Effect of Carboxyl on Vulcanization and Mechanical Properties of Carboxylated Acrylic Rubber Prepared by ^{60}Co-γ-Ray-Induced Polymerization

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ABSTRACT: Acrylic acid carboxylated acrylic rubber (ACM) and itaconic acid carboxylated acrylic rubber were prepared by ^{60}Co-γ-ray-induced emulsion copolymerization. The polymers were characterized using FTIR and ^{13}C NMR spectroscopies. The acid value was determined with nonaqueous titration method. The molecular weight and the polydispersity index of the polymers were measured using gel permeation chromatography. The influence of the cure-site (carboxyl) on the vulcanization and mechanical properties of the ACM was researched by means of rheometric study, gel fraction analysis, mechanical property tests, and dynamic mechanical thermal analysis. The results show that the crosslink density of polymers increases with amounts of the carboxyl cure-site. The itaconic acid carboxylated ACM has better cure characteristics and mechanical properties than the acrylic acid carboxylated ACM has. In addition, the comparison of ACM prepared by ^{60}Co-γ-ray-induced polymerization with ACM prepared by chemical-initiator-induced polymerization has been investigated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5587–5594, 2006

Key words: radiation polymerization; acrylic rubber; carboxyl; crosslink; mechanical properties

INTRODUCTION

Acrylic rubber (ACM) is of great interest in recent years because of its superior properties such as heat and oil resistance.[1,2] It has become a very important material for individual application or blending with many other polymers.

Vulcanization is a crucial step for processing acrylic rubber, as well as many other kinds of rubbers, for which suitable cure-site monomers should be introduced into the polymer chain. Acrylic rubbers containing different types of cure-site monomers and their cure behavior with different crosslinking agents were reviewed by Vial.[3] Among a large quantity of the compounds, several monomers with active cure-sites (such as epoxy, chlorine, and carboxyl), are widely used for industrial applications. Monomers containing carboxylic and epoxy cure-sites are relatively safe, whereas the use of chlorinated monomers gives rise to serious problems of toxicity and corrosion.[4]

Epoxy ACM,[1,5–13] as well as carboxylated ACM, have been studied intensively in recent years. Brown[14] reported the carboxylic elastomers and their crosslinkage with different curing systems. Majerus

and Pitochelli[15] used a difunctional carboxylate epoxy to crosslink two series of acrylic copolymers (ethyl acrylate–acrylic acid and butyl acrylate–acrylic acid) and investigated the influence of microstructure on the tensile behavior. Senuma[16] crosslinked ethylene-acrylic acid copolymer using dicumyl peroxide and carried out swelling measurement. Giannetti et al.[4] studied the ammonium salt-catalyzed crosslinking mechanism of acrylic rubber containing both epoxy and carboxyl cure-sites. Mishra et al.[17–19] blended ethylene-acrylic rubber containing carboxyl cure-site with different types of grafted low-density polyethylene (LDPE) and studied the shrinkability of the blends. In these researches, 4,4′-diamino diphenyl methane (MDA) was used as coupling agent for the maleic anhydride (MA)-grafted LDPE in the reaction between carboxyl groups and acid anhydride groups to form crosslinking; for the glycidyl acrylate (GA)-grafted LDPE and acrylamide (AM)-grafted LDPE, the carboxyl groups reacts with the epoxy groups and the amide groups, respectively, to form the interchain crosslinking. Khatua and Das[20] blended ethylene-acrylic rubber containing carboxyl cure-site with polyurethane (AU) and used 4,4′-diamino diphenyl methane/diphenylguanidine as the curing system to vulcanize the rubber. In the blends, the interchain crosslinking between the rubber and the AU was formed by the reaction of the carboxyl group with the secondary amide. However, there have been few

TABLE I
Recipes of the Emulsion

	Sample codes	BA (g)	AcN (g)	AA (g)	IA (g)	SDS (g)	OP-10 (g)	Distilled water (g)
Induced by gamma-ray[a]	NC-ACM	88	12	/	/	1.5	3.0	150
	AC-ACM1	88	12	2.70	/	1.5	3.0	150
	AC-ACM2	88	12	4.05	/	1.5	3.0	150
	AC-ACM3	88	12	5.40	/	1.5	3.0	150
	AC-ACM4	88	12	6.75	/	1.5	3.0	150
	AC-ACM5	88	12	8.10	/	1.5	3.0	150
	IC-ACM1	88	12	/	2.44	1.5	3.0	150
	IC-ACM2	88	12	/	3.66	1.5	3.0	150
	IC-ACM3	88	12	/	4.88	1.5	3.0	150
	IC-ACM4	88	12	/	6.10	1.5	3.0	150
	IC-ACM5	88	12	/	7.32	1.5	3.0	150
Induced by $K_2S_2O_8$[b]	CAC-ACM5	88	12	8.10	/	1.5	3.0	150
	CIC-ACM5	88	12	/	7.32	1.5	3.0	150

