Effects of Aluminum Ionomer Surface Layers on Polymer Properties

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Synopsis

Bulk samples of carboxylic acid containing copolymers may be treated with solutions of aluminum isopropoxide, $Al(OC_3H_7)_3$, to produce ionically gelled surface layers. The behavior of treated specimens is different from that of untreated specimens in tests which measure friction coefficient, stress crack resistance, and tensile strength. In several instances the results are compared to those produced by CASING, another technique for producing crosslinked surface regions.

INTRODUCTION

Copolymers containing a relatively small concentration of pendant carboxylic acid groups are easily neutralized in the melt or in solution by monovalent and divalent metal bases.[1-6] The resultant salt copolymers have been named ionomers. Neutralization with trivalent metal bases results in an insoluble, infusible material.[1,6,7] Since the conventional (mono- and divalent counterion) ionomers possess a number of interesting and useful properties, synthesis and evaluation of the trivalent form was desirable.

There are some instances where chemical reactions can be carried out on preformed solid polymer substrates. Complete penetration of the reactant is only possible if the cross-sectional area is quite small, as in thin films or fibers. In some cases it is not necessary to carry the reactions out through the entire cross section to achieve the desired results. An example of such a process is CASING (Crosslinking by Activated Species of INert Gases).[8,9] The penetration depths of a few microns achieved by this process are adequate to produce sizable increases in adhesive joint strengths for treated polyethylene.

The use of a liquid reagent or solvent is not a widely employed technique. If complete reaction is to be achieved, the liquid must be a good solvent, which leads to severely swollen substrates from which solvent removal can be very difficult. If the carrier liquid is not a good solvent, little penetration occurs. However, this method was chosen in the hope that effects similar to those produced by CASING could be achieved.

In employing polymer substrates containing functional groups, a wide variety of synthetic opportunities arise in terms of solvent, reagent func-

TABLE I
Composition and Properties of Ethylene–Acrylic Acid Copolymers

Copolymer	COOH/100 CH_2	CH_3/100 CH_2	Density, (g/cc)	Melt index
E/AA-1	0.66	~2.0	0.926	4.8
E/AA-2	1.57	~2.0	0.935	5.0
E/AA-3	2.78	>1.5	0.946	4.8
		<2.0		

tional group content, and functional group type. In producing a cross-linked surface structure, salt-forming functional groups in particular offer numerous possibilities for reaction with trifunctional reagents.

EXPERIMENTAL

Polymers

Three ethylene–acrylic acid copolymers (E/AA) were used in this study. They contain 1.3, 3.1, and 5.3 mole-% acid and have been previously characterized.[5] Their properties are given in Table I. The copolymers were compression molded into a variety of thicknesses and shapes for testing. All samples were annealed for 15–20 hr in a vacuum oven at 75°C prior to treatment or testing. A branched polyethylene (DYNK) from Union Carbide was used as a reference material.

Another resin employed was a methyl methacrylate–methacrylic acid copolymer (MMA/MAA) provided by Rohm & Haas Co. (SR-5411), which contains about 5 mole-% MAA. Tensile bars ($^1/_8 \times ^1/_2 \times 8^1/_2$ in.) and flex bars ($^1/_8 \times ^1/_8 \times 5$ in.) were injection molded and annealed 24 hr at 85°C under vacuum prior to treatment or testing.

Ethylene Polymers—Surface Treatment

Aluminum isopropoxide, $Al(OC_3H_7)_3$, was chosen as the crosslinking reagent. Two carrier solvents with widely different swelling power, benzene and isopropanol, were used. Benzene, as well as being a good swelling agent for the polymer, dissolves appreciable amounts of $Al(OC_3H_7)_3$. Isopropanol not only is a poor swelling agent for the polymer but dissolves a limited amount of the base.

Both solvents were saturated with $Al(OC_3H_7)_3$ at reflux, and the various samples were simply immersed in the boiling solution for specific times. Controls were also run where no $Al(OC_3H_7)_3$ was in the solvent. After immersion, samples were washed in benzene at 30°–40°C to remove excess $Al(OC_3H_7)_3$ and dried under vacuum at 75°C for 15–20 hr. Benzene was such a strong swelling agent that additional tests were made using lower temperatures to avoid distortion of the samples.

