

# Preparation and Characterization of Acrylonitrile–Styrene–Methylmethacrylate Terpolymer as a Compatibilizer for Rubber Blends

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**ABSTRACT:** Acrylonitrile-co-styrene-co-methylmethacrylate (AN-S-MMA) terpolymer was prepared by bulk and emulsifier-free emulsion polymerization techniques. The bulk and emulsion terpolymers were characterized by means of Fourier transform infrared spectroscopy,  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography, thermal gravimetric analysis, and elemental analysis. The kinetics of the terpolymerization were studied. The terpolymers were then incorporated into butadiene–acrylonitrile rubber (NBR)/ethylene propylene diene monomer rubber (EPDM) blends and into chloroprene rubber (CR)/EPDM blend. The terpolymers were then tested for potential as compatibilizers by using scanning electron microscopy and differ-

ential scanning calorimetry. The terpolymers improved the compatibility of CR/EPDM and NBR/EPDM blends. The physicochemical properties of CR/EPDM and NBR/EPDM blend vulcanizates revealed that the incorporation of terpolymers was advantageous, since they resulted in blend vulcanizates with higher 100% moduli and with more thermally stable mechanical properties than the individual rubbers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3143–3153, 2003

**Key words:** acrylonitrile–styrene–methylmethacrylate; terpolymer; compatibilizer; rubber blends; butadiene–acrylonitrile rubber; ethylene propylene diene monomer rubber; chloroprene rubber

## INTRODUCTION

The morphology of uncompatibilized blends is unstable: the dispersed phase coarsens when the melt is subjected to low shear conditions, e.g., during certain molding conditions, which has a deleterious effect on the final blend properties.<sup>1</sup> Interfacial agents are often used to compatibilize immiscible polymer blends. They are known to reduce the interfacial tension, homogenize the morphology, and improve the adhesion between phases. Terpolymer of methylmethacrylate–glycidylmethacrylate–ethylacrylate has been used as an effective compatibilizer for blends of polybutylene terephthalate (PBT) with styrene acrylonitrile copolymer.<sup>2</sup> Terpolymers of ethylene–acrylic ester–glycidylmethacrylate have been used as compatibilizers for PBT and polyolefin “PO” (80:20) blends.<sup>3</sup> Polypropylene–ethylene propylene rubber block (PP-EPR) has been added to blends of isotactic polypropylene (PP) with ethylene propylene diene terpolymer (EPT). It has been considered that it forced compatibility of the two components through chemically bonded blocks.<sup>4</sup> In this article, acrylonitrile–styrene–methylmethacrylate terpolymer was synthesized by bulk and emulsifier-free emulsion polymerization techniques.<sup>5–8</sup> The effect of the prepared terpolymer on the compatibility

of chloroprene rubber (CR)/ethylene propylene diene monomer rubber (EPDM) and butadiene–acrylonitrile rubber (NBR)/EPDM blends was investigated. The physicochemical properties of those blends were examined before and after thermal aging.

## EXPERIMENTAL

### Materials

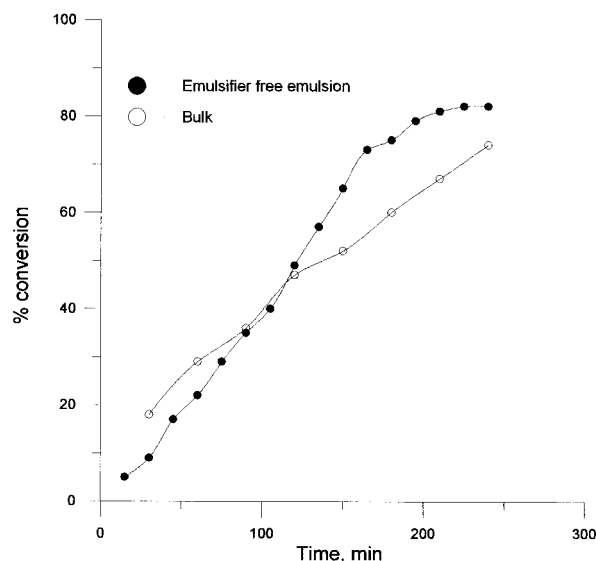
Acrylonitrile, styrene, and methylmethacrylate monomers (products of Merck, Darmstadt, Germany) were purified by being passed over active alumina (Fluka, Buchs, Switzerland). Dibenzoyl peroxide (Merck) was reprecipitated from chloroform. The raw rubbers used were as follows: (1) Vestalon 6505 (EPDM), a product of Esso Chimie (Toronto, Canada); (2) Krynac<sup>®</sup> 3345 (NBR), of 33% acrylonitrile content and 45 Mooney viscosity (ML 1+4/100°C), a product of Bayer Chemical Company, Leverkusen, Germany; and (3) Butachlor MC10 (CR), of 46 Mooney viscosity (ML 1+4/100°C) and of very low crystallization rate, a product of Enichem Spa, Milan, Italy.

### Techniques

Emulsifier-free emulsion terpolymerization of acrylonitrile, styrene, and methylmethacrylate (AN-S-MMA)

The emulsifier-free emulsion terpolymerization of AN-S-MMA was conducted in a 250-mL round-bot-

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**Figure 1** Percent conversion vs time of emulsifier-free emulsion terpolymerization (at 50°C) and bulk terpolymerization (at 65°C) of AN-S-MMA.

tomed three-necked flask fitted with a mechanical stirrer, nitrogen inlet, and a condenser. AN (10 mL), S (5 mL), and MMA (5 mL) were terpolymerized in aqueous medium (100 mL distilled water) at a stirring rate of 300 rpm. using ammonium persulfate (1.0%, by weight, of the aqueous phase) as the initiator. The polymerization reaction lasted for 240 min at 50°C plus another 60 min at 65°C for complete polymerization. The resultant (AN-S-MMA) emulsion was precipitated in methanol, washed several times with distilled water, and finally dried at 50°C for 36 h. The conversion to polymer was calculated gravimetrically.<sup>9</sup>

#### Bulk terpolymerization of AN, S, and MMA

The bulk terpolymerization of AN (100 mL), S (50 mL), and MMA (50 mL) was carried out in a nitrogen flushed 500 mL round-bottomed flask without any

stirring at 65°C using dibenzoyl peroxide (0.1%, by weight of the monomer). The polymerization reaction lasted 240 min, after which a highly viscous solution resulted.

#### Purification

The terpolymerization products, obtained using the bulk and the emulsifier-free emulsion polymerization techniques, were precipitated in methanol from chloroform solution, dried at 40°C for 24 h and then subjected to a Soxhlet extraction of homopolymers with acetone to constant weight (for 36 h to remove the homopolymers and the remaining impurities).

