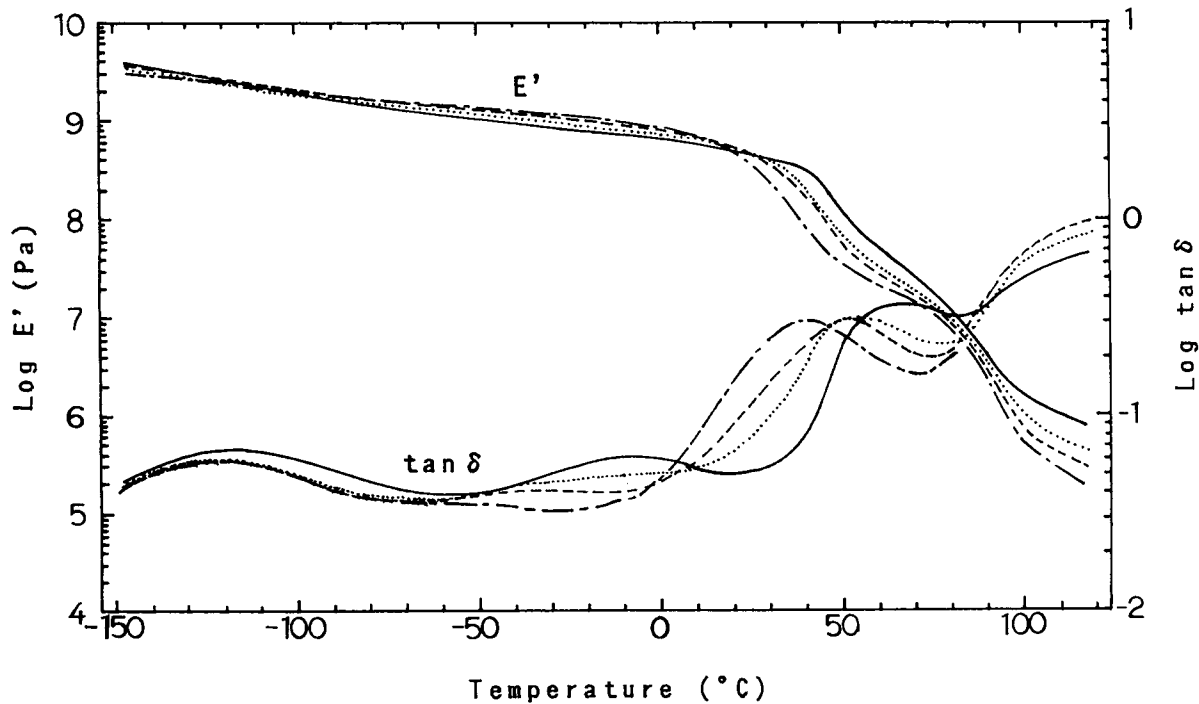


Figure 7 Dynamic viscoelastic behaviors of Na-EMAA with sodium carboxylates of (· · · · ·) 0, (---) 1.75, (· · · · ·) 3.50, and (—) 5.25×10^{-2} mol/100 g. E' = storage modulus.

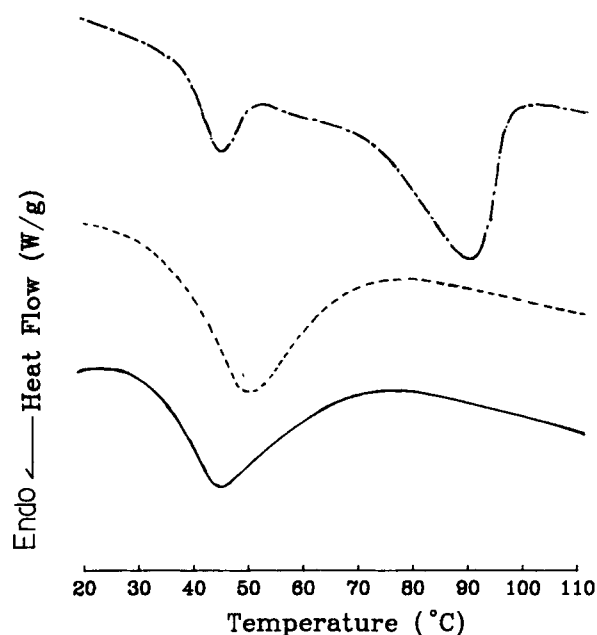


Figure 8 Differential scanning calorimetric chart of (—) Na-EEA-*g*-MAH (α), (---) Na-EEA, and (-·-·-) Na-EMAA with sodium carboxylates of 1.75, 5.25, and 5.25×10^{-2} mol/100 g, respectively.

