BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1734—1738 (1969)

Properties of Butyl Acrylate Copolymer with Metal Ionic Crosslinkage

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(Received July 31, 1968)

Some properties of the butyl acrylate-acrylic acid copolymer, which has ionic crosslinkage with a mono- or divalent cation, were observed. The organic solvent resistance tends to increase with an increase in the degree of neutralization with metal ions at room temperature and at 50°C. The tensile and flow properties exhibit a linear increase with the amounts of metal ions incorporated. The activation energies of the melt viscosity were 7.5, 10.5, and 22.0 kcal/mol for 1, 1/4, and 1/2 of metal-ion equivalents respectively. The stress relaxation behavior was observed at the temperature of 92°C; it was found that relaxation at the highest rate takes place at the initial stage of the relaxation process.

As the linear polymers showing a rubbery elasticity generally have a small cohesive energy density between the molecules, there are some deficiencies of their mechanical, thermal, and chemical properties. Therefore with an eye to practical application, some attempts have been made here to improve the above-mentioned properties by crosslinking reaction. A number of ways for crosslinking reaction have been reported, such as by radiation, a chemical reaction incorporating some functional groups, vulcanization with sulfur or peroxide, and introduction of metal ions.

In recent years, many types of ionic polymers containing covalent and ionic bonds have been introduced. For example, butadiene - acrylic acid(1) and butadiene - acrylonitrile - acrylic acid copolymers(2) were vulcanized with zinc oxide. They are called carboxyl rubber. Styrene-acrylic acid(3) and α-olefin-unsaturated carboxylic acid copolymers(5) were crosslinked with monovalent and sometimes divalent cations, and so they were called "Ionomers."

This paper will deal with some properties of the butyl acrylate - acrylic acid copolymers, which has an ionic crosslinkage with a mono- or divalent cation. The properties investigated here include the temperature dependence of the organic solvent resistance, the mechanical, and viscous flow properties, and the stress relaxation behavior.

Experimental

Samples. The butyl acrylate (BA)-acrylic acid (AA) copolymer used in this study was prepared by emulsion polymerization; the BA/AA composition in this copolymer was 89/11 by mol%. The intrinsic viscosity was

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1) H. P. Brown, *Ind. Eng. Chem.*, **47**, 1006 (1955).

2) H. B. Brown, *Rubber Chem. Technol*, **30**, 1347 (1957).

3) M. Morawetz, *J. Polymer Sci.*, **29**, 307 (1958).

4) W. Cooper, *ibid.*, **28**, 195 (1958).

5) Goodrich, Brit. Pat. 707425 (1954).

around 1.0 in dioxane.

The ionic crosslinking reaction of this copolymer with a mono- or divalent cation such as sodium hydroxide or zinc acetate was performed in a solvent medium; these samples, purified with an excess of the solvent at room temperature, were dried under a vacuum at 50°C. The test specimens were prepared by compression-molding into the various types desired. Some of the properties of these samples are summarized in Table 1.

TABLE 1. SAMPLES

Code	Metal	Neutralized equivalent	Molding temp. (°C)
BAA	—	0	100
BAA-Zn-1/4	Zn	1/4	150
BAA-Zn-1/2	Zn	1/2	200
BAA-Na-1/4	Na	1/4	120
BAA-Na-1/2	Na	1/2	150
BAA-Na-1	Na	1	200

Tensile Properties. The tensile properties were measured by an Instron-type tensile tester. The crosshead travel speed was 50 mm/min. The test specimens were a modified type 25 mm long, 4 mm wide, and 0.5 mm thick. A conditioning chamber was used for high-temperature tests.

Viscous Flow Properties. For the purpose of investigating the temperature dependence of the characteristics of these ionic linkages, the viscous flow deformation was measured by means of a Williams parallel-plate plastometer at various temperatures. Test specimens were compression-molded into a standard disk 4 mm diameter and 2 mm thick. The temperature range investigated was 120 to 220°C, especially 180°C, while the compression load was varied between 2 and 50 kg. Assuming a Newtonian flow, the melt viscosity, η_m(poise), was calculated by using the following equation:

$$1/h^4=(8\,F/3\,\eta_m V^2)t+C \qquad (1)$$

where h is the thickness (cm) at time t (min) under a load of F (dyn), V is the volume of the specimen, and C is a constant.

Stress-relaxation. In oder to investigate the ionic crosslinking behavior under stress at high temperatures, the tensile stress relaxation was measured. The apparatus used was the tensile tester described above, and the temperature of the controlling chamber was 70—90°C. The stress decay with time was analysed by means of an auto-recording chart.