#### Solvolysis of the AN-S-MMA terpolymers

The terpolymers obtained from the bulk and the emulsifier-free emulsion polymerization techniques were subjected to a large series of low polarity to high polarity solvents. It was found that hot chloroform and dimethyl sulfoxide were the most suitable solvents for the AN-S-MMA terpolymers obtained with the bulk and the emulsifier-free emulsion polymerization techniques, respectively, at 40°C.

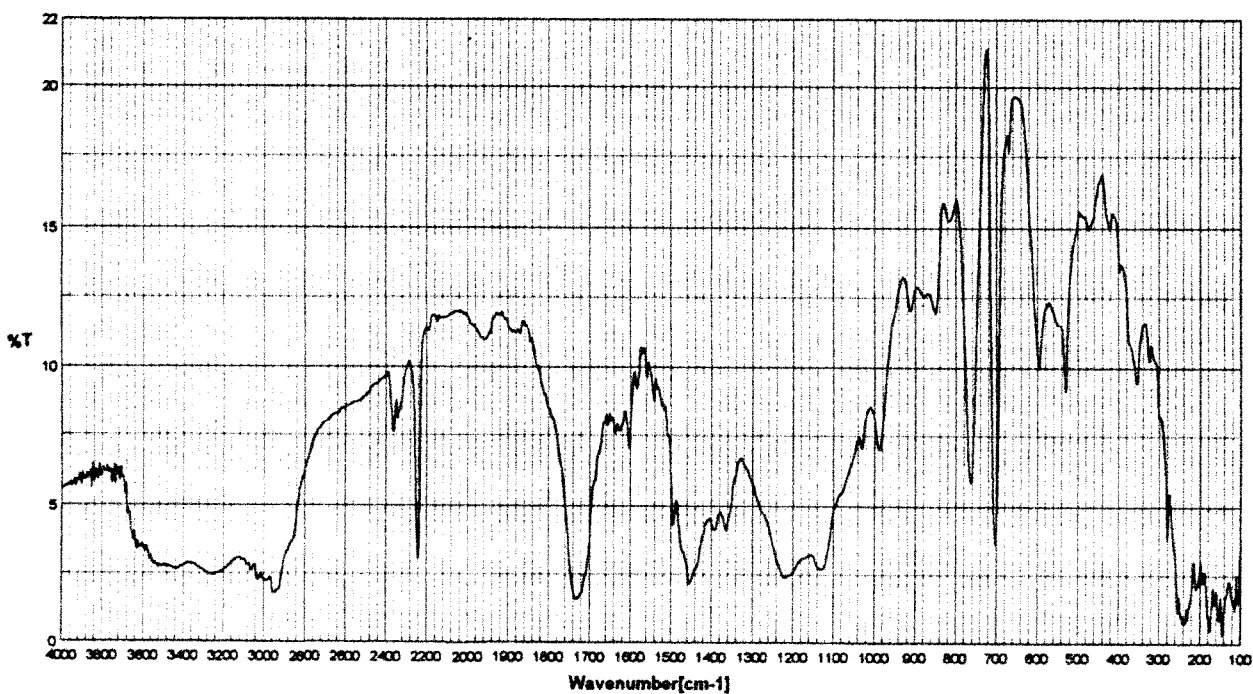
#### Gel permeation chromatography (GPC)

Number-average molecular weights ( $M_n$ ) and polydispersity ( $M_w/M_n$ ) were determined with a Waters GPC instrument (Waters Millipore Corporation, Milford, MA, USA) equipped with a series of five Styragel columns (100, 500, 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup> Å). Those columns were calibrated with a narrow molecular weight distribution (PIB) linear standards. The GPC instrument was connected to a Waters 410 differential refractometer (DRI) and Waters 2478 λ dual absorbance (UV) detectors.  $M_n$  and  $M_w/M_n$  values were determined with the DRI detector.

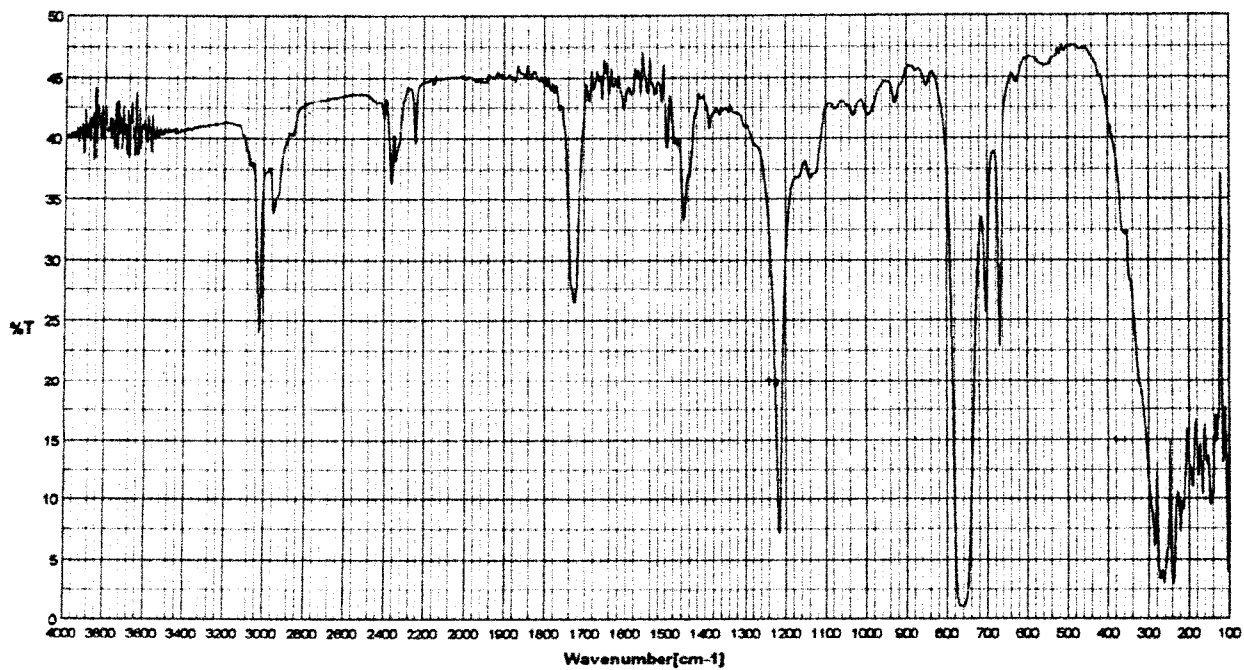
**TABLE I**  
Elucidation of AN-S-MMA Terpolymer Composition

Monomer		Elemental analysis (N %)	FT IR bands (cm <sup>-1</sup> )	<sup>13</sup> C-NMR bands (ppm)
AN	Bulk <sup>a</sup>	15.21	2240 1450	120
	Emulsion <sup>a</sup>	11.06	2240 1450	120
S	Bulk		1605 3027	140 1.8
	Emulsion		2945 1450	140
MMA	Bulk		1720 1029	1.5 1.8
	Emulsion		1720 1029	1.5 1.8

<sup>a</sup> Bulk and emulsion refer to the methods by which the AN-S-MMA terpolymer was prepared.