[a] The polymerization was carried out at room temperature under nitrogen (at a dose rate of 50 Gy/min).
[b] The polymerization was carried out at 70°C under nitrogen (the weight ratios of $K_2S_2O_8$/monomers are 0.277/100 for CAC-ACM5 and 0.281/100 for CIC-ACM5).

reports concerning the effect of type and amount of carboxyl cure-sites on the crosslinking and mechanical properties of the carboxylated acrylic rubber.

γ-ray-induced polymerization, as one of the most convenient methods, has many advantages.[21] It can be carried out at room temperature, under normal pressure, and the reaction is hardly influenced by the variation of temperature. Because there is no chemical initiator in the polymerization process, the final products are not ''contaminated.'' In aqueous emulsion polymerization, the primary free radicals for initiating the polymerization are generated from water and the monomer by γ irradiation.[22]

In the present study, the acrylic rubbers containing different types and amounts of carboxylic monomers were prepared by ^{60}Co-γ-ray-induced emulsion co-polymerization, and hexamethylenediamine carbamate was used as the curing agent. The aim is to research the effect of carboxyl on the vulcanization and mechanical properties of the rubbers. In addition, the comparison of ACM prepared by ^{60}Co-γ-ray-induced polymerization with that prepared by chemical-initiator ($K_2S_2O_8$)-induced polymerization has been investigated.

EXPERIMENTAL

Materials

Butylacrylate (BA), acrylonitrile (AcN), acrylic acid (AA), itaconic acid (IA), sodium dodecylsulfate (SDS), stearic acid, acetone, and ethanol were purchased from Shanghai Chemical Reagent (China). Poly(ethylene glycol) monooctylphenyl ether (OP-10) was obtained from the Fuhua (China). Hexamethylenediamine carbamate (Diak #1), di-*ortho*-tolyl guanidine (DOTG), and carbon black (N550) were provided by Shanghai Chinaway Chemical (China). BA, AcN, and

AA were distilled in vacuum before use. Distilled water was used for preparing aqueous emulsion, and all the other reagents were used without further purification.

Preparation of the polymers

Five series of ACM have been prepared in this study, i.e., ACM not been carboxylated (NC-ACM), acrylic acid carboxylated ACM prepared by ^{60}Co-γ-ray-induced polymerization (AC-ACM), itaconic acid carboxylated ACM prepared by ^{60}Co-γ-ray-induced polymerization (IC-ACM), acrylic acid carboxylated ACM prepared by $K_2S_2O_8$-induced polymerization (CAC-ACM), and itaconic acid carboxylated ACM prepared by $K_2S_2O_8$-induced polymerization (CIC-ACM).

The ingredients in all the samples of the above five series were shown in Table I. First, the ingredients of the sample were mixed in a beaker and emulsified at a speed of about 5000 rpm for 10 min. Then, the polymerization was induced by ^{60}Co-γ-ray or $K_2S_2O_8$. After the polymerization, the latex was filtered and the polymer was allowed to settle as soon as ethanol was added. The products were washed five times and dried at 60°C for 72 h.

Characterization of the polymers

The determination of the acid value was carried out according to the literature,[23] in which the samples were dissolved in acetone and then titrated with KOH–ethanol standard solution. FTIR spectra of the films of the polymers were obtained on a Nicolet-Magna-750 FTIR spectrometer. ^{13}C NMR spectra were recorded on a Bruker-Avance AV400 instrument. The molecular weight was measured by gel permea-

tion chromatography (GPC), equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of columns (HT3, HT4, and HT5). The columns were housed in an oven thermostated at 50°C. DMF was used as the mobile phase at a flow rate of 1 mL/min. The instrument was calibrated with polystyrene standards of molecular weight between 1.31×10^3 and 3.74×10^6 g/mol.