Na-EMAA for the rebound resilience and the UTS against the concentration changes of the sodium carboxylates, but there is a common tendency among them for the rebound resilience and the hardness to increase with higher concentration of sodium carboxylates.

DISCUSSION

In comparison with Na-EEA and Na-EMAA, it was considered that a specific polymer structure provided Na-EEA-*g*-MAH (α) high rebound resilience properties at a concentration of sodium carboxylates lower than 3.50×10^{-2} mol/100 g. By using the data of thermal behaviors in a melted state, DSC, and dynamic viscoelastic behaviors with the other physical properties, the polymer structures were inferred.

As mentioned at the beginning, the ionic cross-linking gives high rebound resilience to the polymers. To recognize if any ionic aggregates are formed through the aggregation of sodium carboxylates in the polymer in the same way as that of ionic aggregates in ethylene ionomers,¹²⁻¹⁴ DSC was measured and is shown in Figure 8. Both Na-EEA-*g*-MAH (α) and Na-EEA had no endothermic peak due to the melting of the ionic aggregates¹⁵ that is detectable in Na-EMAA.

There were hardly any large ionic aggregates formed in both the two polymers, different from Na-EMAA. In addition to it, the endothermic peaks at 45–50°C were assigned to melting polyethylene crystallites that were detectable on the DSC chart of the original EEA and EEA-*g*-MAH. The polar carboxylate esters were assumed to disturb the coagulation of the sodium carboxylates to form large ionic aggregates.

The ionic cross-linkages have a characteristic property in that when sheared up at a high temperature such as 200°C the cross-linkages become loosened to make the polymers fluid. To observe the phenomenon, the behaviors of Na-EEA-*g*-MAH (α) in a melted state were measured in comparison with those of Na-EEA. In Figure 9, the decrease of the MFR per the ionic cross-linking degree of the Na-EEA-*g*-MAH was large when compared with that of Na-EEA, i.e., the ionic cross-linking of Na-EEA-*g*-MAH is stronger than that of Na-EEA. In Figure 10, the dependence of the apparent viscosities on the shear rates of Na-EEA-*g*-MAH (α) was also large as well as it was for Na-EEA, which indicates a characteristic ionic cross-linking.

Na-EEA-*g*-MAH also has another different structure in which there are partially covalent bond cross-linkages. A peroxide is used to graft MAH onto EEA, which inevitably causes the covalent bond cross-linkages in the polymer that are expected to

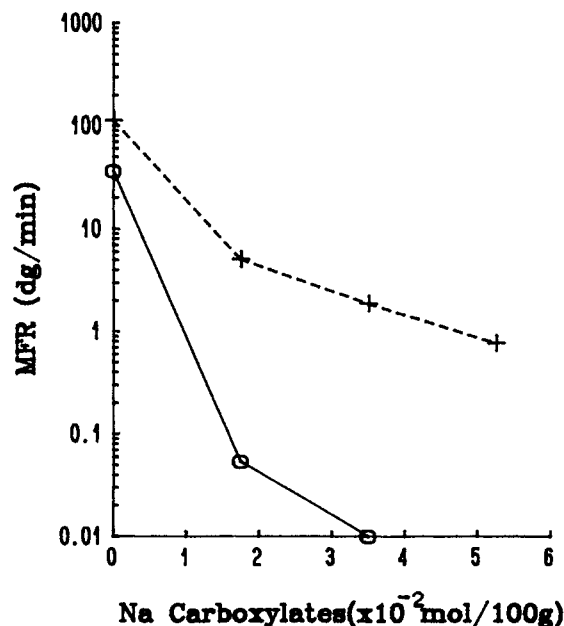


Figure 9 Changes of MFR of (○) Na-EEA-*g*-MAH and (+) Na-EEA with concentrations of sodium carboxylates.