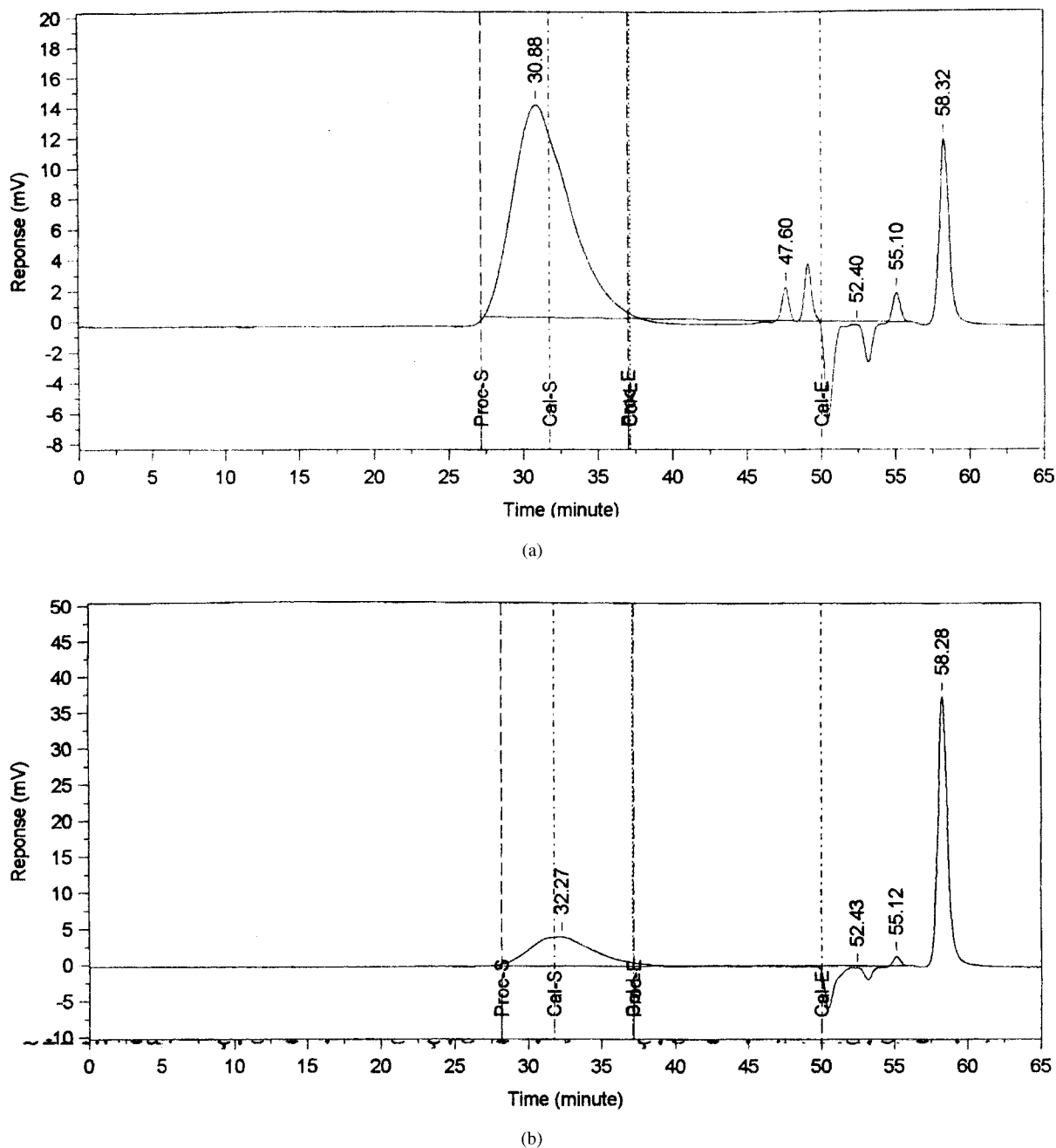


(a)



(b)

Figure 2 FTIR spectra of AN-S-MMA terpolymer prepared by different techniques: (a) emulsifier-free emulsion polymerization; (b) bulk polymerization.



**Figure 3** GPC traces of AN-S-MMA terpolymer polymerized with different techniques: (a) bulk polymerization; (b) emulsifier-free emulsion polymerization.

### $^{13}\text{C}$ nuclear magnetic resonance (NMR) spectroscopy

The terpolymer functional group characteristics were determined with  $^{13}\text{C}$ -NMR spectroscopy (Varian Gemini-300 MHz, Varian Associates, Palo, Alto, CA, USA) using  $\text{CDCl}_3$  as solvent for a 15 h run time.

### Mixing, vulcanization, and testing of rubber

The rubbers were mixed with curatives and other compounding ingredients on a two-roll mill. The base

recipe contained 5 phr zinc oxide, 1.5 phr stearic acid, high abrasion furnace 40 phr black (HAF), 5 phr processing oil, 2 phr sulfur, and 1 phr N-cyclohexyl 2-benzothiazole sulfenamide (CBS). The rheometric characteristics<sup>10</sup> were assessed with a Monsanto oscillating disk rheometer (R-100) at  $152 \pm 1^\circ\text{C}$ . The blends were then cured in a hydraulic press at the same temperature. The physicomechanical properties were determined with a Zwick-1101 tensile tester.<sup>11</sup> Thermal aging<sup>12</sup> was carried out in an air circulating electric oven at  $90^\circ\text{C}$ .