Several methods were used to characterize the gel layer. Thickness was determined by Soxhlet extraction of the sol fraction from thin (less than 3 mils) films in condensing xylene for 24 hr and weighing the remaining gel.

In most cases this skin was coherent and thick enough to determine its density in a gradient column.

Large sections of treated thin films of the 3.1 mole-% acid were examined by transmission and attenuated total reflectance (ATR) infrared spectroscopy.

The CASING treatment was carried out on films of E/AA 1, 2, and 3 and DYNK using a 100-watt, 1.0 mm (Hg) He plasma with varying bombardment times.

Methyl Methacrylate Copolymer—Surface Treatment

It was observed that simple immersion of the MMA/MAA specimens in $Al(OC_3H_7)_3$ solutions resulted in a surface layer that was milky and tended to shrink and crack after drying. A benzene presoak was found to circumvent this, and relatively clear, coherent films were produced. The samples were washed after reaction and vacuum dried for 24 hr at 85°C. Some films were treated with solutions of $LiOCH_3$ or $KOCH_3$ which yield a neutralized surface layer but no crosslinking.

The CASING treatment on these samples was limited to a 10-min bombardment in a 1.0-mm, 100-watt He plasma.

Ethylene Copolymers—Testing

The coefficients of friction on treated and control copolymer films were determined against glass using a specially constructed sled. A detailed discussion of the apparatus is in preparation and is beyond the scope of this work. The film is mounted between two circular plates, one of which contains three holes at 120° intervals, while the other has raised cylindrical studs at comparable locations. Locking the plates results in the sample film-covered studs protruding through the holes; the film on these studs provides the bearing surface to be tested. Stud length is minimized and hole diameter maximized within the design to yield minimum deformation of the film samples. The sled is lowered onto the glass plate mechanically to prevent accidental abuse of the film. Sliding resistance at a variety of loads is measured by an Instron apparatus which also provides the translational motion. The rate of travel of the sled was 0.05 in./min.

Tensile tests were performed according to ASTM D1708 on both treated and untreated samples. Single lap-shear adhesive joint specimens were made by laminating treated and untreated thin films of E/AA-2 between aluminum using a conventional epoxy adhesive cured at 60°C.

Methyl Methacrylate Copolymers—Testing

The cantilever beam method was used to determine the minimum stress necessary to produce crazing, since it provides outer fiber stresses that vary from zero at the weighted end to a maximum at the fulcrum.