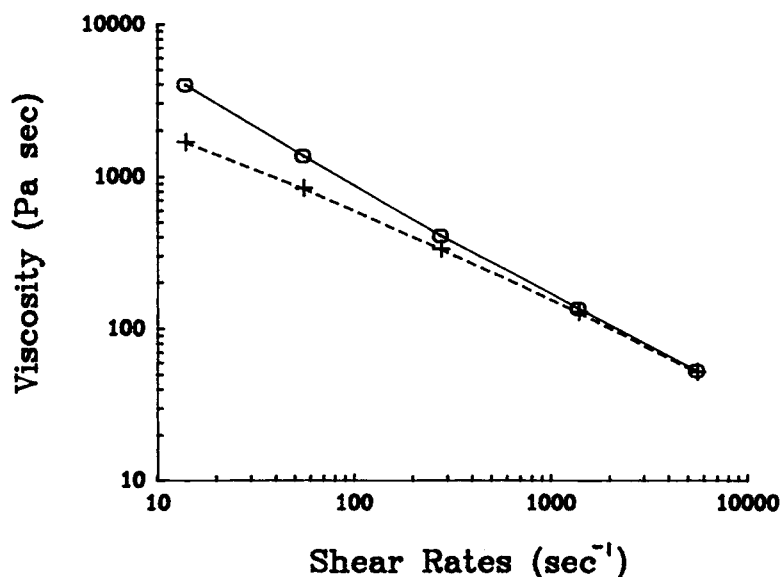


Figure 10 Capillary flow curves of (O) Na-EEA-*g*-MAH (α) and (+) Na-EEA at a 1.75×10^{-2} mol/100 g sodium carboxylate concentration.

have the effect of increasing the rebound resilience. In Figure 9, the MFR of the unneutralized EEA-*g*-MAH (α) is lower than that of the EEA, which shows the possibility of covalent bond cross-linkages in the EEA-*g*-MAH (α).

To investigate the effect of the covalent bond cross-linkages on the rebound resilience of Na-EEA-*g*-MAH, EEA itself was first cross-linked with sev-

eral amounts of the peroxide to measure the rebound resilience including the hardness, the UTE, and the UTS, as shown in Figures 11 and 12. EEA was cross-linked with 0.5 g/100 g peroxide, which is larger than the amount usually used for grafting MAH onto EEA, and saponified with variable amounts of NaOH to examine the properties of the obtained cross-linked and saponified EEA as shown in Figure

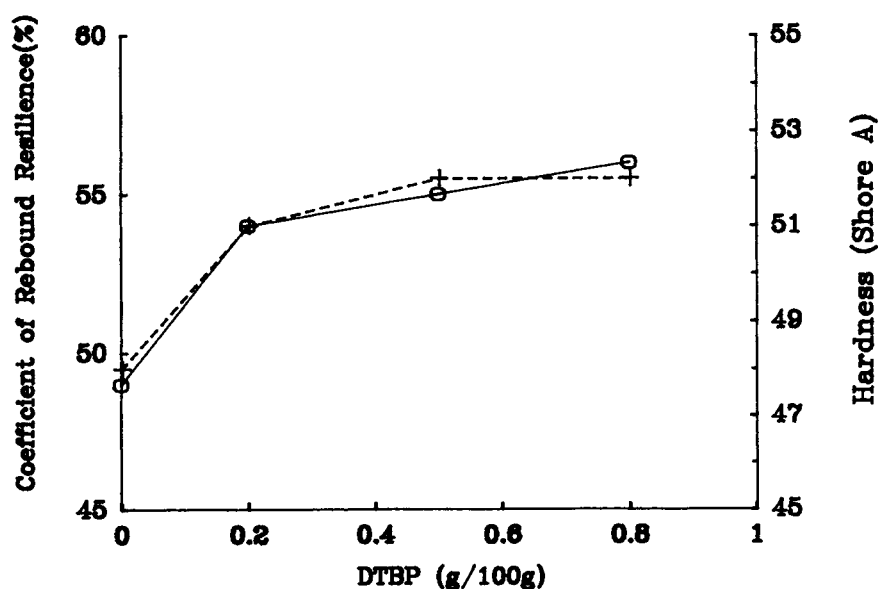


Figure 11 (O) Coefficient of rebound resilience and (+) hardness of EEA cross-linked with concentrations of DTBP.