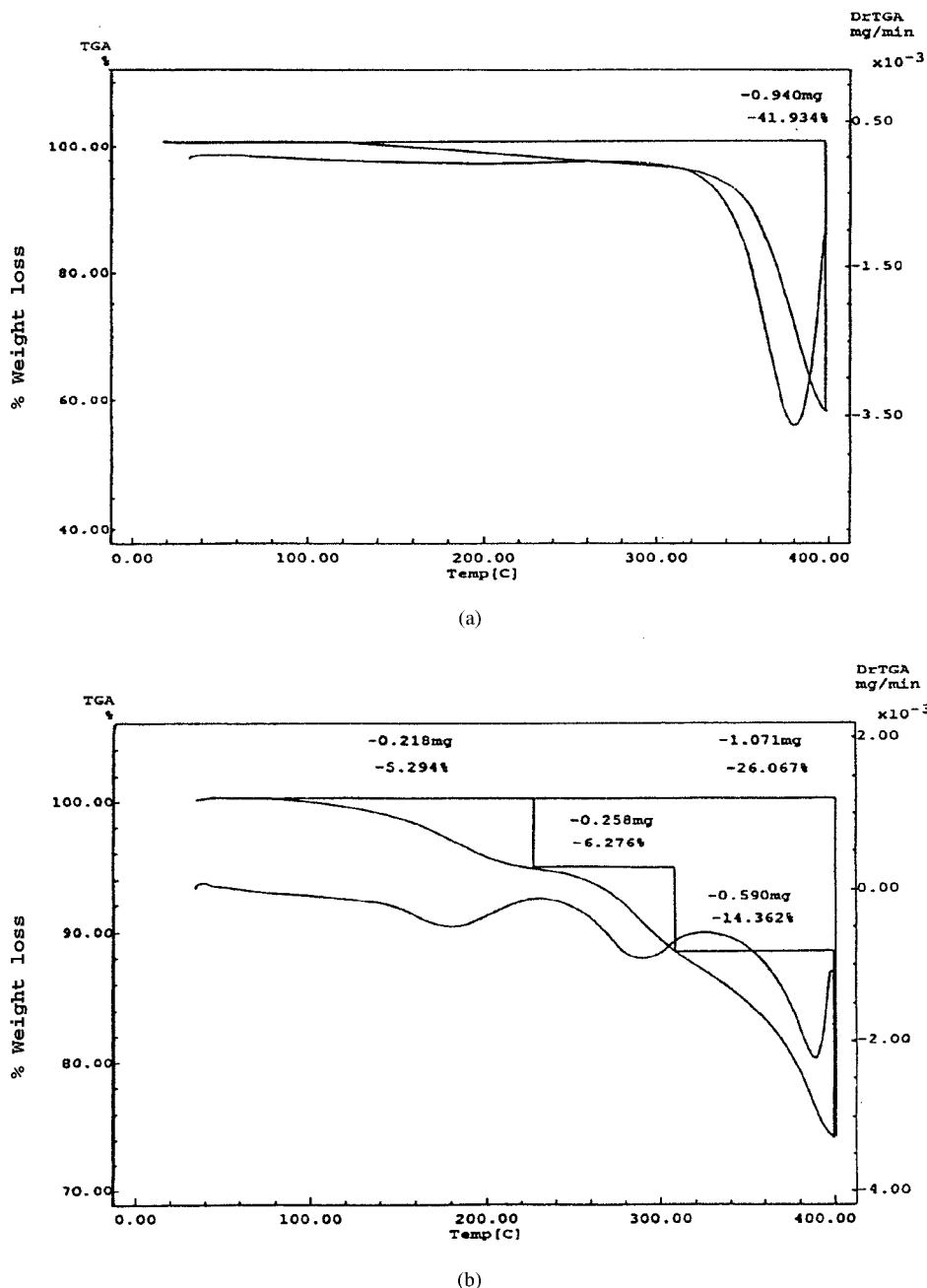


Figure 4 TGA thermographs of AN-S-MMA terpolymer polymerized with different techniques: (a) bulk polymerization; (b) emulsifier-free emulsion polymerization.

## RESULTS AND DISCUSSION

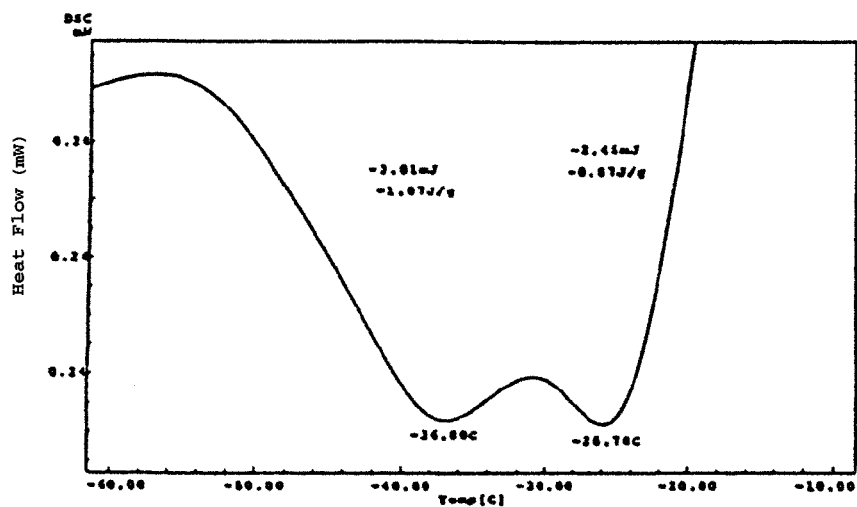
### Kinetics of terpolymerization of AN-S-MMA using bulk and emulsifier-free emulsion polymerization techniques

Trials of bulk and emulsifier-free emulsion terpolymerization of AN-S-MMA were carried out at 65 and 50°C, respectively, for different time intervals of 30, 60, 90, ..., 240 min. The conversion to polymer was determined gravimetrically. Figure 1 shows, in the case of emulsifier-free emulsion terpolymerization, that the conversion time curve was characterized by a short induction period (~20 min), followed by a con-

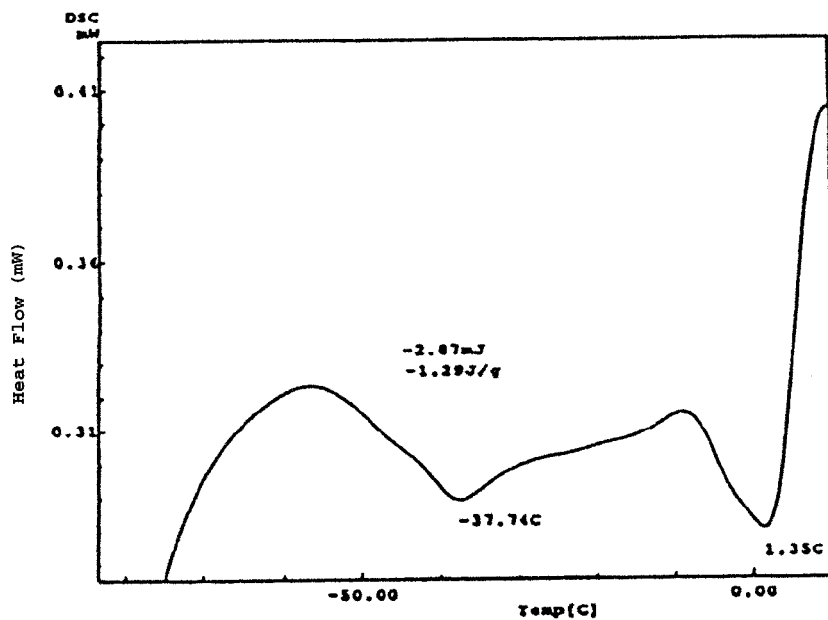
stant rate of polymerization, approaching a maximum beyond which the rate of emulsion terpolymerization of AN, S, and MMA went to zero. In case of bulk terpolymerization, the terpolymer (AN-S-MMA) conversion to 73% was the highest obtainable conversion at 65°C, due to gelation of the polymerization system.