Results and Discussion

Organic-solvent Resistance. The organic-solvent resistance of these polymers has been observed in various solvents at room temperature and at 56°C, 6 hr after immersion in the solvents. The results are illustrated in Table 2, along with the cohesive energy density (CED) of these solvents.

TABLE 2. ORGANIC SOLVENT RESISTANCE

Solvent	CED	BAA		BAA-Zn-1/4		BAA-Zn-1/2	
		23	56	23	56	23	56(°C)
Ethanol	12.7	d	d	g	d	s	g
Butanol	11.4	d	d	g	d	s	s
Acetone	10.0	d	d	g	g	s	s
Dioxane	9.9	d	d	g	d	s	g
MEK	9.2	d	d	g	g	s	s
Butyl Acetate	8.5	d	d	s	g	s	s
Benzene	9.2	d	d	s	g	s	s
Cyclo-hexane	8.2	d	d	s	s	s	s

d: dissolved, g: gel-like solution, s: swelling

It has been found that the parent BA-AA copolymer can be dissolved easily in all the solvents investigated, but the solubility of ionically-crosslinked copolymers tends to decrease as the degree of neutralization with metal ions increases. Judging from the above observation, ionic crosslinkage with a divalent metal has quite a strong network structure and can not be broken at about 50°C in these solvents. In the case of small amounts of metal ions, however, they can be dissolved at high temperatures in ethanol or butanol, either of which is a hydrogen-bond-scission reagent with a cohesive energy density of about 12.

TABLE 3. TENSILE PRORERTIES

Temp. (°C)	Sample	Tensile strength (kg/cm^2)	Modulus at 75% (kg/cm^2)	Elongation (%)	Breaking energy (kg-cm/cm^2)	App. deg. of crosslinking (mol/cm^3)
23	BAA	1.5	0.1	5300	2.4	1.6×10^{-6}
	BAA-Zn-1/4	4.2	0.5	1500	55	7.0×10^{-6}
	BAA-Zn-1/2	15	4.4	500	56	4.5×10^{-5}
	BAA-Na-1/4	3.9	0.3	6900	92	4.7×10^{-6}
	BAA-Na-1/2	20	0.8	600	64	1.2×10^{-5}
	BAA-Na-1	37	8.1	400	55	1.2×10^{-4}
93	BAA	0.5	3.1[a]	1000	0.2	—
	BAA-Zn-1/4	3.4	3.4[a]	1850	2.2	—
	BAA-Zn-1/2	8.5	3.2	1500	12	—

[a] 10% modulus

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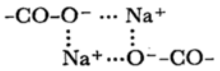
6) P. J. Flory, *Chem. Revs.*, **35**, 51 (1944).

Tensile Properties. It is generally well known that the tensile propetries of elastomers change remarkably with the increase in the density of crosslinking. Table 3 shows these values measured at 23 and 93°C. The apparent density of crosslinking (ν_a) was calculated by using Eq. (2), which is based on the kinetic theory of rubber elasticity:⁶⁾

$$f=\nu_a \boldsymbol{R} T(\alpha-1/\alpha^2) \qquad (2)$$

where f is the tensile stress; $\boldsymbol{R}$, the gas constant; T, the absolute temperature, and α, the extension ratio defined as the ratio of extended to unstrained length.

It is obvious that, at low temperatures, the tensile strength, the modulus, and the breaking energy increase, but the elongation decreases with an increase in the metal present. Therefore, these properties depend on the equivalent of metal used, *i. e.*, the degree of the neutralization of carboxylic acid. However, it seems that the values tested here are mostly somewhat lower than those of other practical rubbers. Figure 1 illustrates the variation in the tensile strength with a neutralized equivalent for both Na and Zn at room temperature. Figure 2 shows the density of crosslinking calculated from Eq. (2) against, the neutralized equivalent. It was observed that the density of crosslinking by metal ions increases exponentially with the neutralization amount for an acidic group and that there is a considerable difference between the monovalent Na and the divalent Zn. At the high temperature of 93°C, deformation by viscous flow and by a fall in tensile properties were generally observed. However in a copolymer with a large amount of metal, the retention of tensile strength is large at a high temperature, and so this type of linkage is fairly strong. The above facts suggest the following structures of the crosslinkage of these copolymers. For Zn^{2+}, it may be $-COO^-\ Zn^{2+}\ OOC^-$. For Na^+, the structure may be:



$$\begin{array}{l} -CO-O^- \cdots Na^+ \\ \qquad\ \vdots \qquad\ \ \vdots \\ \qquad Na^+ \cdots O^- -CO- \end{array}$$

as has been suggested by Morawetz,³⁾ where ion-dipole interaction between two ion pairs forms a quadrupole ion. Moreover, these structures may be the cause of a higher level of tensile strength and modulus compared to those of the parent copolymer.

