

Water-Swelling Elastomer Prepared by *In Situ* Formed Lithium Acrylate in Chlorinated Polyethylene

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ABSTRACT: Lithium acrylate (LiAA) was *in situ* prepared in a chlorinated polyethylene (CPE) matrix through the neutralization of lithium hydroxide (LiOH) and acrylic acid (AA) during mixing. The obtained compounds were vulcanized with dicumyl peroxide (DCP). The *in situ* preparation and polymerization of LiAA were characterized with Fourier transform infrared spectrometry. The crosslink density analysis results indicated that the CPE/LiAA vulcanizates contained both covalent bonds and ionic bonds. The effects of the DCP and LiAA contents on the mechanical properties

and water-swelling properties of the CPE/LiAA vulcanizates were studied. The relationship between the LiOH/AA molar ratio and the properties of the CPE/LiAA vulcanizates was investigated. The results showed that LiAA could improve the mechanical and water-swelling properties of CPE/LiAA vulcanizates, providing a new approach to the preparation of water-swelling elastomers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1804–1812, 2004

Key words: chlorinated polyethylene (PE); swelling

INTRODUCTION

A crosslinked polyacrylate resin such as poly(sodium acrylate) (PNaAA) is a water-swelling polymer. The water-absorption ratio of crosslinked PNaAA can be high, over 1000%, and PNaAA has been called a superabsorbent polymer.^{1–4}

Therefore, crosslinked PNaAA resin is used to prepare water-swelling elastomers. Many studies on the preparation of water-swelling elastomers have been reported in recent years, and most of the related publications are focused on mechanical blends of PNaAA and elastomers. PNaAA resin was originally prepared through the homopolymerization or copolymerization of sodium acrylate (NaAA) with other monomers and then was compounded with elastomers.⁵ These methods generally resulted in inhomogeneous dispersions of water-swelling resins in the elastomer matrix and poor mechanical properties because of the poor compatibility between the elastomers and PNaAA resin. In addition, PNaAA resin was easy to extract from the vulcanizates during water swelling. To overcome this drawback, researchers have carried out many studies.^{6–10} For example, Chen et al.¹¹ improved the compatibility between crosslinked PNaAA and chloroprene rubber with a graft copolymer of chloroprene rubber and poly(ethylene glycol). Some methods of improving the compatibility between the elastomer matrix and water-swelling resins have been reported.^{12–14} A

water-swelling elastomer was prepared through the emulsion blending of rubber latex and water-swelling resins; Lin et al.^{15,16} prepared a water-swelling elastomer with good mechanical properties and water-swelling properties through the emulsion blending of a natural rubber latex and a partially hydrolyzed polyacrylamide. Hydrophilic monomers and an initiator were added to a styrene–butadiene rubber latex to obtain a water-swelling elastomer with high water absorptivity and good water-absorbing stability.¹⁷ Some of our previous publications concern the modification of elastomers by *in situ* prepared unsaturated carboxylates.^{18–22} More recently, we have developed water-swelling elastomers through the *in situ* formation of NaAA in ethylene/vinyl acetate copolymer and chlorinated polyethylene (CPE) matrices.^{23,24}

The purpose of this study was to explore a new approach to the preparation of water-swelling elastomers. Lithium acrylate (LiAA) was *in situ* prepared in a CPE matrix through the neutralization of lithium hydroxide (LiOH) and acrylic acid (AA). The *in situ* homopolymerization and graft polymerization of LiAA were initiated with dicumyl peroxide (DCP) at an elevated temperature, and this led to an elastomer vulcanizate. The neutralization of LiOH and AA, the polymerization of LiAA, and the crosslinking reaction of CPE/LiAA compounds were investigated, and the crosslinking structure of the CPE/LiAA vulcanizates was characterized. The effects of the LiAA content, DCP content, and LiOH/AA molar ratio on the mechanical properties and water-swelling properties of the CPE vulcanizates were explored.

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TABLE I
Raw Materials

| Material | Properties | Source |
|--------------------------------|------------------------------|--|
| Chlorinated polyethylene (CPE) | 135B, chlorine content = 35% | Yaxing Chemical Co., Ltd. (Shandong, China) |
| Lithium hydroxide (LiOH) | Chemically pure | Shanghai Chemical Medicine Co., Ltd (Shanghai, China) |
| Acrylic acid (AA) | Chemically pure | Shanghai Wulian Chemical Co., Ltd. (Shanghai, China) |
| Dicumyl peroxide (DCP) | Purity = 99.3% | Shanghai Gaoqiao Petroleum Co., Ltd. (Shanghai, China) |
| Lithium acrylate (LiAA) | | Our laboratory |

EXPERIMENTAL

Materials

The raw materials used in the study are listed in Table I.