The control and treated flex bars were clamped horizontally in a support leaving a $4^1/_2$ in. overhang. The load was applied to the unsupported end
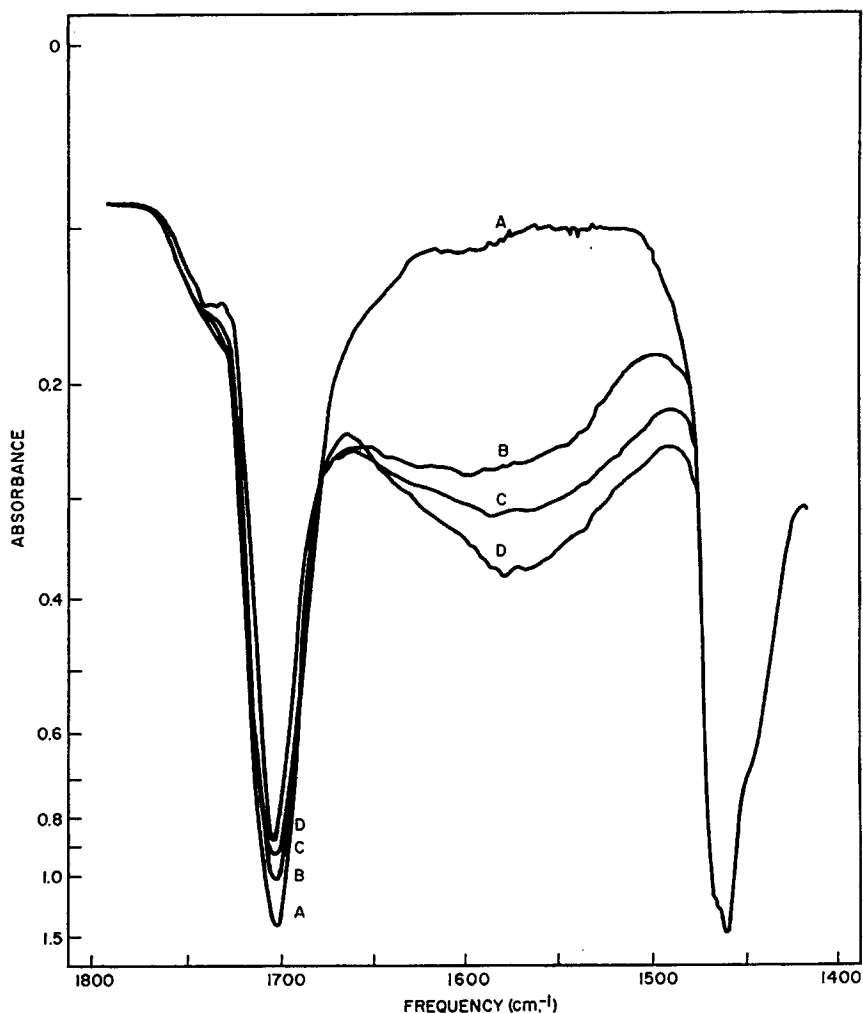
Fig. 1. ATR spectra of E/AA-2 treated in refluxing isopropanol saturated with Al-(OC$_3$H$_7$)$_3$: (A) control; (B) 60 sec; (C) 180 sec; (D) 600 sec.

by hanging a weight through a hole drilled near the end of the specimen. The threshold outer fiber stress S to produce crazing was calculated from

$$S = 6\ M/bd^2$$

where M is the bending moment ($M \equiv$ load $\times$ distance from fulcrum) in inch-pounds and b and d represent the bar width and thickness, respectively. The minimum stress to produce crazing is somewhat time dependent, so an arbitrary loading period of 10 min was chosen as adequate to provide comparative data in studying the effects of these surface treatments.

The stress cracking agent used was ethanol. The solvent was applied to the tension side of the bar via a $1/_4$-in.-wide strip of saturated filter paper for
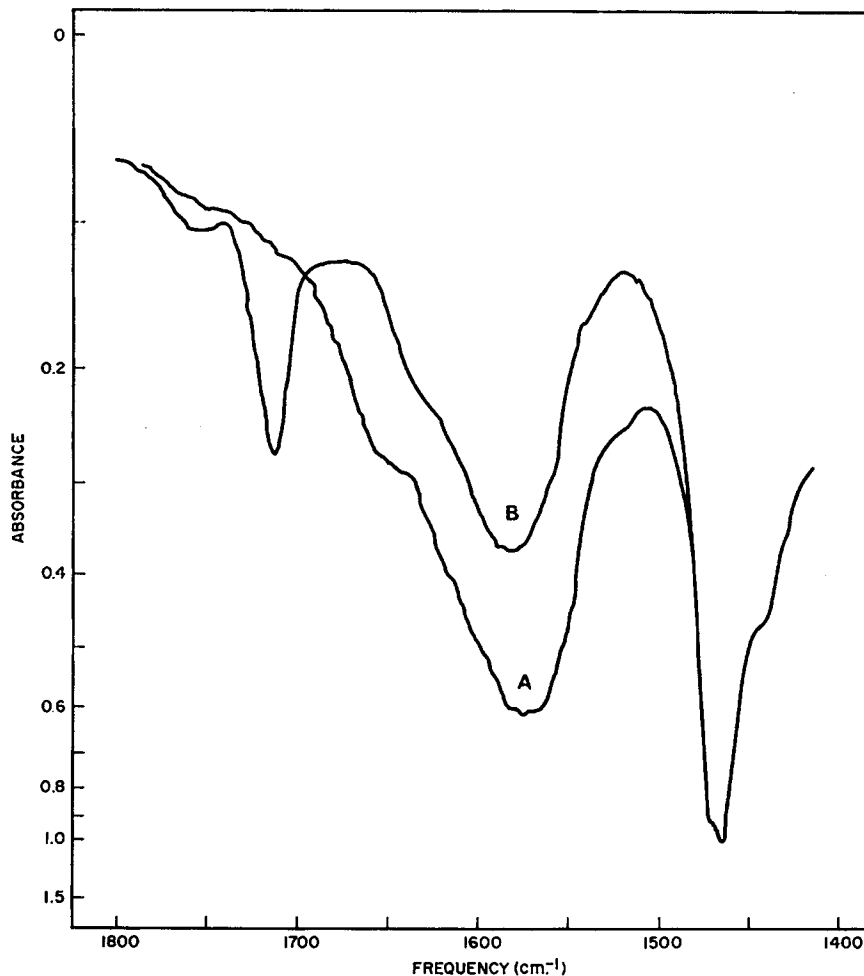
Fig. 2. ATR spectra of E/AA-2: (A) refluxing benzene saturated with $Al(OC_3H_7)_3/$ 1 sec; (B) room temperature, benzene saturated with $Al(OC_3H_7)_3/600$ sec.