Preparation of the blends

The blends were prepared in a two-roll mill equipped with water cooling system. The ACM was firstly masticated in the mill for 3 min. Then the reagents were added in sequence of stearic acid, carbon black, accelerator (DOTG), and curing agent (Diak #1). Each chemical was well mixed before adding another with the mixing times of 3, 10, 3, and 5 min, respectively.

Molding

Test specimens (about 2-mm thick) were prepared by compression molding at 175°C in a frame-and-plate mold for 40 min for all the blends and cooled immediately by flowing water through the platens under pressure. Then, the samples were removed from the mold and the standard dumbbell-shaped test pieces were punched out from the molded cured sheets.

Rheometric study

The cure characteristics of the blends were obtained from a Moving Die Rheometer (MDR-2000E) at 175°C with an oscillating angle of 1° and an oscillating frequency of 1.7 Hz. The testing time was 200 min for acrylic acid carboxylated ACM and 40 min for itaconic acid carboxylated ACM.

Testing of the cured ACM

Hardness was measured on a Shore A Rubber Durometer. Tensile tests were carried out by a universal testing machine (JPL-2500N). Gel fraction was determined via Soxhlett extraction with acetone for 72 h. Dynamic mechanical thermal analysis was performed on a DMTA instrument (Perkin–Elmer-Pyris Diamond) in a tensile mode at the frequency of 1 Hz and with the heating rate of 5°C/min.

RESULTS AND DISCUSSION

Characterization of the polymers

Acid value

Acid value is an important parameter for vulcanization since carboxyl is used as the cure-site in the pre-

TABLE II
Acid Values of the Polymers

Samples	Acid value (mol/kg)
NC-ACM	0
AC-ACM1	0.174
AC-ACM2	0.232
AC-ACM3	0.355
AC-ACM4	0.397
AC-ACM5	0.510
IC-ACM1	0.087
IC-ACM2	0.119
IC-ACM3	0.125
IC-ACM4	0.130
IC-ACM5	0.138
CAC-ACM5	0.914
CIC-ACM5	0.322

sent experiment. Titration results (Table II) showed that the polymers containing different amounts of carboxyl groups were successfully prepared. The acrylic acid carboxylated ACM has higher acid value than has the corresponding itaconic acid carboxylated ACM. The reason could be due to the different copolymerization reactivity ratios of the two carboxylic monomers. Results also show that ACM prepared by $K_2S_2O_8$-induced copolymerization has higher acid value than the corresponding one induced by ^{60}Co-γ-ray has. The reason is not clear at present.

FTIR spectrum

FTIR spectra of copolymers are presented in Figure 1. The strong absorption peak at 1720 cm^{-1} shows the stretching vibration of carbonyl (C=O) of BA, and the peak at 2240 cm^{-1} is from —CN. The broad peak with V_{max} at 3252 cm^{-1} is from the —OH vibration in carboxyl groups of the polymers, which is not present in the sample NC-ACM, since it does not contain carboxyl group. This proved that the tercopolymers (BA/AcN/AA and BA/AcN/IA) have been produced. In addition, the content of the carboxyl in the polymers were estimated according to the intensity of the —OH vibration peak, which is consistent with the titration results.