### Elucidation of AN-S-MMA terpolymer composition

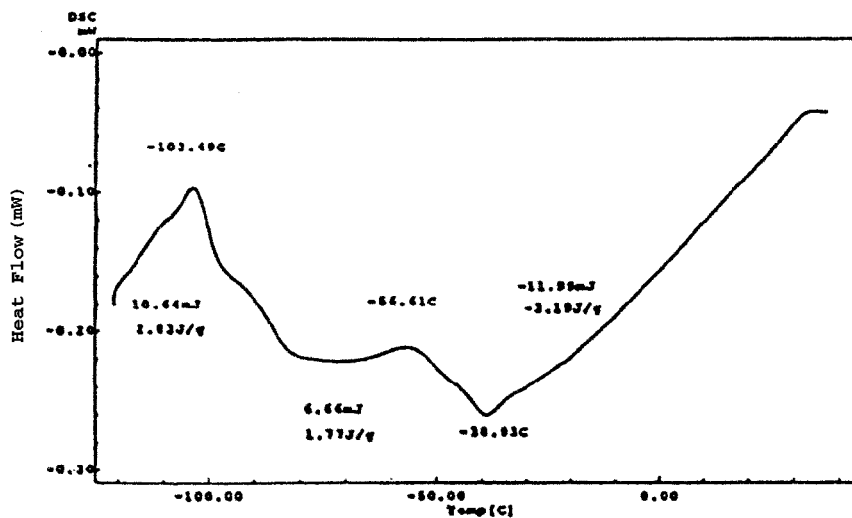
Elucidation of the AN-S-MMA terpolymer composition, prepared by bulk or emulsifier-free emulsion



(a)

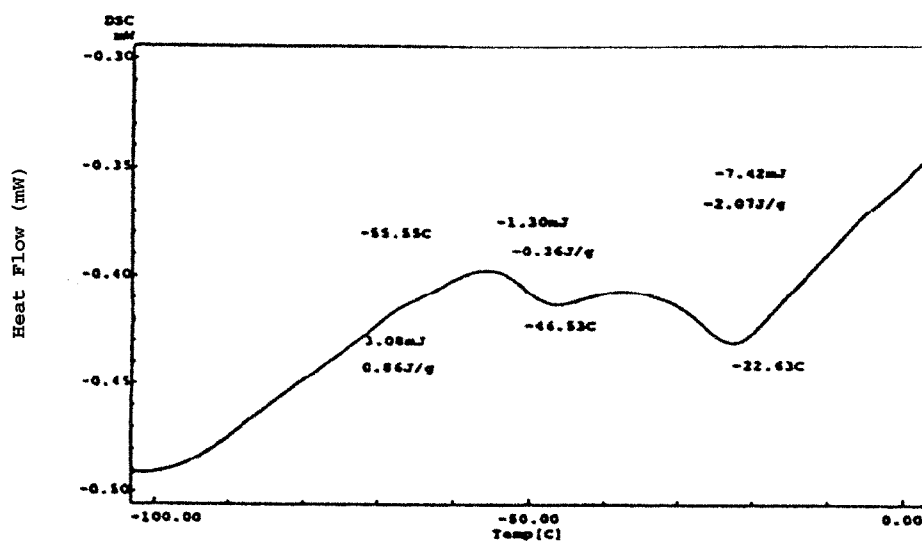


(b)

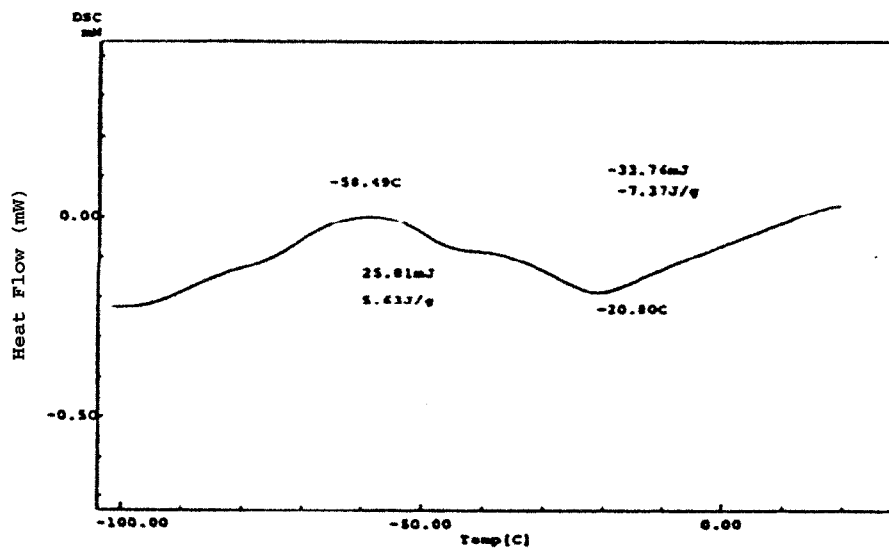


(c)

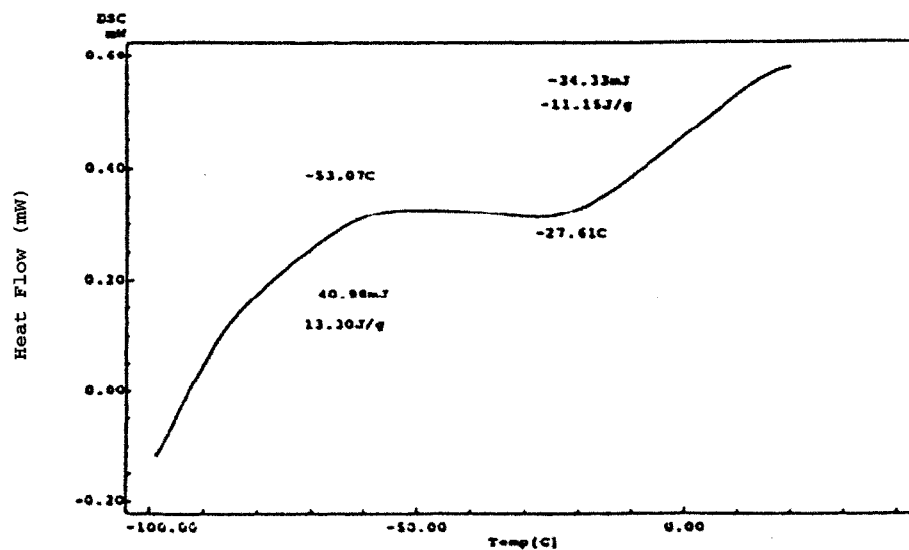
Figure 5 DSC thermographs of CR/EPDM blends with and without compatibilizer: (a) without; (b) bulk AN-S-MMA; (c) emulsifier-free emulsion AN-S-MMA.