the duration of the loading period. The filter paper strip assures intimate contact over a uniform area and reduces the crazing at the specimen corners where the stress pattern is complex. At the end of the test, the load was removed, and the sample was taken from the clamp, wiped clean, and examined for crazes.

The tensile bars were annealed and treated in the same manner as the flex bars. The samples were fractured on an Instron apparatus in accordance with ASTM D638.

RESULTS AND DISCUSSION

Figures 1 and 2 show the 1800–1400 cm^{-1} portion of the ATR spectrum of the treated 3.1 mole-% acid copolymer. Both the COOH (1705 cm^{-1})
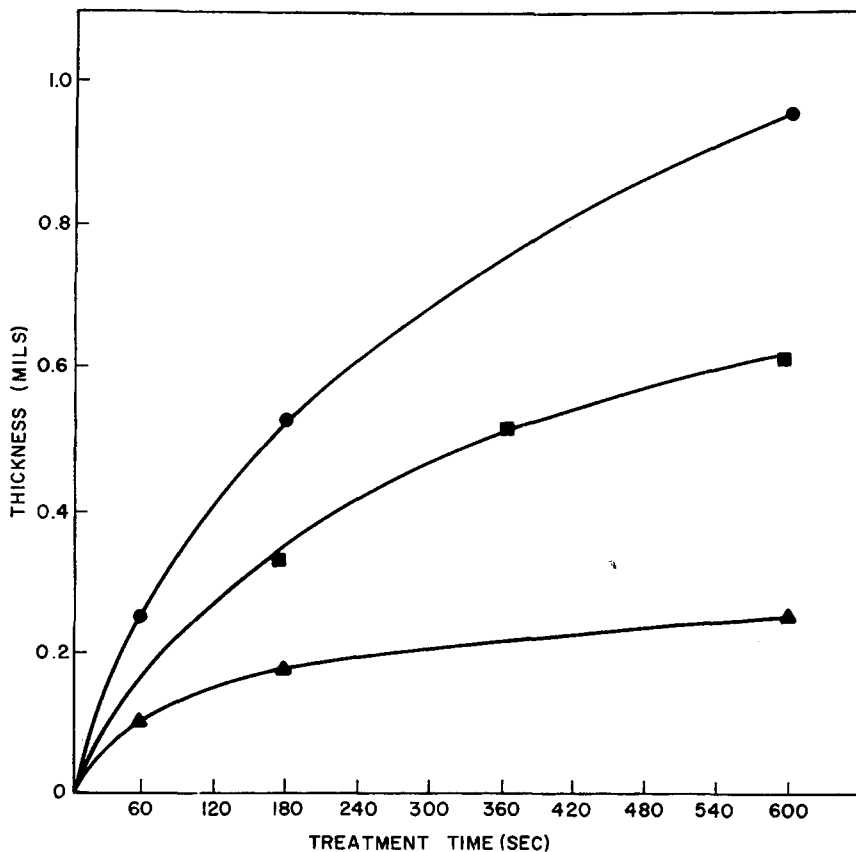
Fig. 3. Gel layer thickness as a function of treatment time in isopropanol–Al(OC₃H₇)³
at 82°C: (●) E/AA-1; (■) E/AA-2; (▲) E/AA-3.