Sample preparation

The mixture of CPE and the additives was prepared in a Haake RC90 rheometer (Germany) at a rotor speed of 32 rpm and an initial temperature of 60°C. LiOH was added to CPE first. After the dispersion of LiOH in CPE, AA was slowly added, followed by the addition of DCP. The whole compounding process lasted about 20 min. The resultant compound was press-cured at 170°C for 10 min and cut into specimens for measurement.

The LiAA contents shown in all the figures are the theoretical values calculated from the LiOH and AA contents. The neutralization degree was supposed to be 100%, and the LiOH/AA molar ratio was 1.0.

Infrared transmission spectra analysis

Infrared transmission spectra were obtained with a Paragon 1000 Fourier transform infrared (FTIR) spectrometer from PerkinElmer Corp. (Boston, MA). The sample of AA was prepared via the casting of AA onto a KBr disc. The CPE gum, LiAA/CPE, and LiOH/AA/CPE compounds were prepared via compression molding as thin films at room temperature, and the LiAA/CPE and LiOH/AA/CPE vulcanizates were prepared via compression molding at 170°C for 10 min.

Curing characteristics

The curing curves were recorded at 170°C with a UR 2030 rheometer (U-CAN Dynalex, Inc., Taiwan, China). The relative curing degree was represented by the difference between the maximum torque value (MH) and the minimum torque value (ML) of the curing curve, and the curing rate (C_R) was calculated as follows:

$$C_R = (M_{90} - M_{10}) / (t_{90} - t_{10}) \quad (1)$$

where M_{90} is equal to a torque value $[(MH - ML) \times 90\% + ML]$; M_{10} is equal to a torque value $[(MH - ML) \times 10\% + ML]$; and t_{90} and t_{10} are the times at M_{90} and M_{10} , respectively.

Determination of the crosslink density

The crosslink density was determined by equilibrium swelling. A sample was dried for 12 h at 80°C in a vacuum oven, and the initial weight was measured. It was swollen in xylene at 23°C for 72 h to achieve a swelling equilibrium and was weighed. It was vacuum-dried for 36 h at 80°C to remove all the solvent and was reweighed. The volume fraction of the elastomer in the swollen gel (V_r), which was used to represent the crosslink density of the vulcanizate, was determined as follows:

$$V_r = \frac{M_0 \phi (1 - \alpha) / \rho_r}{M_0 \phi (1 - \alpha) / \rho_r + (M_1 - M_2) / \rho_s} \quad (2)$$

where M_0 is the sample mass before swelling; M_1 and M_2 are the sample masses before and after drying, respectively; ϕ is the mass fraction of the elastomer in the vulcanizate; α is the mass loss of the gum CPE vulcanizate during swelling; and ρ_r and ρ_s are the elastomer and solvent densities, respectively.

As reported previously,¹⁸ elastomer vulcanizates reinforced with unsaturated carboxylates contain both ionic crosslinks and covalent crosslinks, so it is significant to distinguish the ionic crosslink density from the covalent crosslink density as follows:

$$V_r = V_{r1} + V_{r2} \quad (3)$$

where V_{r1} and V_{r2} are the relative covalent crosslink and ionic crosslink densities and V_r is the relative gross crosslink density.

For the determination of the covalent crosslink density, an elastomer sample was swollen in an xylene/chloroacetic acid mixed solvent for 5 days to destroy ionic crosslinks, and then it was swollen in xylene for 72 h. V_{r1} was calculated from eq. (2); V_{r2} was calculated by the subtraction of V_{r1} from V_r with eq. (3), and was used to represent the ionic crosslink density.

Mechanical properties

The tensile tests were carried out according to ASTM D 412 in an Instron series IX 4465 materials tester, with a grip separation rate of 500 mm/min, with specimens 2 mm thick.

The Shore A hardness was determined with a hand-held Shore A durometer according to ASTM D 2240.

The mechanical properties in the water-swelling state (after water swelling) were measured after the removal of the surface water via blotting with filter paper at the swelling equilibrium state. The tensile strength after water swelling (T_{ws}) was determined as follows:

$$T_{ws} = F/bh \quad (4)$$

where F is the tensile force at rupture and b and h are the sample width and thickness in the swelling equilibrium state, respectively.

Water-swelling ratio

The measurements of the water-swelling ratio were performed with a square sample, with a side length of 25 mm and a thickness of 2 mm, by the immersion/gain method. First, a samples was dried for 12 h at 80°C in a vacuum oven, and its original weight (M_0) was recorded. Then, the sample was immersed in an excess amount of deionized water at 23°C. The weight of the wet sample (M_t) was determined after the removal of the surface water via blotting with filter paper at different times, until a swelling equilibrium was reached.