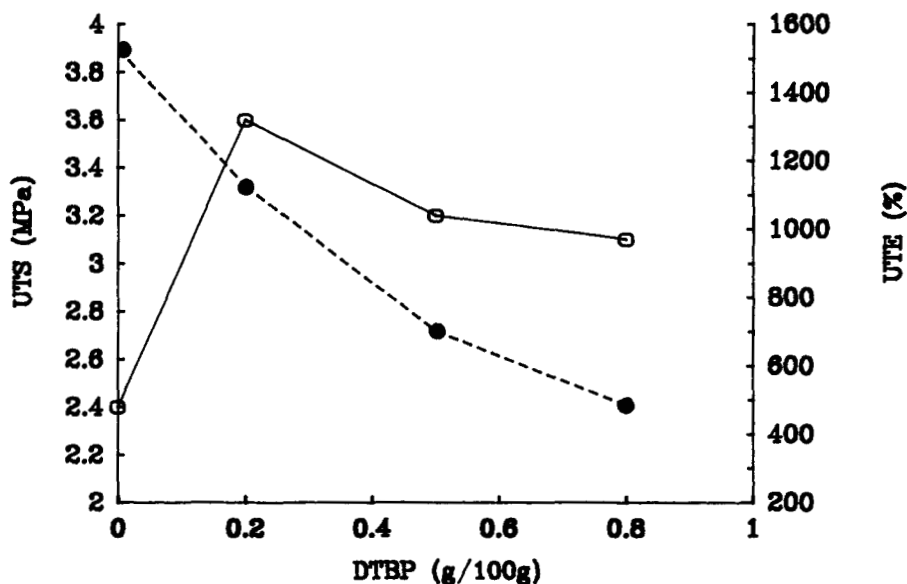


Figure 12 (○) UTS and (●) UTE of EEA cross-linked with concentrations of DTBP.

13. Both the cross-linked EEA and the cross-linked and saponified EEA showed less rebound resilience than that of Na-EEA, i.e., the increase of the rebound resilience by the saponification of the previously peroxide-cross-linked EEA is smaller than that by saponifying the original EEA. It is inferred that the covalent bond cross-linking in the polymer

locally restricts the mobility of the polymer molecules not to freely enable the formation of interchain ionic cross-linkages. Therefore, the covalent bond cross-linkages in Na-EEA-*g*-MAH (α) assumedly reduce the increase of the rebound resilience by the neutralization of the grafted MAH.

As a noteworthy point obtained from the data as

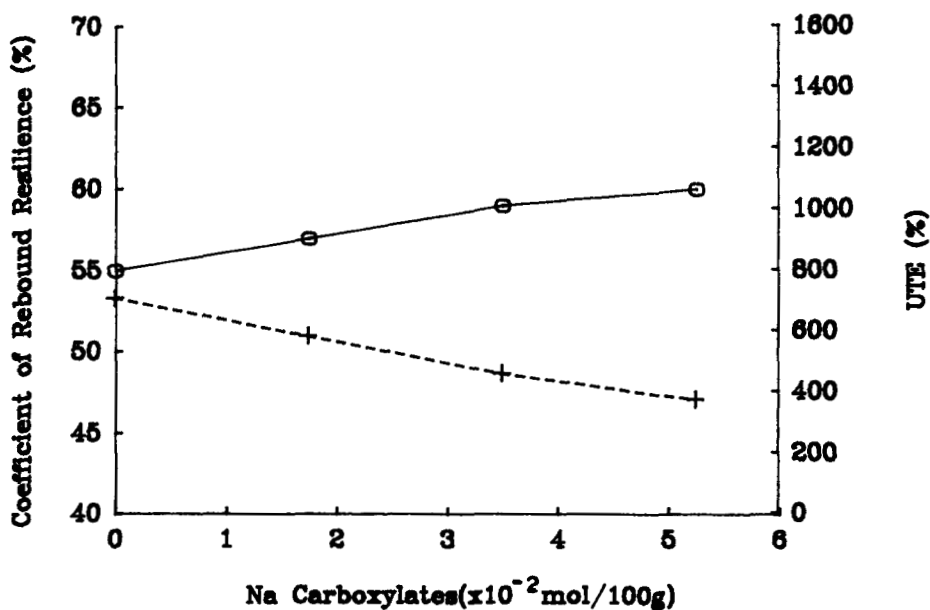


Figure 13 (○) Coefficient of rebound resilience and (+) UTE of cross-linked and saponified EEA with concentrations of sodium carboxylates.