and COO^- ($\sim$ 1570 cm^{-1}) groups absorb in this region giving an excellent
analysis of the surface layer neutralization. This technique probes ap-
proximately 1 micron deep into the surface of the material. The spectra
show that either hot or cool benzene treatment, through increased swelling
power and greater concentration of $Al(OC_3H_7)_3$, converts almost all of the
acid groups at this depth to the salt. On the other hand, for the isopro-
panol-treated sample the conversion is low and increases only slowly with
immersion time. For a 2-mil film of E/AA-1, the total neutralization
determined by transmission is 40% for a 10-min treatment in benzene at
40°C.

Figure 3 and Table II give the results of the extraction and density mea-
surements. Apparently at lower acid contents, the low "crosslink" density
gel formed is still permeable to diffusion of the isopropanol carrier. This
permits reagent to be continuously carried to the interior of the specimen.
On the other hand, as the acid content of the substrate increases or the reac-

TABLE II
Gel Layer Thickness

Copolymer	Solvent[a]	Temp, °C	Time, sec	Thickness, mils	Density, g/cc
E/AA-1	I	82	60	0.266	0.944
	I	82	180	0.529	0.942
	I	82	600	0.980	—
	B	40	20	0.04	—
	B	40	60	0.13	—
	B	40	600	0.457	—
E/AA-2	I	82	180	0.350	0.968
	I	82	360	0.512	—
	I	82	600	0.600	0.960
	B	40	600	0.377	—
E/AA-3	I	82	60	0.098	0.990
	I	82	180	0.175	—
	I	82	600	0.258	0.980
	B	25	600	0.155	0.980

[a] I = Isopropanol; B = benzene.

TABLE III
Tensile Test Results of E/AA-3[a]

Treatment (solvent/time/temp)[b]	Young's modulus, psi	Yield strength, psi	Break strength, psi
None	8,350	1,120	3,385
Controls (solvent but no Al(OC$_3$H$_7$)$_3$)	8,750	1,160	3,450
B–Al(OC$_3$H$_7$)$_3$/300 sec/25°C	10,514	1,193	3,990
I–Al(OC$_3$H$_7$)$_3$/60 sec/82°C	8,875	1,170	3,600

[a] Sample dimensions 0.187 × 0.128 in.
[b] B = Benzene; I = isopropanol.

tion rate is increased, as in the benzene solvent, the neutralization and gelation rapidly forms a "tight" network of high "crosslink" density which does not swell and which seals the substrate to extensive penetration. For convenience, this process will be referred to as CMS (Crosslinking by Multivalent Salts).

One of the areas of significant departure between conventional CASING and CMS is the increased skin thickness achieved by solvent diffusion. To determine if the effects of this crosslinking could be detected in the mechanical properties of large samples, tensile tests were performed. The results of the tensile tests on the 5.3 mole-% acid copolymer are shown in Table III. Even a relatively thin skin of metal ion-crosslinked material affects the modulus and strength.

The adhesive joint single lap-shear tests indicate that the isopropanol—Al(OC$_3$H$_7$)$_3$-modified surface layer is tougher than the original copolymer. These results, shown in Table IV, are not as dramatic as achieved by CAS-

TABLE IV
Single Lap-Shear Tests on Laminated Joints of E/AA-2[a]

Treatment (solvent/time/temp)[b]	Joint strength, psi
Control	2,200
B–Al(OC$_3$H$_7$)/1 sec/80°C	1,680
B–Al(OC$_3$H$_7$)/2 sec/80°C	1,613
I–Al(OC$_3$H$_7$)/60 sec/82°C	2,450
I–Al(OC$_3$H$_7$)/180 sec/82°C	2,500

[a] Joints: Al–epoxy adhesive–E/AA film–epoxy adhesive–Al.
[b] I = Isopropanol; B = benzene.