The water-swelling ratio (SR) was calculated as follows:

$$SR = (M_t - M_0)/M_0 \times 100\% \quad (5)$$

RESULTS AND DISCUSSION

FTIR spectroscopy analysis

The *in situ* preparation of LiAA, through the neutralization of LiOH and AA in CPE, was confirmed by FTIR spectra. Figure 1(a–d) shows the FTIR spectra of CPE gum, AA, a CPE/LiAA (100/39) compound, and a CPE/LiOH/AA (100/21/36) compound, respectively. CPE shows absorption peaks at 662 and 1273 cm^{-1} , which are characteristic of the stretching vibrations of C—Cl and C—H bonds, respectively.^{25,26} AA has a characteristic absorption peak at 1712 cm^{-1} , which is attributed to the C=O stretching vibration, and a peak at 1640 cm^{-1} , which is attributed to the C=C stretching vibrations.²⁷ When the hydrogen in the $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—OH}$ group is substituted by a cation, the C=O

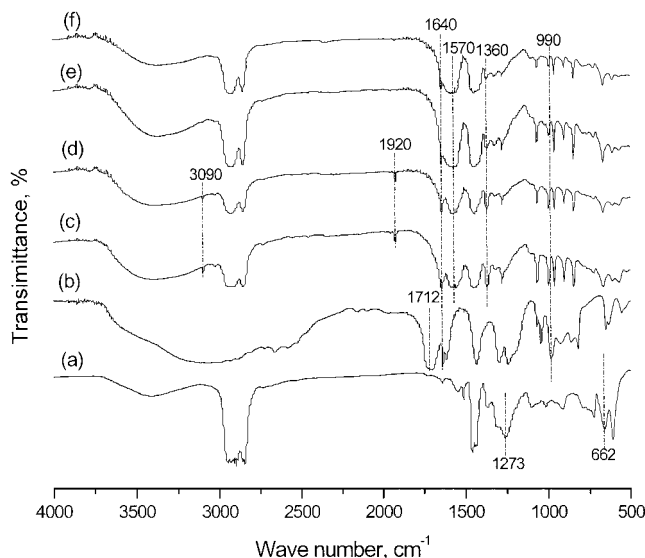


Figure 1 FTIR spectra of (a) CPE gum, (b) AA, (c) a CPE/LiAA (100/39) compound, (d) a CPE/LiOH/AA (100/21/36) compound, (e) a CPE/LiOH/AA (100/21/36) vulcanizate, and (f) a CPE/LiAA (100/39) vulcanizate.

and C—O bonds attached to the same C atom are equalized to $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—O}^-$.²⁸ The carboxylate anion has two strongly coupled carbon–oxygen bonds that give rise to the separate asymmetric and symmetric stretching vibrations. For LiAA, the asymmetric stretching vibration band is at 1570 cm^{-1} , and the symmetric stretching vibration band is at 1360 cm^{-1} . The absorption peaks at 990 cm^{-1} can be ascribed to the C—H out-of-plane bending vibration from =CH_2 . The weak absorption bands at 3090 and 1920 cm^{-1} might be due to DCP.

When AA and LiOH were mixed in a molar ratio of 1:1 in CPE gum, the characteristic absorption bands of AA shifted, and the characteristic absorption bands of LiAA appeared. The spectrum of the CPE/LiOH/AA compound [Fig. 1(d)] is the same as that of the CPE compound containing directly added LiAA [Fig. 1(c)]. This implies that AA reacted with LiOH to form LiAA.

Figure 1(e, f) shows the FTIR spectra of a CPE/LiOH/AA (100/21/36) vulcanizate and a CPE/LiAA (100/39) vulcanizate, respectively. The spectra of the CPE vulcanizates change in the peaks at 1640, 990, and 1360 cm^{-1} in comparison with the spectrum of the CPE compounds. The relative intensities of the =CH_2 absorption peaks at 1640 and 990 cm^{-1} obviously became weak, and this indicates that the C=C bonds reacted to a great extent during vulcanization. The absorption peak at 1360 cm^{-1} becomes weak, and this

indicates that the $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—O}^-$ group in poly(lithium acrylate) (PLiAA) formed an ion crosslink and that the symmetric stretching vibration of the carbon–oxygen