Viscous-flow Properties. In order to investigate the properties of the crosslinkage by metal ions introduced between the parent backbone of BA-AA copolymer, deformation under a load was measured at high temperatures by means

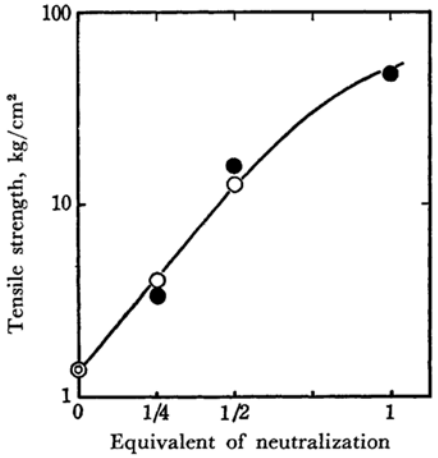


Fig. 1. Dependence of tensile strength on equivalent of neutralization.
◎ BAA ○ BAA-Zn ● BAA-Na

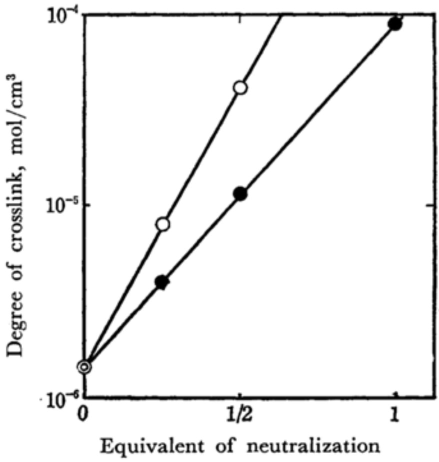


Fig. 2. Dependence of degree of crosslinking on equivalent of neutralization.
◎ BAA ○ BAA-Zn ● BAA-Na

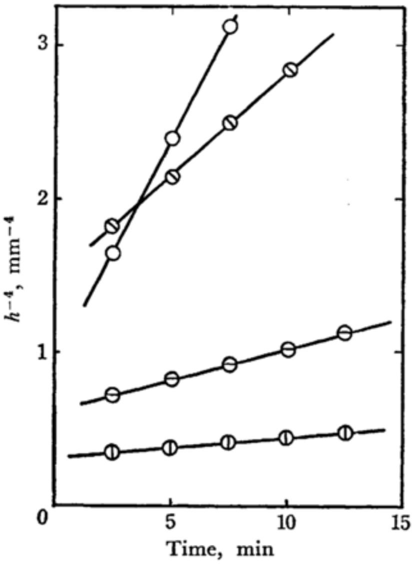


Fig. 3. Relationship between h^{-4} and t.
○ BAA, 150°C. ⦶ 120°C of, ⊖ 150°C of, ⊘ 180°C of BAA-Zn-1/4

of a Williams parallel-plate plastometer. In the measurement of the melt viscosity using various samples with different quantities of metal ions, the load and temperature were varied between 1.9—51.5 kg and 118—250°C respectively. The linear relationship between h^{-4} and t, according to Eq. (1), is shown in Fig. 3. Assuming this flow deformation to be Newtonian from the relationship shown in Fig. 3, η_m was calculated by Eq. (2); the results are listed in Table 4. η_m apparently exhibits a sharp increase with the quantity of metal ions at the same temperature. The temperature dependence of the η_m of various samples is illustrated in Figure 4. The apparent activation energies were calculated from the gradient of these curves according to Arrhenius' equation and are shown in the last column of Table 4.