shown in Figure 12, the covalent bond cross-linkages made the UTE decrease remarkably¹⁶ with decreasing UTS except at the initial stage. In cases of Na-EEA and Na-EMAA, the UTE decreases but the UTS, rather, increases with increase of the sodium carboxylate concentration, as shown in Figures 3 and 4. Na-EEA-*g*-MAH (α), however, shows different behavior in that both UTE and UTS decrease with its increase, as mentioned before. For an example, at a 1.75×10^{-2} mol/100 g sodium carboxylate, the UTE of Na-EEA decreased until it reached 73% of the original EEA and that of the cross-linked and saponified EEA decreased to 38% of it. The UTE of Na-EEA-*g*-MAH (α) decreases until at 23% to the original EEA-*g*-MAH (α), which is close to the level of the cross-linked and saponified EEA, i.e., the UTE of the Na-EEA-*g*-MAH (α) indicates, as a whole, the decreasing ratio due to the covalent bond cross-linking effect of the cross-linked and saponified EEA when compared with Na-EEA.

How the differences in the structures of Na-EEA-*g*-MAH (α), Na-EEA, cross-linked and saponified EEA, and Na-EMAA reflect on the IR spectra of

their sodium carboxylates was also investigated. The changes of the absorption bands of the carbonyl groups of carboxylate anions near 1560 cm^{-1} were observed with the concentration of sodium carboxylates. There were some differences found in the absorption bands depending on the kinds of sodium carboxylates that the polymers contain. In Figure 14, the peak absorption bands of Na-EEA-*g*-MAH (α), Na-EEA, cross-linked and saponified EEA, and Na-EMAA were near ν_{co} 1570 cm^{-1} , ν_{co} 1560 cm^{-1} , ν_{co} 1560 cm^{-1} , and from ν_{co} 1527 cm^{-1} to ν_{co} 1538 cm^{-1} , respectively. The absorption bands of Na-EMAA have the lowest wavenumber among them, being the bands of carbonyl groups of the carboxylate anions based on the ionic aggregation of the sodium carboxylates of Na-EMAA with low degrees of neutralization such as 10, 20, and 30 mol %.¹⁷⁻¹⁹ The absorption bands of Na-EEA and cross-linked and saponified EEA show a typical wavenumber of sodium monocarboxylates such as sodium acrylates. That of Na-EEA-*g*-MAH (α) is the highest wavenumber among them, being the bands of the carbonyl groups of the sodium dicarboxylates, such as