ING ordinary polyethylene. However, this is to be expected since the untreated ethylene—acrylic acid copolymers in this test show a much greater joint strength than the untreated parent homopolymer. Hot benzene is too strong a swelling agent, and the joint strength is actually decreased. It is doubtful that these particular treatments represent the optimum conditions for bonding.

The frictional force observed is a complex function of displacement. For all the untreated polyethylenes the drag increases to a peak value in 0.02 to 0.05 in. of displacement and falls to a more or less stable plateau with further motion. In the plateau region the force may show small steady increases, decreases, or no change.

Table V shows the friction coefficients at various loads for the untreated, CMS-treated, and CASING-treated ethylene polymers. Both treatments effectively reduce the apparent frictional coefficients although there are some differences in the nature of the reduction. CASING leaves the general shape of the force–displacement curve unaltered and achieves the major portion of its effect after very short bombardment times. The CMS treatment removes the peak from the force–displacement curve and only achieves its greatest effect at long treatment times. It is not possible to attribute the differences between the results of the two treatments solely to the chemistry of the processes. In general, the CMS treatment produces thicker gel layers, and this alone may be responsible for the observations.

At this point, these results cannot be interpreted on a theoretical basis.

Current understanding of environmental stress cracking indicates the dual role of the surrounding liquid. The liquids wet conventional polymers but only those with appropriate cohesive energy density are strong swelling agents. Crosslinking the surface region of polymers should reduce swellability, thereby increasing resistance to environmental stress cracking. The MMA/MAA system was chosen for this study because of the well-known sensitivity of PMMA to environmental stress cracking. In addition, the nature of the polymer (glassy) and the test method (cantilever beam) dictate smaller stresses than used in the evaluation of environmental stress crack resistance for flexible polymers. Under these conditions the surface layer is more likely to remain intact. As a final added point of interest, the formation of crazes which eventually lead to failure in tension

TABLE V
Surface Layer Treatment and Sliding Friction

| Polymer treatment (process, time, solvent/thickness) | Friction coefficient at load[a] | | | | | |
| | 78 g | | 200 g | | 400 g | |
	peak	plateau[b]	peak	plateau[b]	peak	plateau[b]
DYNK						
Virgin	11.0	5.3	6.5	3.8	5.5	4.5
CASING, 60 sec/-	6.8	1.9	7.5	1.5	4.0	1.3
CASING, 600 sec/0.05 mils	10.0	1.3	6.1	0.9	4.7	1.1
CASING, 1800 sec/0.08 mils	6.2	1.3	6.3	1.2	3.3	0.8
E/AA-1						
Virgin	12.0	4.9	6.8	3.9	4.7	3.4
CASING, 60 sec/-	11.0	1.0	5.6	1.2	3.1	0.9
CASING, 600 sec/0.03 mils	12.0	1.3	—	—	—	—
CASING, 1800 sec/0.11 mils	8.6	1.1	5.9	1.0	3.8	0.9
CMS, 20 sec, B/-	c	4.1	c	4.7	c	3.2
CMS, 60 sec, B/0.20 mils		2.4		3.3		3.7
CMS, 600 sec, B/0.46 mils		0.8		1.2		1.0
CMS, 600 sec, I/0.95 mils		0.8		1.2		1.0
E/AA-2						
Virgin	14.0	9.0	8.6	4.0	4.6	3.5
CASING, 60 sec/-	6.2	1.7	6.2	1.6	2.9	1.2
CASING, 600 sec/0.06 mils	—	1.3	—	1.7	—	—
CASING, 1800 sec/0.11 mils	4.2	1.2	4.3	1.2	—	—
CMS, 20 sec, B/-	c	3.6	c	4.0	c	3.8
CMS, 60 sec, B/0.15 mils		4.1		4.8		4.3
CMS, 600 sec, B/0.37 mils		0.5		1.4		1.8
CMS, 600 sec, I/0.60 mils		0.9		—		—
E/AA-3						
Virgin	d	6.2	d	2.8		
CMS, 600 sec, I/0.20 mils	c	0.9	c	0.9		