(a)

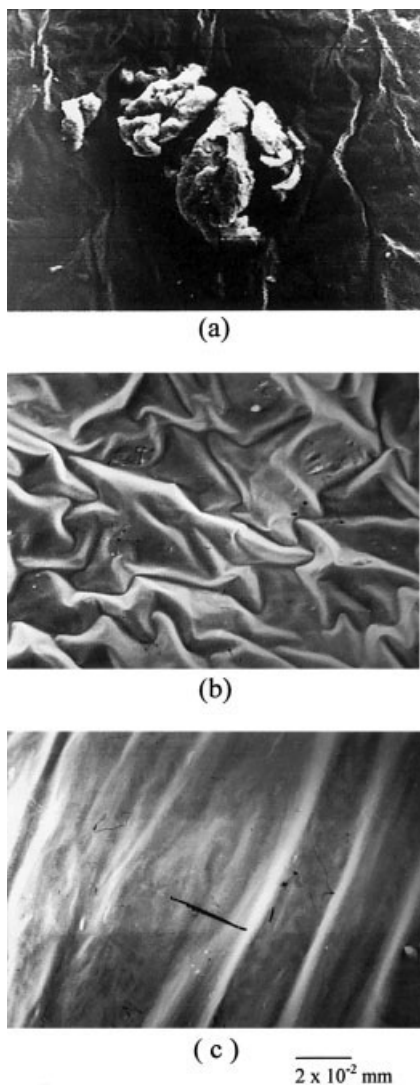


(b)



(c)

**Figure 6** DSC thermographs of NBR/EPDM blends with and without compatibilizer: (a) without; (b) bulk AN-S-MMA; (c) emulsifier-free emulsion AN-S-MMA.



**Figure 7** SEM micrographs of CR/EPDM with and without compatibilizer: (a) without; (b) bulk AN-S-MMA; and (c) emulsion AN-S-MMA.

polymerization of AN, S, and MMA, was confirmed by elemental analysis and Fourier transform infrared (FTIR) and  $^{13}\text{C}$ -NMR spectroscopy. The confirmation of the characteristic functional groups of AN ( $-\text{C}\equiv\text{N}$ ), S ( $-\text{C}_6\text{H}_5$ ), and MMA ( $=\text{C}=\text{O}$ ) is shown in Table I and Figures 2(a,b) and 3(a,b).

#### Gel permeation chromatography

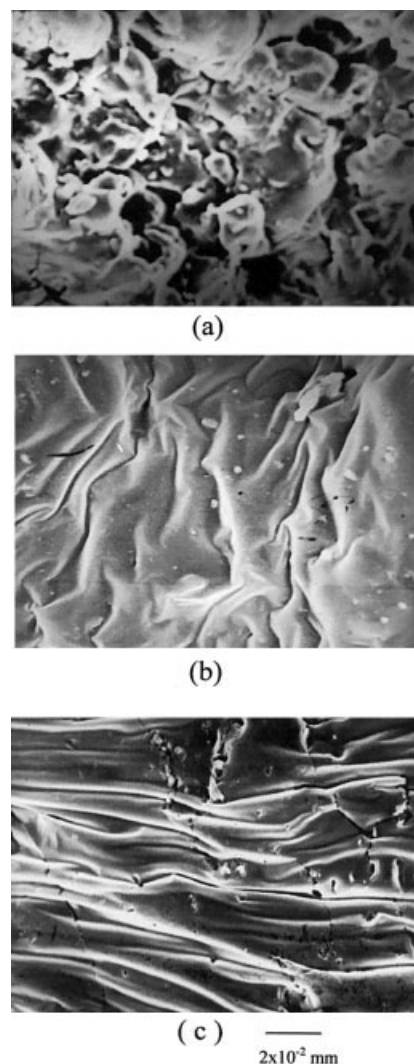
Figure 3(a,b) shows the GPC traces of the AN-S-MMA terpolymer. The refractive index (RI) trace of the bulk polymerized sample shows a major peak associated with the AN-S-MMA and indicates a number average molecular weight ( $M_n$ ) of 50 K and polydispersity index ( $M_w/M_n$ ) = 1.7. The RI trace of the emulsion polymerized sample also shows a major peak associated with the AN-S-MMA and indicates  $M_n$  of 35 K and  $M_w/M_n$  = 1.75. The RI traces indicate the formation of monomodal AN-S-MMA terpolymer.

#### Thermal gravimetric analysis (TGA) of the AN-S-MMA terpolymer

Figures 4(a) and 4(b) show the TGA traces of AN-S-MMA terpolymer prepared by bulk and emulsion terpolymerizations. The terpolymer prepared by the emulsion polymerization technique loses 5.3% of its original weight at 180°C and 6.3% at 240°C. The bulk prepared terpolymer shows a smooth thermal degradation trace up to 300°C, although it softens at 100°C. The thermal behavior variation of the two AN-S-MMA types is attributed to the method of preparation (bulk or emulsion terpolymerization) that affects the molecular weight and crystallinity of the AN-S-MMA terpolymers obtained.

#### Compatibility of CR/EPDM and NBR/EPDM blends

CR/EPDM, as well as NBR/EPDM rubber blends, were mixed with and without bulk or emulsion AN-



**Figure 8** SEM micrographs of NBR/EPDM with and without compatibilizers: (a) without; (b) bulk AN-S-MMA; (c) emulsion AN-S-MMA.



TABLE II  
Formulations, Rheometric Characteristics, and Physico mechanical Properties of CR/EPDM and NBR/EPDM Blends with and Without Bulk or Emulsion AN-S-MMA Terpolymer

	S1	S2	S3	S4	S5	S6	S7	S8	S9
Ingredients (phr)									
CR	100	50	50	50	0	0	0	0	0
EPDM	0	50	50	50	100	50	50	50	0
NBR	0	0	0	0	0	50	50	50	100
Bulk AN-S-MMA	0	0	10	0	0	0	10	0	0
Emulsion AN-S-MMA	0	0	0	10	0	0	0	10	0
Rheometric characteristics at 152°C									
Maximum torque (dNm)	96	78	78	78	53	63	67	62	91
Minimum torque (dNm)	6	8	10	10	6.5	8	8	8	7
Cure time ( $t_{c90}$ ) (min)	38	48	48	48	46.5	8	17	12.5	18
Scorch time ( $ts_2$ ) (min)	5	5.5	4.5	4	2	3.2	3.2	3.2	3.7
Cure rate index ( $\text{min}^{-1}$ )	3	2.4	2.3	2.3	2.3	20.8	7.3	10.8	7
Physico mechanical properties									
Tensile strength (MPa)	6.6	7.6	7	7.9	10.3	8.6	6.2	6	9.2
100% modulus (MPa)	1.9	3	3.5	3.8	1.3	2.2	2.5	2.6	1.8
Elongation at break (%)	270	210	200	205	380	395	300	300	395

S-MMA terpolymer (the compatibilizer) using a Bra-bender plasticorder at 140°C and 40 rpm for 3 min. Each blend was then masticated on a laboratory two-roll mill for 2 min at 80°C. The compatibility of those blends was examined with differential scanning calorimetry (DSC). Also, the morphology of rubber blends were examined with scanning electron microscopy (SEM).