^{13}C NMR spectrum

The representative copolymers (containing more carboxyl) AC-ACM5 and IC-ACM5 were characterized using ^{13}C NMR. Figure 2 shows the ^{13}C NMR spectra of the copolymers with the assignments. The characteristic peaks of —CN, —COOH, and —COOC$_4$H$_9$ groups were clearly observed, which further conforms the molecular structures of the tercopolymers.
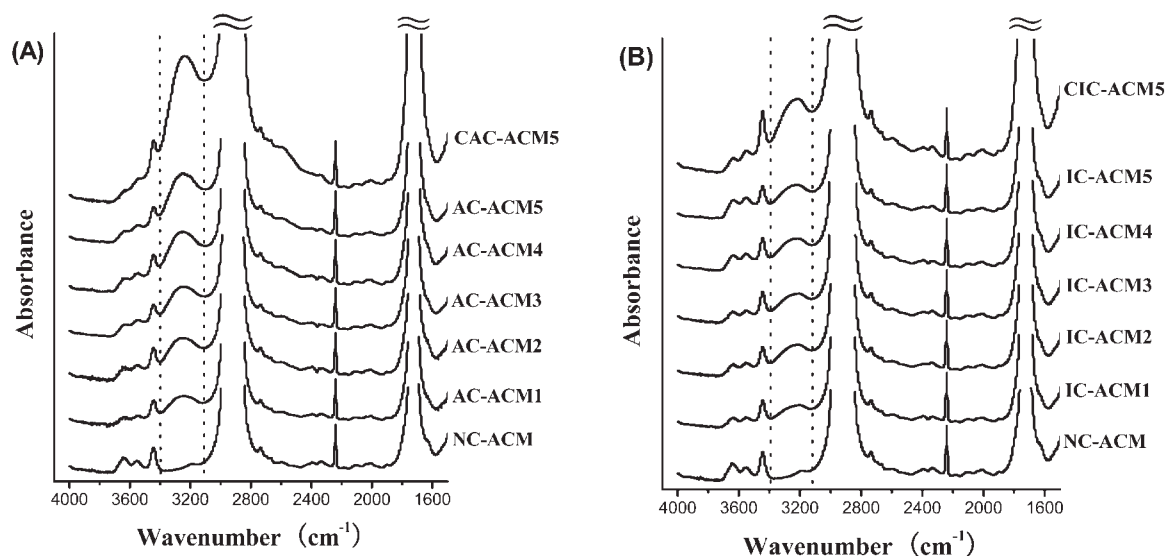
Figure 1 FTIR spectra of the polymers: (A) acrylic acid carboxylated ACM and (B) itaconic acid carboxylated ACM.

GPC analysis

Molecular weight and polydispersity index (PDI = M_w/M_n) are important parameters for rubber materials. Generally, the polymer used as rubber is expected to have a high molecular weight and a suitable PDI. According to the literature, the irradiation emulsion polymerization process can easily lead a higher molecular weight than do chemical-initiator-

induced polymerization.[24] In the present work, the same result was observed. The ACM prepared by ^{60}Co-γ-ray irradiation has a higher molecular weight and a narrower PDI relative to the ACM prepared by chemical method (Table III). The GPC traces were presented in Figure 3.

Testing of the blends

Torque rheometry

According to the literature, the polymer containing carboxyl as a cure-site could be crosslinked by diamines.[14] In this present study, the Diak #1 was used as curing agent. The curing curves are showed in Figure 4. The cure characteristic parameters are given in Table IV.

It can be seen that the IC-ACM is cured faster than that of the AC-ACM. The curing curves of IC-ACM reach a plateau in about 10 min, much faster than AC-ACM (about 1 h). As a result, the optimum cure time (t_{90}) of the AC-ACM is much longer than that of IC-ACM. This is probably caused by the different reactivity of carboxyl group in the two kinds of polymers. The pendent carboxyl groups on IC-ACM molecular chains are longer than those on AC-ACM molecular chains. Therefore, the carboxyl groups
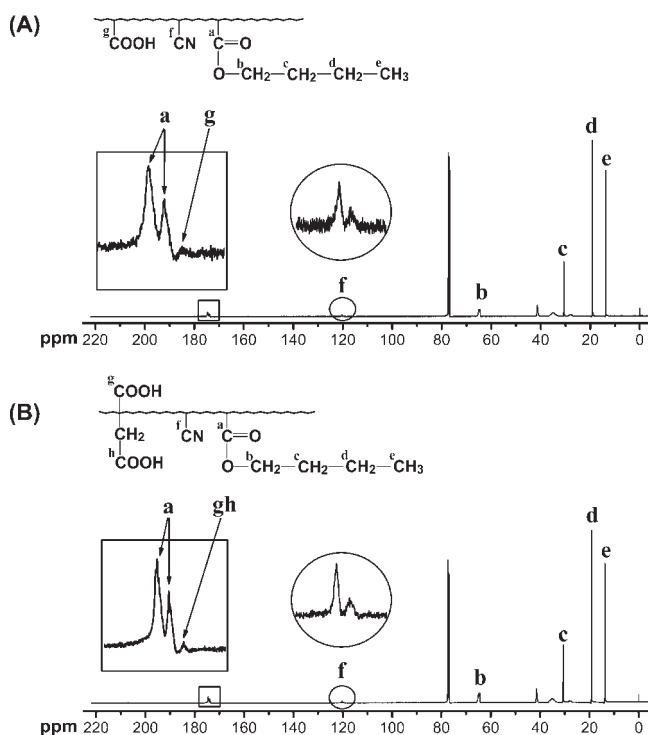

Figure 2 ^{13}C NMR spectra of the polymers: (A) AC-ACM5 and (B) IC-ACM5.