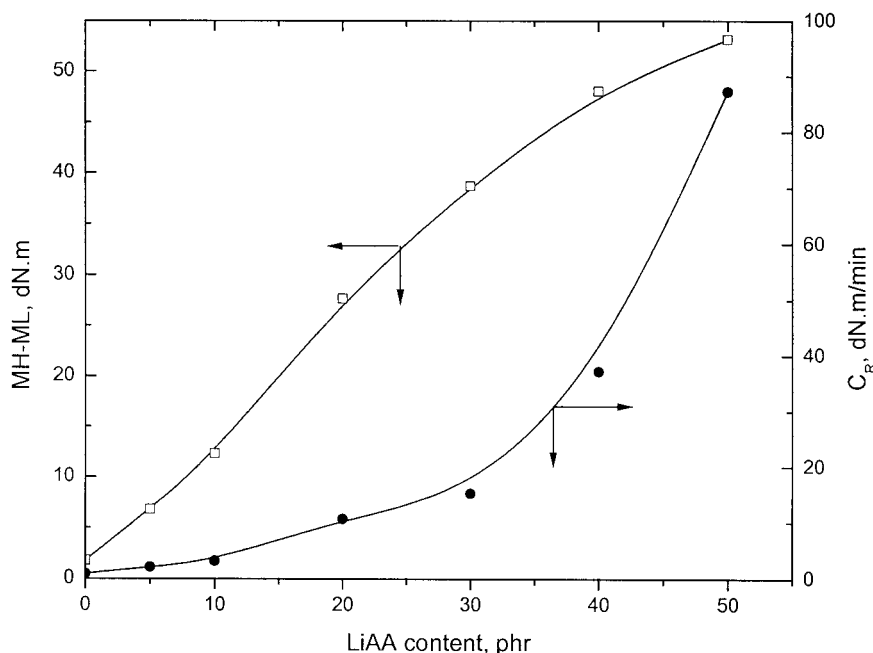


Figure 2 C_R and the curing degree of CPE/LiAA compounds (formulation: 100 phr CP, 1.0 phr DCP 1.0, and variable LiAA).

bonds became weak. Therefore, the polymerization of LiAA can be confirmed from the FTIR spectra.

Curing characteristics

The values of C_R and $MH - ML$ were calculated according to the curing curves of the CPE/LiAA compounds, and they are recorded in Figure 2. C_R and the degree of the compounds increased with increasing LiAA content.

Crosslink density

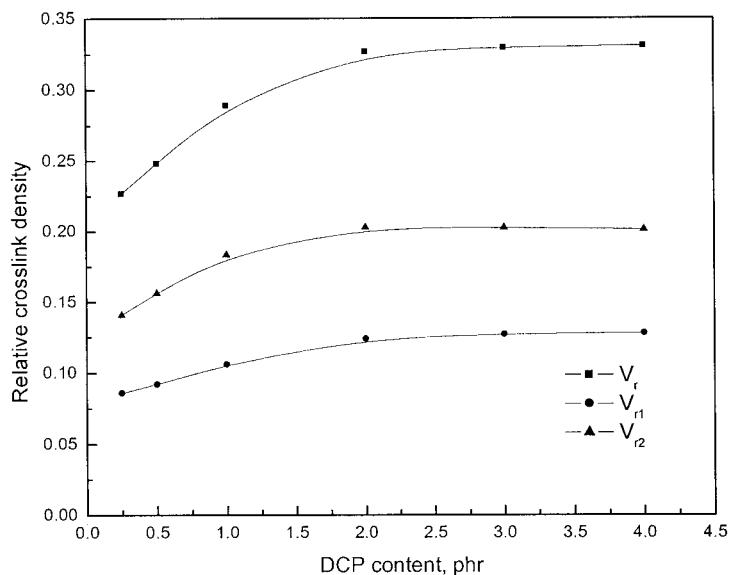
In the compounds of an elastomer and metallic methacrylate, DCP can initiate the crosslinking reaction of an elastomer and the polymerization of metallic methacrylate, including both homopolymerization and graft polymerization.²⁹ Therefore, there are both ionic crosslink bonds and covalent crosslink bonds in a CPE/LiAA vulcanizate; the covalent crosslink bonds are due to the crosslink reaction of the CPE elastomer, and the ionic crosslink bonds result from the graft polymerization of PLiAA onto CPE. The effect of the DCP content on the crosslink densities of CPE/LiAA vulcanizates is shown in Figure 3(a). At a given LiAA content of 39 phr, the ionic crosslink density was higher than the covalent crosslink density, and the gross crosslink density, ionic crosslink density, and covalent crosslink density all increased with increasing DCP content. This result was about the same as that reported for ethylene-propylene-diene rubber/zinc dimethacrylate vulcanizates.³⁰

The effects of the LiAA content on the crosslink density of CPE/LiAA vulcanizates are shown in Figure 3(b). When the DCP content was 1.0 phr, both the gross crosslink density and the ionic crosslink density of CPE/LiAA vulcanizates increased with increasing LiAA content, but the covalent crosslink density showed a slight decrease. These experimental results indicated that the free radical of DCP not only initiated the covalent crosslinking of CPE molecular chains but also initiated the homopolymerization and graft polymerization of LiAA. The graft polymerization of LiAA onto CPE chains could form ionic crosslinks in the vulcanizates.