[a] Load = total sled weight.
[b] Plateau values are averages; friction may tend to increase or decrease with travel.
B = Benzene as the $Al(OC_4H_7)_3$ solvent, $T = 40°C$; I = isopropanol is the $Al(OC_3H_7)_3$ solvent, $T = 82°C$.
[c] CMS samples show no peak in coefficient.
[d] Low-frequency stick slip defies accurate measurements.

for glassy polymers often are initiated at the sample surface. A surface layer treatment may well hinder such initiation, enhancing the tensile strength of the material.

The results of the ethanol-induced stress cracking tests are shown in Table VI. Annealing markedly increases the threshold crazing stress, as expected. The increases in this value with ionic surface crosslinking are measurable, and the CASING process appears to be very effective in this respect. It can be seen that these results fit in quite well with the existing theory of environmental stress cracking. A crosslinked surface is much less permeable than the base resin itself, which limits the action of the solvent.

TABLE VI
Threshold Fiber Stress of SR 5411 (MMA/MAA) Copolymer[a]

Sample	No. tested	S, psi
As molded	5	1570
Annealed	4	2497
CMS (30/30/30)[b]	5	2768
CMS (180/60/60)[b]	5	2870
CASING (10 min, 1.0 mm He, 100 W)	5	3200
Univalent salt	5	2308

[a] Test method: cantilever beam/ethanol.
[b] Times in sec for: presoak/Al(OC$_3$H$_7$)$_3$–benzene (room temp)/wash benzene.

TABLE VII
Tensile Strength and Elongation of SR 5411 (MMA/MAA)

Sample	No. tested	TS, psi	ϵ_b, %
As molded	5	10,557	3.96
Annealed	5	11,298	4.56
CMS (30/30/30)[a]	5	11,867	4.96
CMS (180/60/60)[a]	5	11,862	>5.0
CASING (10 min, 1.0 mm He, 100 W)	4	11,770	5.0

[a] CMS treatment key same as in Table VI.

The average tensile strengths and elongations (ϵ_b) of control and treated methacrylate copolymers are shown in Table VII. The CASING treatment gives a small increase in strength, while the CMS treatment gives a slightly greater increase in strength. Of particular note is the manner in which the increase is achieved. The moduli of the treated and control samples are the same, but the elongations are greater for the treated specimens.

For these large test pieces, the volume fraction of crosslinked material is small, and significant stiffening is not expected. Rather, a greater strain is allowed before the failure crack is initiated. This pattern fits with the proposed action of the localized surface-layer crosslinking: interference with the generation of failure craze/cracks at the surface. Thus, behavior also agrees in general with the increases in threshold craze stress found in the environmental stress cracking tests.

CONCLUSIONS

Copolymers containing carboxylic acids as pendant groups may be converted to their aluminum salts by reaction with Al(OC$_3$H$_7$)$_3$. This reaction is carried out by diffusing the base into the polymer substrate using a suitable carrier solvent. The resultant ionomer is essentially crosslinked by the trivalent cation.

The presence of this ionic gel layer or a covalent gel layer as generated by CASING decreases the friction coefficient of the samples while increasing their tensile strength and resistance to environmental stress cracking.

These investigations indicate that the potential of polymer surface-layer treatment extends beyond the field of adhesive joining applications.   The results are generally not completely understood on a theoretical basis. The mechanisms of adhesion and plowing (friction) and solvent action (stress cracking) are themselves incompletely understood, and the tests do not measure a single property that can be simply connected to some parameter.   What is important is that these results fit within the general framework of the current "state of the art."

No efforts have been made to optimize the effects of treatment in any given test.   In view of the results to date, some further improvement in properties may be attained by suitable development studies.

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