TABLE III
Values of M_n, M_w, and PDI of the Polymers

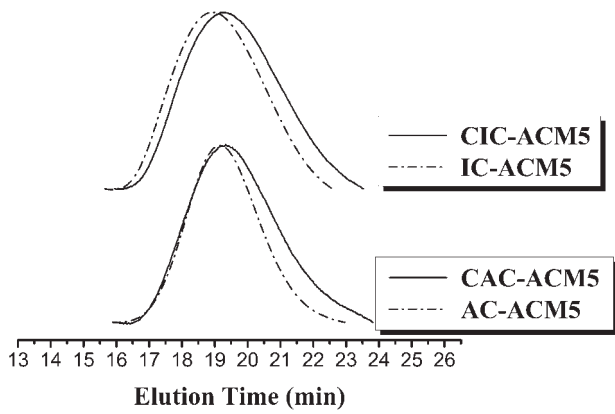| Samples	M_n (g/mol)	M_w (g/mol)	PDI
AC-ACM5	661936	822926	1.2432
CAC-ACM5	527075	735945	1.3963
IC-ACM5	687873	902382	1.3118
CIC-ACM5	543499	763035	1.4039

Figure 3 GPC traces of the polymers.

in IC-ACM have more free mobility and higher reactivity.

The effect of the carboxyl amounts on the cure characteristics of AC-ACM and IC-ACM is shown in Figure 4. With the increase of the carboxyl amounts, the crosslinking becomes fast; meanwhile, the cross-link density also increases. As a result, the t_{90} and the scorch time ($t_S{}^2$) become shorter and the maximum torque (M_H) increased.

The effect of curing agents on vulcanization could be seen from AC-ACM5B and IC-ACM5B (see Fig. 4). The torque of AC-ACM5B and IC-ACM5B remains nearly constant due to the absence of the curing agent.

The cure characteristics of the ACM prepared by $K_2S_2O_8$-induced polymerization (CAC-ACM5 and CIC-ACM5) are similar to the corresponding samples prepared by ^{60}Co-γ-ray-induced polymerization (AC-ACM5 and IC-ACM5), except that the former has the lower M_H. It could be attributed to the lower molecular weight and wider PDI of CAC-ACM5 and CIC-ACM5 compared with those of AC-ACM5 and IC-ACM5, which decreases the strength of the rubbers and lowers M_H.
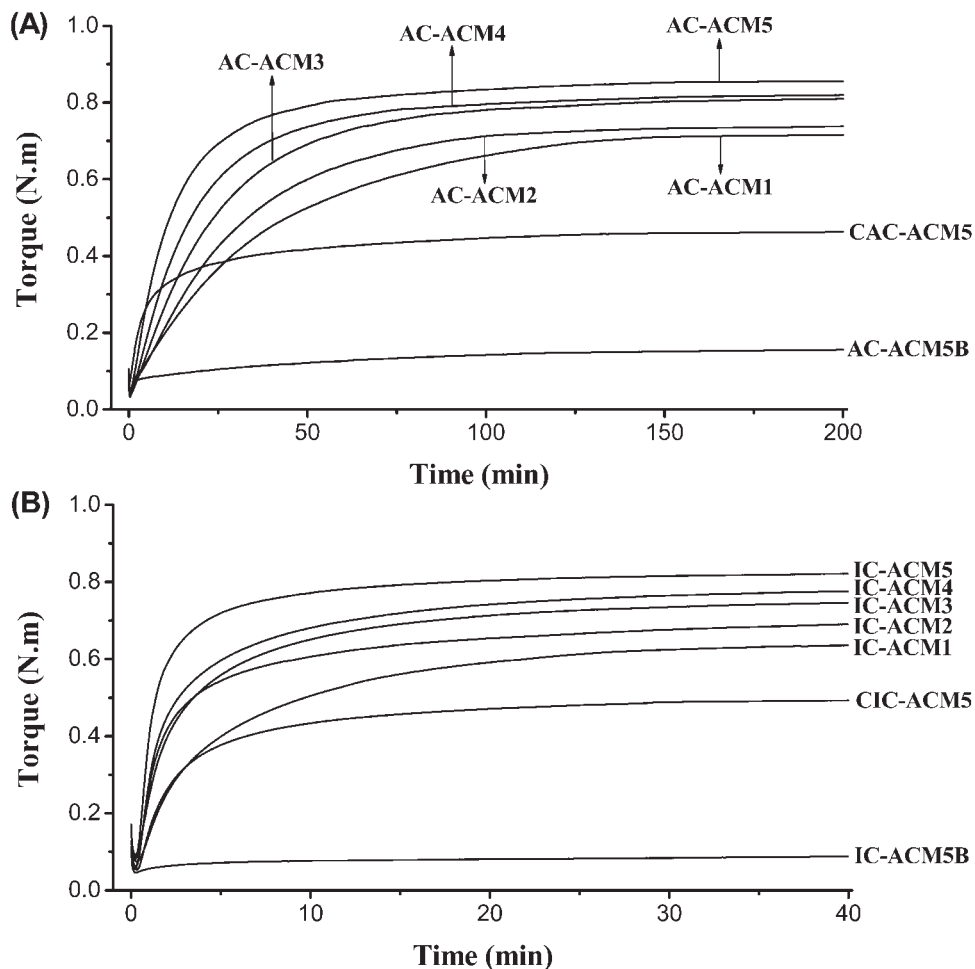