#### Differential scanning calorimetry

Figure 5(a) shows the DSC thermograph without using any compatibilizer for the CR/EPDM blend. The glass transition temperatures ( $T_g$ ) of CR and EPDM appeared at -26 and -37°C, respectively. The  $T_g$  of CR disappeared, upon using bulk or emulsion AN-S-MMA terpolymer as a compatibilizer, and there was one endothermic peak for the blend, which appeared at -38 or -39°C, respectively [Figs. 5(b) and 5(c)]. Figure 6(a) shows the DSC thermograph, without using any compatibilizer, of the NBR/EPDM blend. The  $T_g$ s of NBR and EPDM appeared at -23 and -47°C respectively. However, the  $T_g$ s of the NBR/EPDM blend, compatibilized with either bulk or emulsion AN-S-MMA terpolymer, appeared at -21 and -28°C, respectively [Figs. 6(b) and 6(c)]. The results obtained from the DSC study indicate that the AN-S-MMA terpolymer prepared either by bulk or emulsifier-free emulsion polymerization, was effective compatibilizer for CR/EPDM and NBR/EPDM rubber blends.

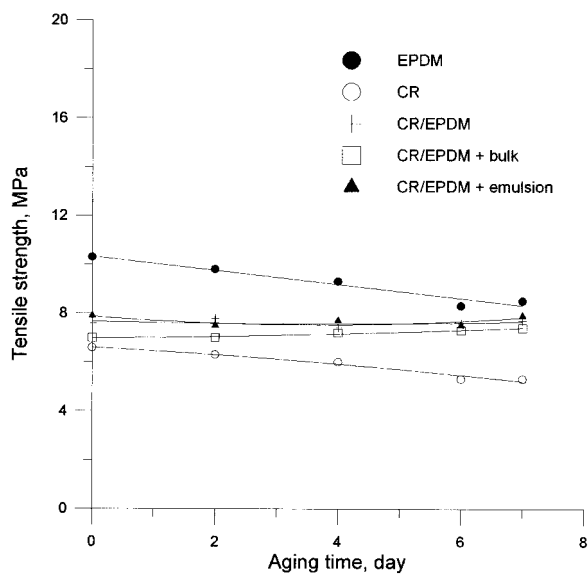
#### Scanning electron microscopy

SEM was also used to examine the compatibility of the blends. EPDM domains were formed and separated from the continuous phase (CR) in the absence of a compatibilizer, forming an incompatible blend [Fig.

7(a)]. However, using bulk or emulsion AN-S-MMA terpolymer resulted in compatible CR/EPDM blends [Figs. 7(b) and 7(c)], where only one phase existed. Figures 8(a-c) indicate that the terpolymer was also an effective compatibilizer and improved the morphology of the NBR/EPDM blends. Those results confirmed the results obtained with DSC.

#### Rheological and mechanical properties of CR/EPDM and NBR/EPDM rubber blends

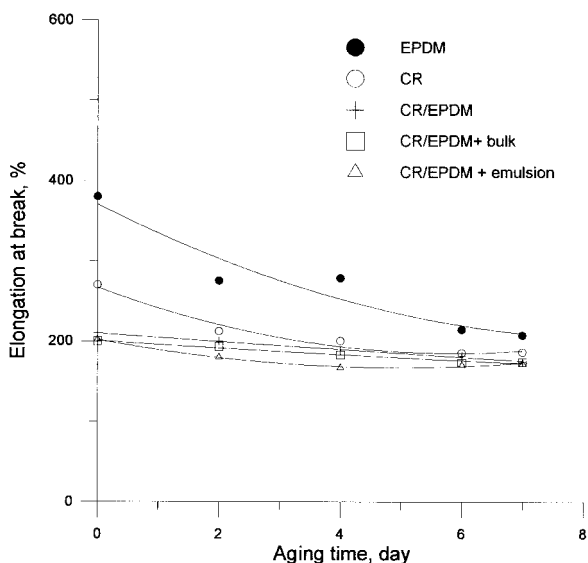
CR/EPDM and NBR/EPDM rubber blends and other compounding ingredients were mixed, with and without bulk or emulsion AN-S-MMA terpolymer, on a two-roll mill and then vulcanized in a hydraulic press at  $152 \pm 1^\circ\text{C}$  for their cure times. The formulations, rheometric characteristics and physicochemical properties of the blends and their vulcanizates are listed in Table II. From Table II, it is evident that blending of CR and EPDM rubbers resulted in a blend (S2) with maximum torque of medium value, but with minimum torque of higher value than those of the individual rubbers (S1 and S5). Addition of bulk or emulsion AN-S-MMA terpolymer to that blend resulted in an increase in the minimum torque (S3 and S4). This can be attributed to the increase of plasticity of the blend. The blending of CR with EPDM increased and improved the scorch time of EPDM. CR/EPDM blends, with and without the terpolymer, possessed medium tensile strength, higher 100% moduli, and lower values of elongation at break, than those values of the individual rubbers. On the other hand, the blending of NBR with EPDM resulted in blends (S6, S7, and S8) with short cure times (8, 17, and 12.5 min), lower tensile strengths, and higher moduli than those values of the individual rubbers. The rubber mixes under investigation were then subjected to thermal aging at 90°C. Figures 9 and 10 show that the



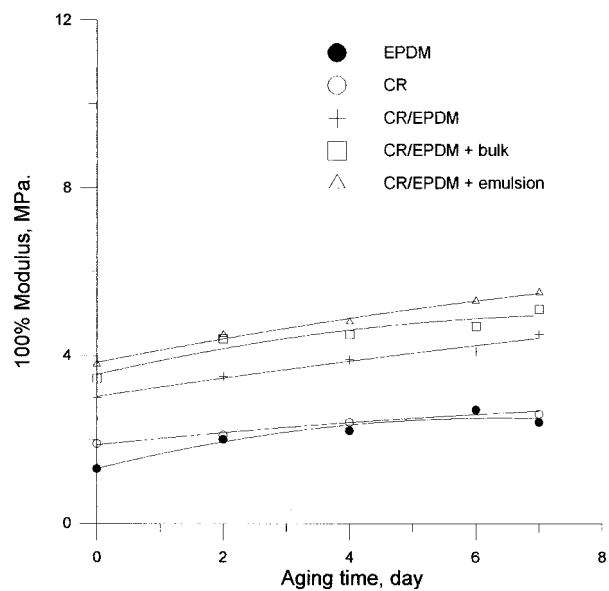
**Figure 9** Tensile strength vs aging time of CR/EPDM vulcanizates with and without bulk and emulsion AN-S-MMA.

tensile strength and elongation at break of EPDM and CR individual rubbers decreased as the aging time increased. However, the CR/EPDM blend vulcanizates, compatibilized with bulk or emulsion AN-S-MMA terpolymer, showed thermally stable tensile strength and elongation at break. Figure 11 illustrates that the blends compatibilized with bulk or emulsion AN-S-MMA terpolymer possessed higher moduli than those of individual rubbers throughout the aging periods. This can be attributed to the effective compatibilizer that, in turn, enhanced the co-curing of the individual rubbers.