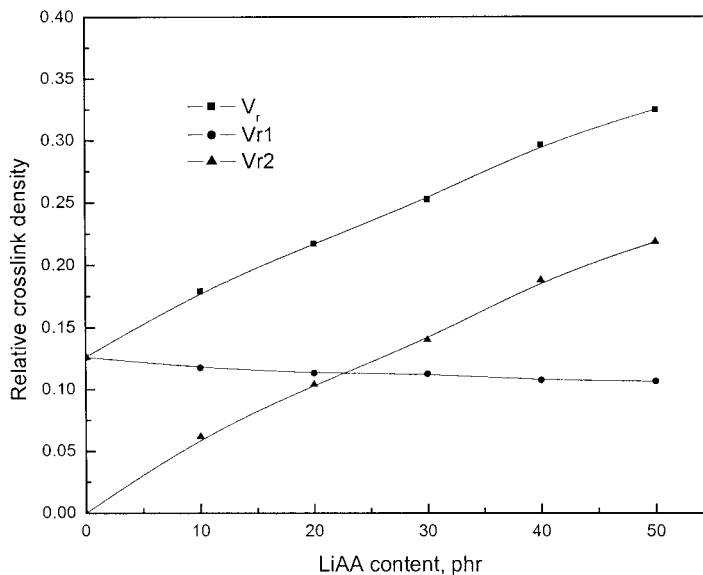
Mechanical properties

Figures 4–6 show the mechanical properties of the CPE/LiAA vulcanizates. As shown in Figure 4, the tensile strength of the vulcanizates increased with increasing DCP content, and it reached the maximum value of 27.7 MPa at a DCP content of 1.0 phr. The elongation at break of the vulcanizates decreased with increasing DCP content. When the samples were swelled and reached water-swelling equilibrium, the tensile strength decreased markedly, and the elongation at break increased slightly, compared with those before water swelling. The tensile strength and elongation at break after water swelling decreased with increasing DCP content.

The effect of the LiAA content on the mechanical properties of CPE/LiAA vulcanizate is shown in Figure 5. When the LiAA content was 0–40 phr, the



(a)



(b)

Figure 3 Crosslink density of CPE/LiAA vulcanizates: (a) the effect of the DCP content (formulation: 100 phr CPE, 39 phr LiAA, and variable DCP) and (b) the effect of the LiAA content (formulation: 100 phr CPE, 1.0 phr DCP, and variable LiAA).

tensile strength of the vulcanizates increased with increasing LiAA content and was greater than 28 MPa at the LiAA content of 40 phr. Thereafter, the tensile strength of the vulcanizates decreased with increasing LiAA content. The elongation at break decreased with increasing LiAA content. When the CPE/LiAA vulcanizate was in the state of a water-swelling equilibrium, the tensile strength was very low, but the elongation at

break had a small increase in comparison with that before water swelling. The tensile strength and elongation at break after water swelling decreased with increasing LiAA content.

The experimental results show that LiAA had a reinforcing effect on CPE. The reinforcing effect was due to the graft polymerization of LiAA onto CPE chains and could lead to ionic crosslinks. When the

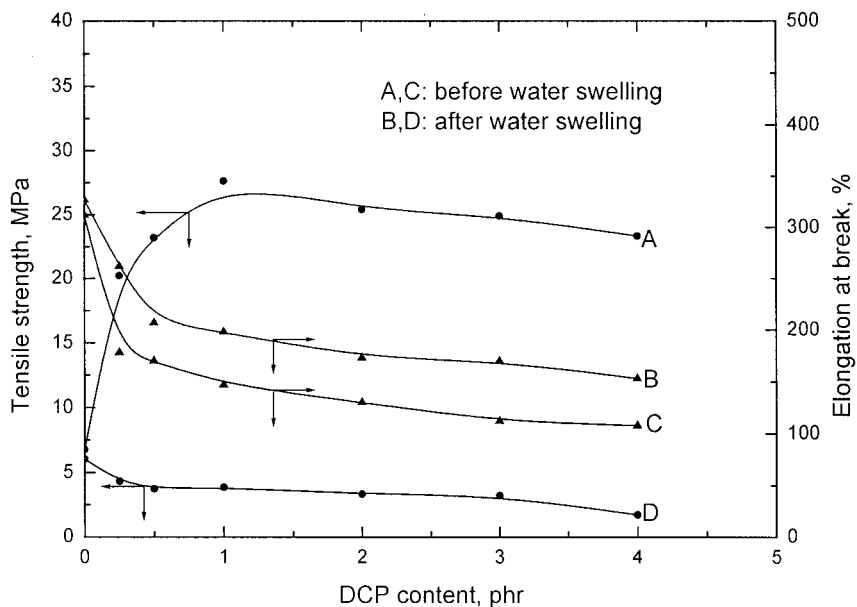


Figure 4 Effect of the DCP content on the mechanical properties of CPE/LiAA vulcanizates (formulation: 100 phr CPE, 39 phr LiAA, and variable DCP).