Figure 4 Curing curves of filled ACM which was composed of 100/70/2/1/1 (w/w) ACM/carbon black (N550)/stearic acid/DOTG/Diak #1: (A) acrylic acid carboxylated ACM and (B) itaconic acid carboxylated ACM. AC-ACM5B has the same composition with AC-ACM5 except the absence of Diak #1, the same situation as IC-ACM5B and IC-ACM5.

TABLE IV
Cure Characteristics of the Filled ACM

Mix no.	M_L (N · m)[a]	M_H (N · m)[b]	t_S1 (min)[c]	t_S2 (min)[c]	$t10$ (min)	$t90$ (min)
AC-ACM1	0.036	0.716	5.68	12.96	3.48	91.72
AC-ACM2	0.033	0.738	5.72	11.32	3.84	71.64
AC-ACM3	0.035	0.810	4.68	8.64	3.76	63.04
AC-ACM4	0.033	0.820	3.56	6.40	2.92	51.80
AC-ACM5	0.037	0.856	2.44	4.28	2.08	42.56
IC-ACM1	0.074	0.636	1.26	2.34	0.92	17.78
IC-ACM2	0.059	0.690	0.66	0.98	0.58	13.14
IC-ACM3	0.091	0.746	0.82	1.26	0.66	13.38
IC-ACM4	0.055	0.776	0.66	0.94	0.58	12.78
IC-ACM5	0.082	0.821	0.58	0.78	0.54	6.98
CAC-ACM5	0.062	0.463	1.76	4.72	0.80	57.08
CIC-ACM5	0.054	0.493	0.98	1.90	0.66	12.66

[a] The minimum torque.
[b] The maximum torque.
[c] The scorch time.

Gel fraction

The gel fraction was analyzed via Soxhlett extraction with acetone for 72 h. Since the blends contained the fillers (carbon black, curing agent, and accelerator), the results of gel fraction contribute to the blends, and not to the polymers.

Results of the gel fraction analysis are shown in Figure 5. AC-ACM5B and IC-ACM5B have the lowest gel fraction because these two samples do not contain curing agent and are not cured. Interestingly, the gel fraction of the samples AC-ACM5 and CAC-ACM5 are also very low. But the gel fraction of the samples IC-ACM5 and CIC-ACM5 are much higher. From the torque rheometry study, it can be found that the itaconic acid carboxylated ACM has better cure characteristics than has the acrylic acid carboxylated ACM. Herein, the gel fraction result suggests that AC-ACM5 and CAC-ACM5 were only cured to a certain degree during the vulcanization process, and it was not enough to form the complete network structure. Accordingly, the uncrosslinked polymer in AC-ACM5 and CAC-ACM5 could be extracted. However, the network structure was formed in IC-ACM5 and CIC-ACM5, so they had higher gel fraction.

Dynamic mechanical thermal analysis

Figure 6 shows the temperature dependence of loss tangent (tan δ) of the cured blends over the temperature range of −90°C to 180°C at 2 Hz. The loss tangent peaks, corresponding to glass-transition temperature, of the acrylic acid carboxylated ACM are observed at −10.5°C_{min} and 4.8°C_{max}, and at −14.1°C_{min} and −9.4°C_{max} for itaconic acid carboxylated ACM. These peaks are caused by the chain segment motions at glass-transition temperature.[25]

The peaks, corresponding to rubber-transition temperature, are observed at 140°C_{min} and 150°C_{max} for

AC-ACM, but not observed for IC-ACM. The peaks at this temperature range are caused by the relaxation of the polymer chains,[25] which can be restricted by the crosslink network structure. In AC-ACM, the crosslink network is only partially formed and the polymer chains can still move to some extent. However, such relaxation is restricted in the IC-ACM by its complete network structure, and this restriction increases with the crosslink density. As a result, from IC-ACM1 to IC-ACM5, the intensity of transition peak (the broad peak at about 140°C) decreases and disappears in IC-ACM5.