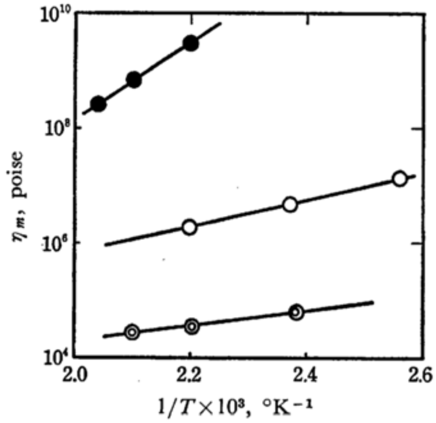


Fig. 4. Temperature dependency of melt viscosity.
◎ BAA ○ BAA-Zn-1/4 ● BAA-Zn-1/2

TABLE 4. MELT FLOW PROPERTIES

Sample	Temp. (°C)	Load (kg)	η_m (poise)	E_{vis} (kcal/mol)
BAA	150	5	8.8×10^4	7.5
	180	3	5.2×10^4	
	200	1.9	3.3×10^4	
BAA-Zn-1/4	150	51.5	1.4×10^7	10.9
	180	51.5	5.3×10^6	
	200	51.5	2.3×10^6	
BAA-Zn-1/2	180	51.5	1.5×10^9	22.0
	200	51.5	6.1×10^8	
	220	51.5	2.2×10^8	

Stress-relaxation Behavior. The stress-relaxation behavior is also a good method for determining the properties of crosslinkage.

If we assume that stress relaxation at high temperatures is due to random network scission, the following relation holds between the stress decay ratio (relative stress) at a constant extension and at a constant number of crosslinking:

$$f(t)/f(0)=n(t)/n(0)=e^{-kt} \tag{3}$$

where $f(0)$ and $n(0)$ are the stress and number of crosslinking, respectively, at the initial stage, and where $f(t)$ and $n(t)$ are those at time t. Figure 5 illustrates a typical stress decay curve with BAA-Zn-1/2 as the sample. From this figure, it can be seen that the highest rate of stress relaxation takes place at the initial stage of the relaxation process, and that this rate decreases with an increase in the metal-ion content. Figure 6 shows the change in the relaxation modulus with the time. At 92°C, the viscous flow was observed with the parent BAA copolymer, which does not contain any metal, whereas the equilibria, E_r were 10^5 and 10^6 with the copolymers containing Zn-1/4 and Zn-1/2 respectively.

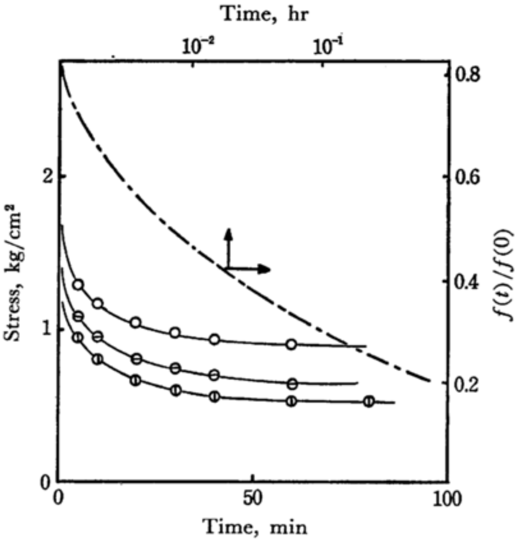


Fig. 5. Typical stress decay curve of BAA-Zn-1/2.
○ 70°C ⊖ 82°C ⦶ 92°C

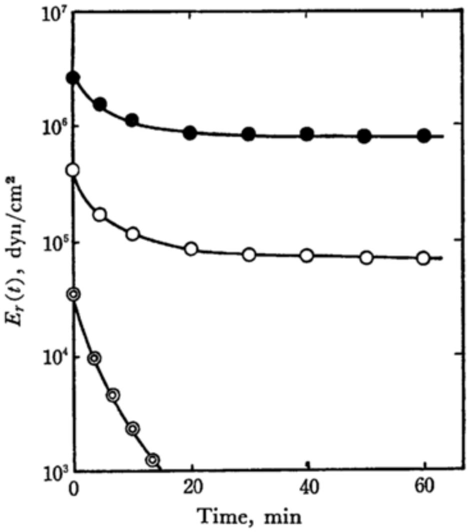


Fig. 6. Relaxation modulus *vs.* time.
◎ BAA ○ BAA-Zn-1/4 ● BAA-Zn-12

We have observed that some types of relaxation take place at the initial stage of the relaxation process. These higher rate-relaxation phenomena can be considered to be due to a partial loosening of the chain entanglement or to a slippage of labile crosslinkage caused by sufficient residual interaction of acrylic acid side groups. Network linkage by divalent metal ions is relatively stable even at high temperatures. For most of the properties tested in this study, the ionically-crosslinked butyl acrylate copolymer exhibits a lower level than do other practical rubbers. However, it is considered that the above deficiencies can be improved by investigating the parent copolymer, vulcanization, the molecular size, the chemical composition of the comonomer, the carboxylate content, the vulcanizate recipe, and the types and quantities of cations.