CPE/LiAA vulcanizates were swelled by water, the ionic crosslinks suffered destruction, the volume of the samples increased, and the water absorbed in the vulcanizates acted as a plasticizer. This resulted in a reduction of the tensile strength and hardness and an increase in the elongation at break. The effects of the DCP and LiAA contents on the mechanical properties were mainly due to the difference in the crosslink structures.

Figure 6 shows the effect of the LiOH/AA molar ratio on the mechanical properties of the CPE/LiAA vulcanizates. The tensile strength increased as the LiOH/AA molar ratio increased from 0.67 to 1.0, it reached the maximum value when the LiOH/AA molar ratio was 1.0, and then it decreased as the LiOH/AA molar ratio further increased. The elongation at break was at the minimum when the LiOH/AA molar ratio was 1.0. It can be concluded that an extra

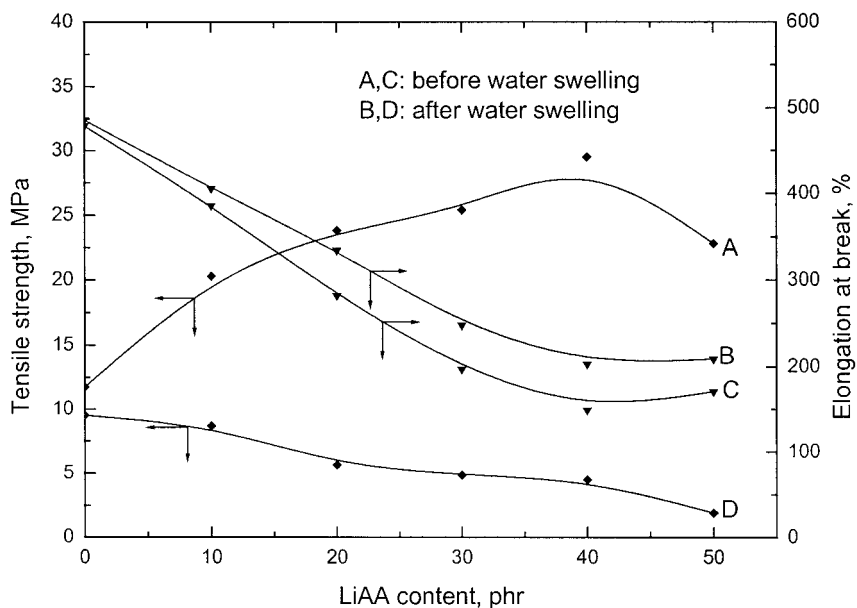


Figure 5 Effect of the LiAA content on the mechanical properties of CPE/LiAA vulcanizates (formulation: 100 phr CPE, 1.0 phr DCP, and variable LiAA).

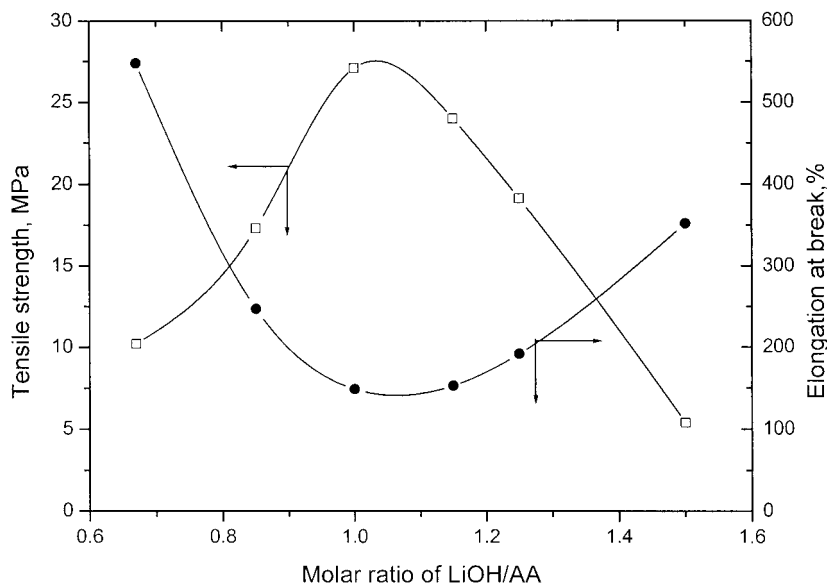


Figure 6 Effect of the molar ratio of LiOH/AA on the mechanical properties of CPE/LiAA vulcanizates [formulation: 100 phr CPE, 1.0 phr DCP, and 39 phr LiAA (0.5 mol); variable LiOH/AA molar ratio].

amount of LiOH or AA could affect the polymerization of LiAA and result in a reduction of the crosslink density of CPE/LiAA vulcanizates.