For the ACM prepared by $K_2S_2O_8$-induced polymerization, the same effects are observed. The rubber-transition peak is strong in CAC-ACM5 but not in CIC-ACM5.

Mechanical properties

It is reported that the crosslinking influences a range of elastomer properties, including modulus, hardness, toughness, tear strength, and tensile strength.[26]
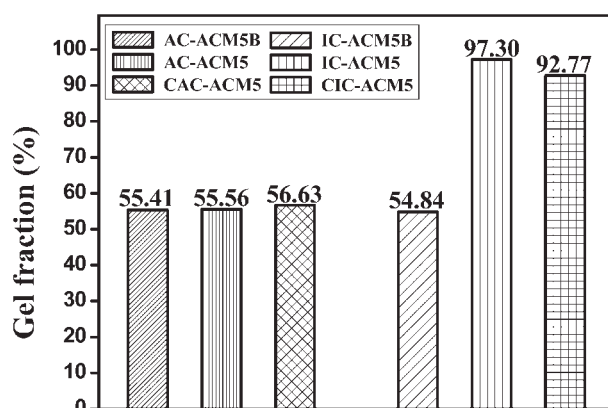

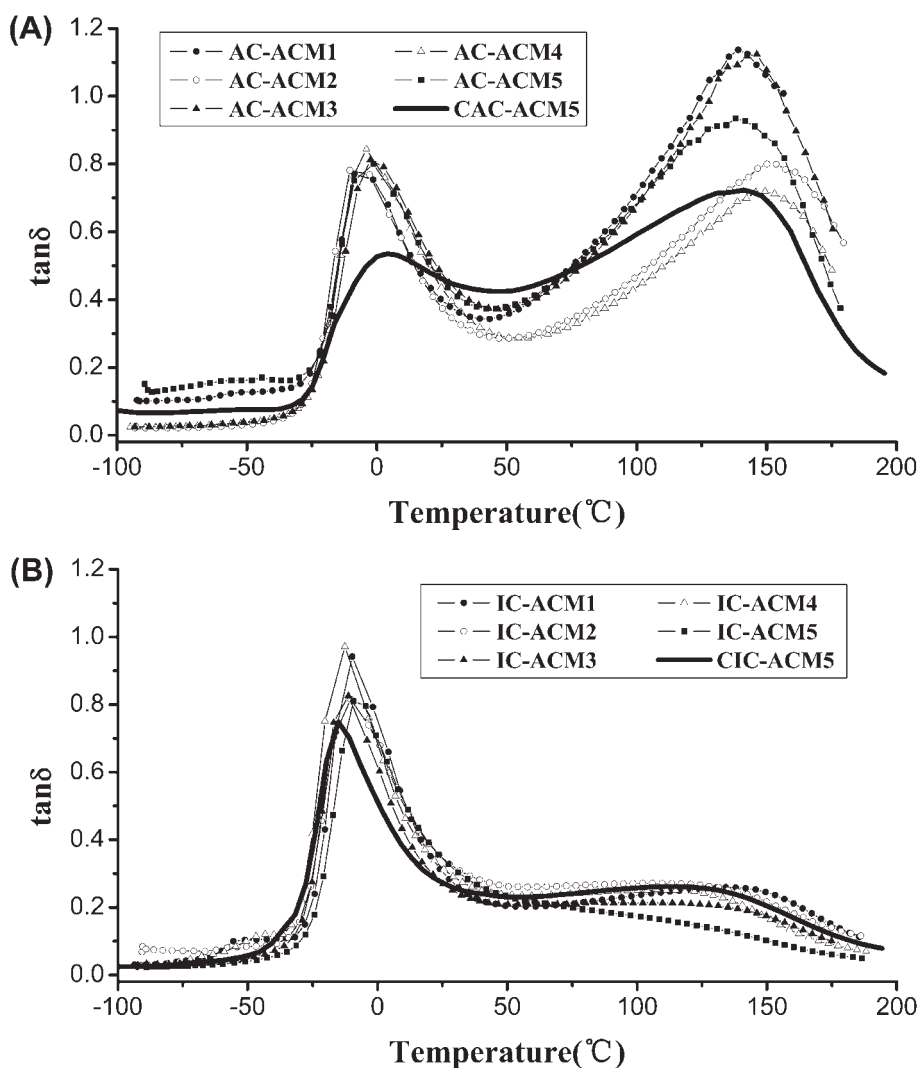**Figure 5**   Gel fraction analysis result of the cured ACM.