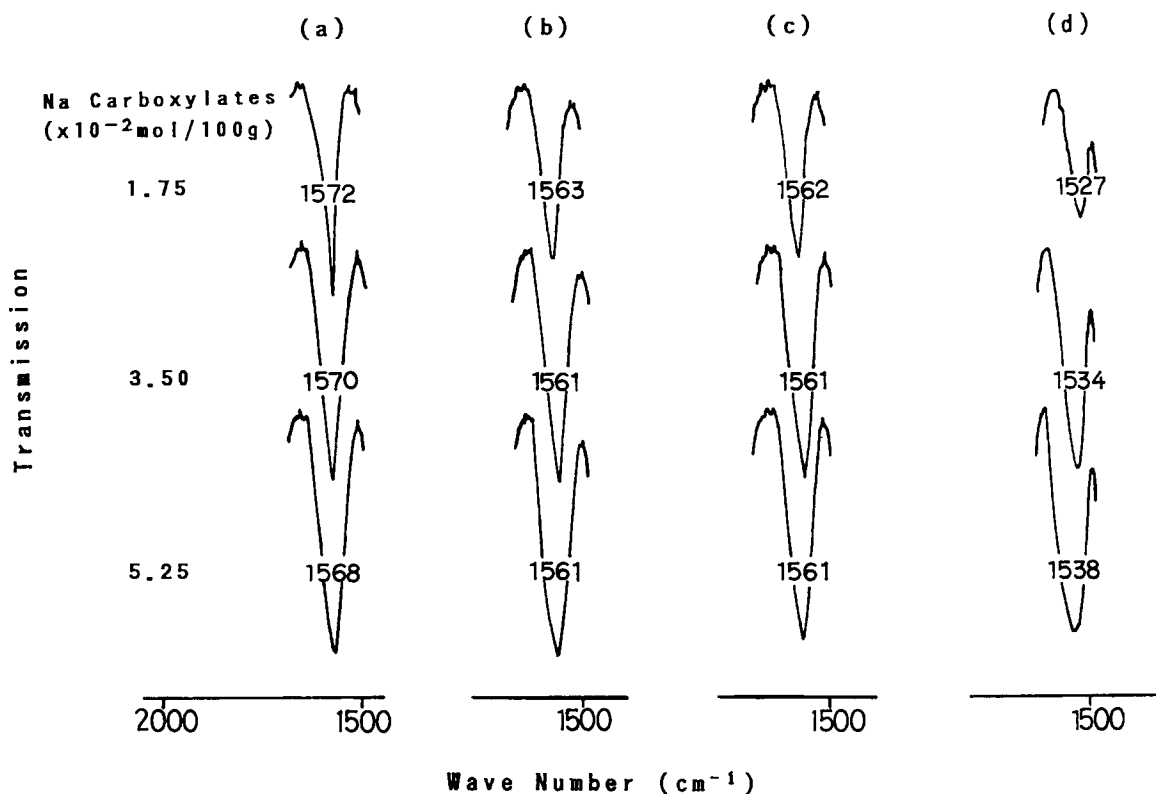


Figure 14 IR spectra of ν_{co} of (a) Na-EEA-*g*-MAH (α), (b) Na-EEA, (c) cross-linked and saponified EEA, and (d) Na-EMAA with sodium carboxylates of 1.75, 3.50, and 5.25 $\times 10^{-2}$ mol/100 g.