Tensile strength of the NBR/EPDM blends compatibilized with bulk or emulsion terpolymer was stable

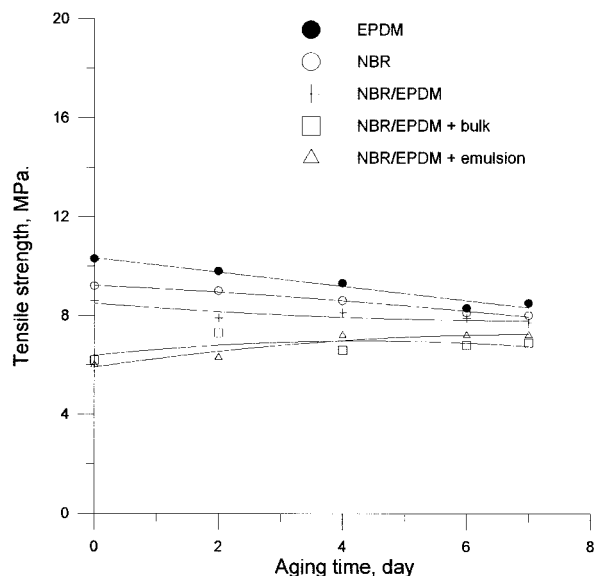


**Figure 10** Elongation at break vs aging time of CR/EPDM vulcanizates with and without bulk and emulsion AN-S-MMA.



**Figure 11** One hundred percent modulus vs aging time of CR/EPDM vulcanizates with and without bulk and emulsion AN-S-MMA.

against thermal aging (Fig. 12). The % elongation at break (Fig. 13) of the individual rubbers, and that of the uncompatibilized blend, decreased with the thermal aging time. However, the compatibilized NBR/EPDM blends possessed thermally stable elongation at break. On the other hand, the compatibilized blends possessed the highest 100% moduli (Fig. 14) throughout the aging periods, indicating that the terpolymer used enhanced the co-curing of NBR and EPDM. Thus, the results obtained revealed that AN-S-MMA terpolymer, prepared either by the bulk or the emul-

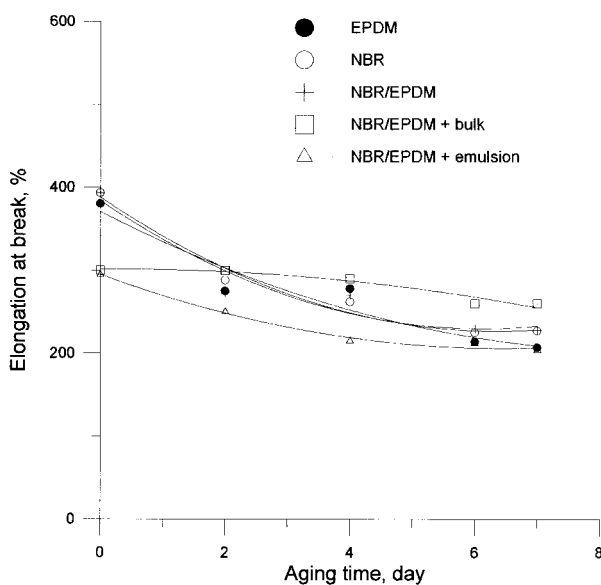


**Figure 12** Tensile strength vs aging time of NBR/EPDM vulcanizates with and without bulk and emulsion AN-S-MMA.

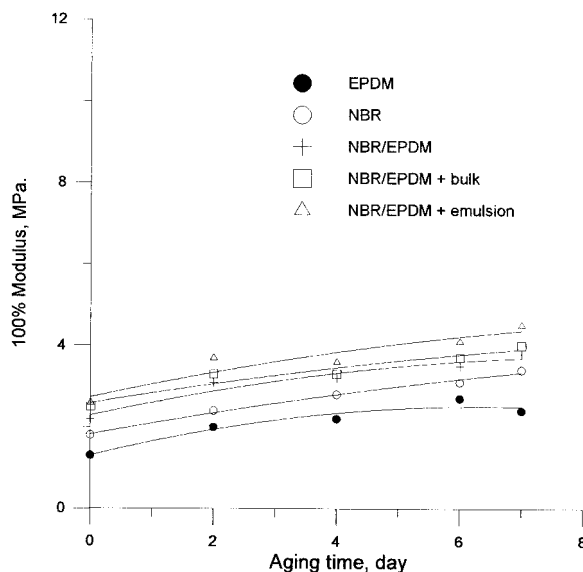
sion polymerization techniques, was an effective compatibilizer for NBR/EPDM blend.

### CONCLUSIONS

1. The % conversion to AN-S-MMA terpolymer prepared with the emulsifier-free emulsion terpolymerization at 50°C, reached a maximum value (80%) after 200 min.
2. The % conversion to AN-S-MMA terpolymer prepared with the bulk terpolymerization at 65°C reached 73% after 240 min.
3. The RI traces of the two AN-S-MMA types indicate the formation of monomodal terpolymer.
4. Bulk and emulsion polymerized AN-S-MMA terpolymers were effective compatibilizers for CR/EPDM and NBR/EPDM blends since they improved the morphology of the blends, as shown by the scanning electron micrographs, and because of the one peak for the compatibilized blend that appeared in the DSC thermographs.
5. AN-S-MMA terpolymers enhanced the co-curing of CR with EPDM and NBR with EPDM,



**Figure 13** Elongation at break vs aging time of NBR/EPDM vulcanizates with and without bulk and emulsion AN-S-MMA.



**Figure 14** Figure 14 One hundred percent modulus vs aging time of NBR/EPDM vulcanizates with and without bulk and emulsion AN-S-MMA.

since the blends possessed higher 100% moduli than the individual rubbers, indicative of effective compatibility.

6. AN-S-MMA terpolymers were advantageous because of the production of thermally stable CR/EPDM and NBR/EPDM compatibilized rubber blends.

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