Figure 6 Temperature dependence of loss tangent of ACM at 2 Hz: (A) acrylic acid carboxylated ACM and (B) itaconic acid carboxylated ACM.

The modulus and hardness increase linearly with crosslink density.[27] The same influences on mechanical properties are observed in present work (see Table V). For each series, the mechanical properties are improved with the increase of the crosslink density.

TABLE V
Mechanical Properties of the Cured ACM

Mix no.	100% Modulus (Mpa)	200% Modulus (Mpa)	Maximum tensile strength (Mpa)	Strength at break (Mpa)	Hardness (Shore A)
AC-ACM1	0.7	1.0	0.9	0.3	15
AC-ACM2	1.1	1.1	1.1	0.2	25
AC-ACM3	1.2	1.1	1.2	0.1	25
AC-ACM4	1.4	1.6	1.7	0.2	27
AC-ACM5	1.6	1.9	2.1	0.5	33
IC-ACM1	2.5	5.1	7.7	7.5	46
IC-ACM2	2.8	6.3	8.7	8.7	51
IC-ACM3	3.2	7.6	9.9	9.7	52
IC-ACM4	3.5	8.9	11.2	11.1	52
IC-ACM5	3.7	10.5	14.3	14.2	56
CAC-ACM5	2.6	2.6	2.7	2.4	38
CIC-ACM5	2.9	6.4	9.3	9.3	47

The mechanical properties are very poor of AC-ACM, but significantly improved in IC-ACM. This result suggests that the network structure is an important factor for the mechanical properties. The network structure of the polymer is mostly affected by the structure of carboxyl in polymer chain. The IC-ACM has better network structure than has the AC-ACM after vulcanization process.

CAC-ACM5 contains more carboxyl groups than has AC-ACM5, so that it has higher crosslink density and better mechanical properties than has AC-ACM5. However, this property does not apply for the well-cured ACM. With less amounts of carboxyl groups, IC-ACM5 still has better mechanical properties than has CIC-ACM5. The reason is that IC-ACM5 has higher molecular weight and narrower PDI so that IC-ACM5 has a higher strength.

CONCLUSIONS

The acrylic rubbers containing different types and amounts of carboxylic monomers have been polymerized by ^{60}Co-γ-ray-induced emulsion copolymerization. The polymers have been characterized and the influence of carboxyl on cure characteristics and mechanical properties of the ACM are studied. The comparison of ACM prepared by ^{60}Co-γ-ray irradiation and by chemical method was performed. The following conclusions can be drawn from this study:

1. Due to the different copolymerization reactivity ratios of the two carboxylic monomers, the acrylic acid carboxylated ACM has higher acid value than has the corresponding itaconic acid carboxylated ACM.
2. ACM prepared by ^{60}Co-γ-ray-induced emulsion copolymerization has lower acid value, higher molecular weight, and narrower PDI than that prepared by $K_2S_2O_8$-induced emulsion copolymerization with the same ingredients.
3. For each series, at a constant level of curing agent, the increasing of carboxyl amounts can improve the maximum torque and shorten the optimum cure time (t_{90}) and scorch time ($t_S{}^2$).
4. The itaconic acid carboxylated ACM has better cure characteristics and mechanical properties than has the acrylic acid carboxylated ACM.
5. The acrylic acid carboxylated ACM prepared by $K_2S_2O_8$-induced polymerization contained more carboxyl groups than that prepared by ^{60}Co-γ-ray-induced polymerization. As a result, it has higher crosslink density and better mechanical properties. However, due to the effect of the molecular weight and the PDI, the itaconic acid carboxylated ACM prepared by ^{60}Co-γ-ray-induced polymerization has better cure characteristics and mechanical properties than that prepared by $K_2S_2O_8$-induced polymerization, though it contains less amounts of carboxyl cure-site.

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