Water swelling

Figures 7–9 show the water-swelling properties of CPE/LiAA vulcanizates. Figure 7 shows the effect of the DCP content, Figure 8 shows the effect of the LiAA

content, and Figure 9 shows the effect of the LiOH/AA molar ratio on the water-swelling ratio of the vulcanizates.

As shown in Figure 7, the water-swelling ratio decreased with increasing DCP content, and the maximum swelling ratio of CPE/LiAA vulcanizates decreased to 162% from about 200% when the DCP content increased from 0.25 to 3.0 phr. Figure 8 indicates that the swelling ratio of the vulcanizates in-

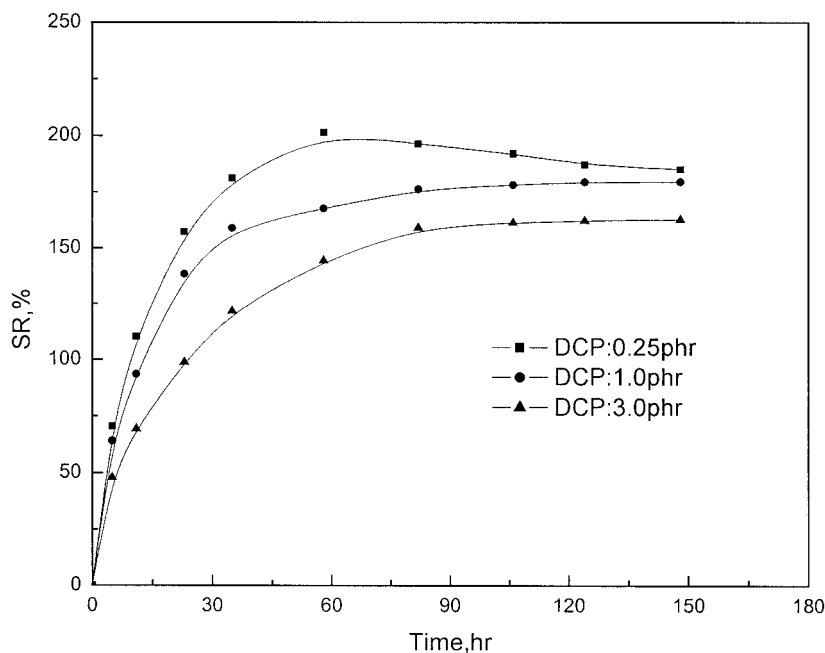


Figure 7 Effect of the DCP content on the swelling ratio of the vulcanizates (formulation: 100 phr CPE, 39 phr LiAA, and variable DCP).

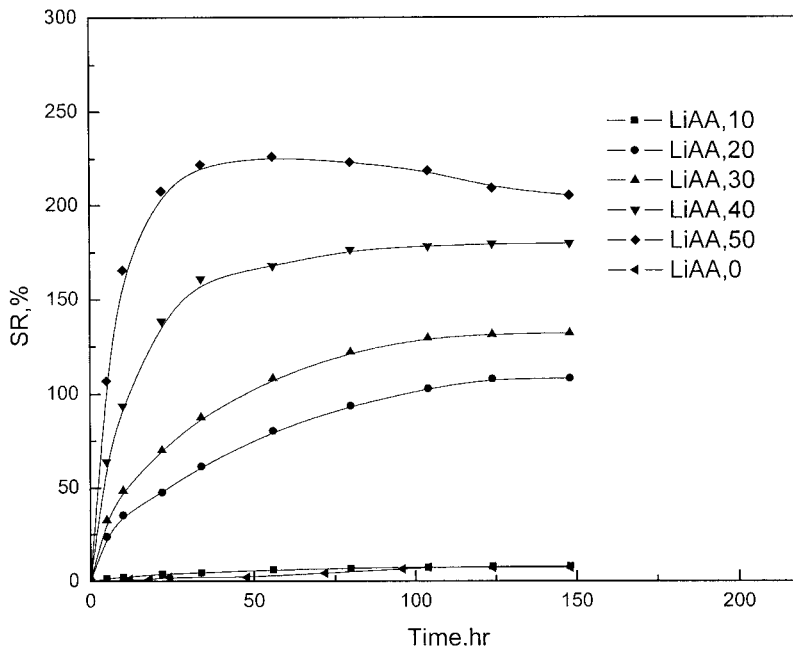


Figure 8 Effect of the LiAA content on the swelling ratio of the vulcanizates (formulation: 100 phr CPE, 1.0 phr DCP, and variable LiAA).

creased greatly with increasing LiAA content. A CPE vulcanizate without LiAA almost did not swell in water. When the LiAA content was 50 phr, the maximum swelling ratio of the CPE/LiAA vulcanizates was higher than 220%. Figure 9 shows that the water-swelling ratio had a maximum value when the molar ratio of LiOH/AA was 1.0.