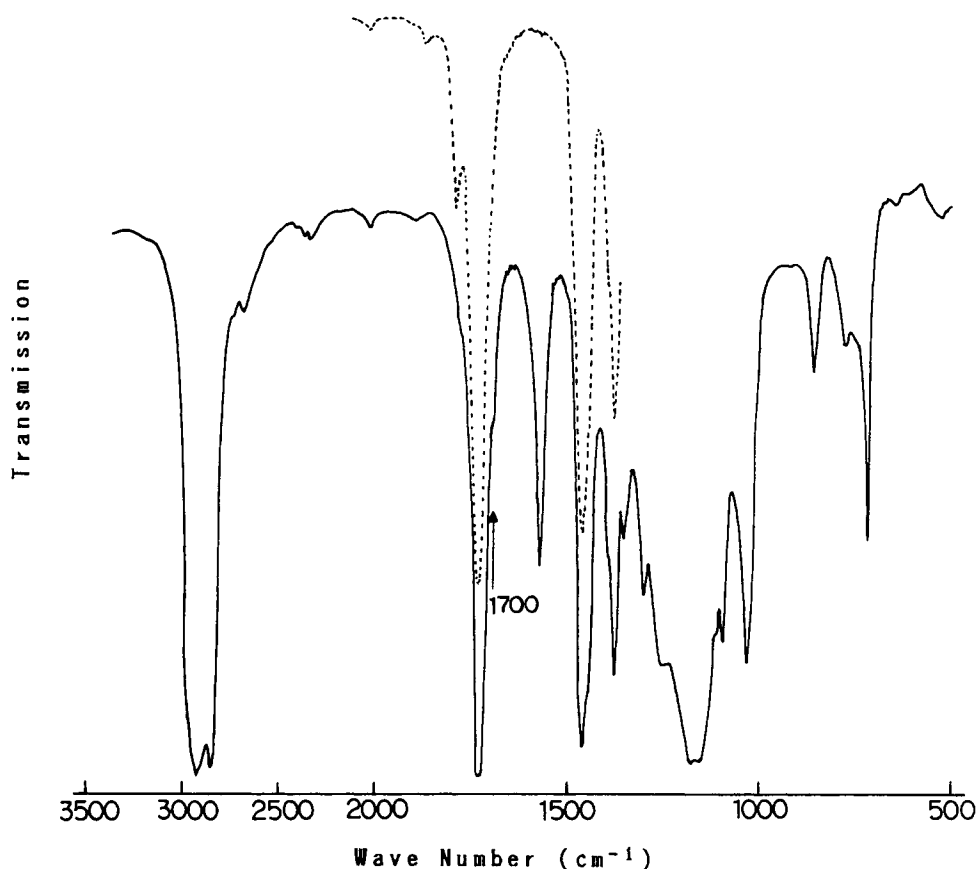


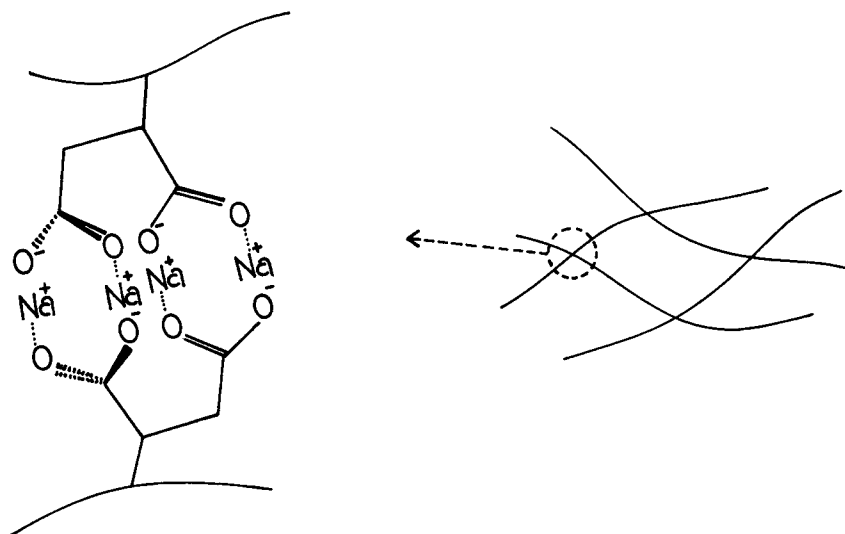
Figure 15 IR spectra of (—) Na-EEA-*g*-MAH (α) and (----) EEA-*g*-MAH (α).

sodium maleates, which show the ionic bonds of a high energy. Its whole IR spectrum, as shown in Figure 15, indicated that there were not any absorbance bands of the acid anhydrides at 1780 cm^{-1} at all, but, partially, a weak absorbance band of the carboxylic acids at 1700 cm^{-1} . The degree of neutralization of the grafted MAH (calculated as dibasic acid) in the polymer at a low concentration of sodium carboxylates or $1.75 \times 10^{-2}\text{ mol}/100\text{ g}$ is 95 mol %. Most of the grafted MAH therefore becomes neutralized in its structure to form the salts. It was also recognized that when neutralized EEA-*g*-MAH (α) with an amount of NaOH equivalent to the $3.50 \times 10^{-2}\text{ mol}/100\text{ g}$ sodium carboxylate concentration under the saponification conditions of the EEA an excess of NaOH could be inevitably consumed to saponify the formed Na-EEA-*g*-MAH (α) and no increase of rebound resilience more than 65% was observed.

From those analyses of the polymer's structures and properties, we are convinced that the high rebound resilience of Na-EEA-*g*-MAH (α) surely depends on the sodium dicarboxylates of the grafted

and neutralized MAH in the polymer. The dicarboxylate salts show strong ionic bond cross-linkages close to covalent bond cross-linkages in the polymer, differing from the ionic bond cross-linkages of the monocarboxylate salts of the other polymers. Furthermore, from the data in which there are no large ionic aggregates in the polymer and a small amount of sodium dicarboxylates provide to the polymer high rebound resilience, the salts are probably well dispersed and effectively form the interchain ionic cross-linkages among the molecules to exhibit the high rebound resilience because of well-dispersed MAH due to a very low self-reactivity ratio²⁰⁻²³ when grafted onto polymers. The structures of the dicarboxylates of the grafted and neutralized MAH are therefore assumed as shown in Scheme 2.

On the basis of the knowledge obtained, a higher rebound resilience can be expected if a greater amount of MAH is grafted onto EEA and neutralized. Then, EEA-*g*-MAH (β) with a $2.55 \times 10^{-2}\text{ mol}/100\text{ g}$ MAH, which was the maximum amount possibly grafted onto EEA using the extruder, was produced and neutralized to obtain the powdered



Scheme 2

compound according to the procedure in the Experimental section. The results of the property evaluation are shown in Figures 1–4. The rebound resilience was 67% as high as was expected when compared with the other polymers.

CONCLUSION

It was concluded that Na-EEA-*g*-MAH has a structure efficiently exhibiting the high rebound resilience both by the strong ionic bond cross-linkages of the sodium dicarboxylates of the grafted MAH close to the covalent bond cross-linkages and by the effective dispersity of the cross-linkages in the polymer. The method of grafting MAH onto a polymer and neutralizing the grafted MAH becomes a good way to improve the rebound resilience in some cases and is expected to be widely applicable to other polymers.

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