As mentioned previously, PLiAA consisting of both grafted PLiAA and homo-PLiAA formed in CPE/LiAA vulcanizates during vulcanization. When the vulcanizates were in contact with water, the —COOLi groups in the PLiAA molecular chains partially ionized and became carboxylate anions (—COO^-) and mobile counteractions (Li^+). Both the —COOLi

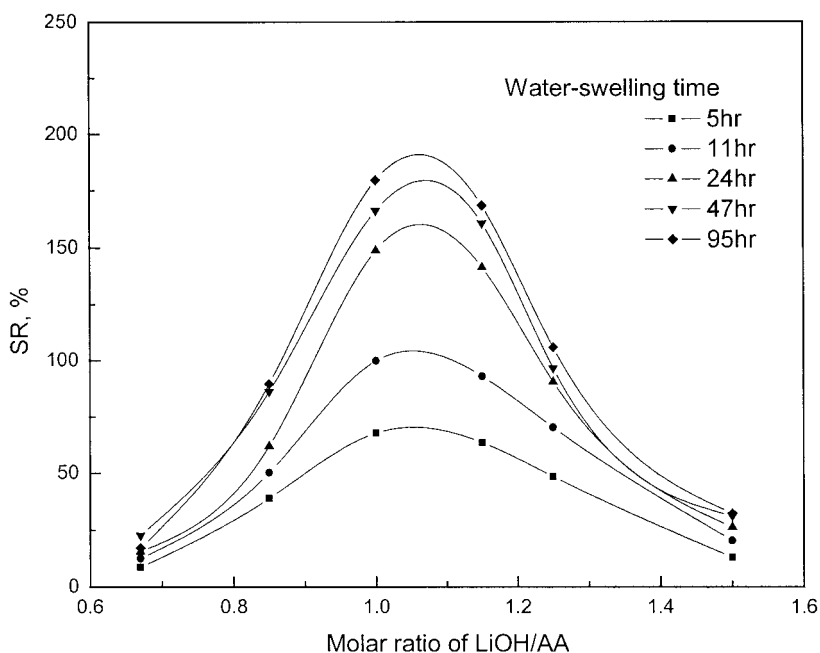


Figure 9 Effect of the LiOH/AA molar ratio on the water-swelling ratio [formulation: 100 phr CPE, 1.0 phr DCP, and 39 phr LiAA (0.5 mol); variable LiOH/AA molar ratio].

groups and the dissociated ions had the ability to attract water molecules. In addition, the repulsion between the carboxylate anions on the PLiAA chains resulted in the expansion of the crosslink network of the elastomer, and the water molecules became clusters of restricted size entrapped in the mesh of the network of the elastomer. When the permeation stress of the water molecules was equal to the elastic stress of the covalent crosslink network of the elastomer, the water-swelling process reached the equilibrium state. Therefore, the water-swelling process was influenced by the crosslink structure, hydrophilic composition (PLiAA), and ionization degree of the —COOLi groups. Therefore, increasing the DCP content led to an increase in the covalent crosslink density and a decrease in the swelling ratio. Increasing the LiAA content led to an increase in the hydrophilic composition and, of course, an increase in the swelling ratio.

When the LiOH/AA molar ratio was not equal to 1.0, the extra LiOH or AA ionized in the presence of water and became water-soluble free ions. These ions could hinder the ionization of the —COOLi group and influence the water-swelling process of the vulcanizates. In addition, the extra amount of LiOH or AA affected the polymerization of LiAA and resulted in the water-swelling properties of the vulcanizates becoming poor.

CONCLUSIONS

LiAA was *in situ* prepared in CPE through the neutralization of LiOH and AA. The *in situ* polymerization of LiAA was initiated by DCP at an elevated temperature. The CPE/LiAA vulcanizates had both covalent and ionic crosslink bonds. The gross crosslink density increased with increasing DCP and LiAA contents. The covalent crosslink density increased with increasing DCP content but decreased slightly with increasing LiAA content. LiAA had a great reinforcing effect on CPE gum, and the tensile strength of the CPE/LiAA vulcanizates was higher than 28 MPa when the NaAA and DCP concentrations were 40 and 1.0 phr, respectively. The vulcanizates had good water-swelling properties, and their maximum water-swelling ratio was greater than 220% when the AA concentration was 50 phr and the DCP concentration was 1.0 phr. The water-swelling ratio increased with increasing LiAA content, but it de-

creased with increasing DCP content. In addition, the water-swelling ratio depended on the LiOH/AA molar ratio and had its maximum value when the LiOH/AA molar ratio was 1.0. The *in situ* preparation and polymerization of LiAA play important roles in the improvement of the mechanical properties and water-swelling properties of CPE/LiAA vulcanizates.

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