

Synthesis and Characterization of Methacrylic Acid and Butyl Acrylate Grafted onto Ethylene-Propylene-Diene Terpolymer

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A multi-component polymer of methacrylic acid (MAA) and butyl acrylate (BA) grafted onto ethylene-propylene-diene (EPDM) terpolymer was synthesized in toluene using benzoyl peroxide (BPO) as initiator. The effect of EPDM/MAA-BA ratio and MAA/BA ratio on the grafting ratio of polymerization was investigated. The products were characterized by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), surface energy, inherent viscosity, and atomic force microscopy (AFM). The results showed that the MAA and BA monomers were successfully grafted onto EPDM. Furthermore, after being grafted, the polarity of the surface of the EPDM-g-MAA-BA increased with increasing grafting ratio, and the morphology of its surface became more smooth.

Keywords butyl acrylate, ethylene-propylene-diene terpolymer, grafting ratio, methacrylic acid, morphology, polarity

Introduction

In recent years, the modification of polymers has received much attention. Among the methods of modification, grafting is one of the most important methods to improve their physicochemical properties.^[1] In particular, the grafting reaction of polar groups onto nonpolar polymers is of great application.^[2,3] Ethylene propylene diene terpolymer (EPDM) is a typical nonpolar rubber. EPDM displays many advantageous features, such as low cost, high thermal decomposition temperature, high specific heat, low brittle temperature, resistance to ozone, and favorable mechanical properties.^[4] It is widely used in different applications, such as waterproof coatings, rubber contact switches, floor heating, electromagnetic interference shielding, various electronic and electrical applications, sidewalls of tires, wires coating, sporting goods, outdoor electrical insulator, and in a variety of automotive applications space^[5–7] due to its saturated hydrocarbon backbone with the presence of double bonds in the side chains.^[8] However, it cannot be used in some

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products due to its nonpolar surface.^[9] Therefore, grafting some polar groups onto EPDM can improve the compatibility between EPDM and other materials to enhance the performance of composite materials.^[10–14]

In recent years, using different organic peroxide systems, grafting of polar groups, such as styrene, acrylonitrile, maleic anhydride, 2-dimethylamino ethylmethacrylate (DMAEMA), tris(2-methoxyethoxy)vinylsilane (TMEVS), polystyrene, poly(methylmethacrylate) (PMMA) and vinyloxyaminosilane, to the EPDM rubber backbone to functionalize the polymer has been studied by various researchers.^[15–27] Grafting of methyl methacrylate (MMA) and styrene (St) onto EPDM has been carried out using solution polymerization to enhance its weatherability, yellow discoloration, and ageing property.^[22] Styrene–EPDM–acrylonitrile (AES)/SAN blends were synthesized for their use as an effective toughening agent for SAN.^[23] Grafting of vinyltriethoxysilane (VTES) onto EPDM/LLDPE blends has been reported for engineering and ablative applications; they enhanced the dynamic vulcanization to withstand high temperature.^[24,25] Maleic anhydride was grafted onto EPDM using a grafting copolymerization method. Then organic/inorganic composite coatings with varied infrared emissivity were obtained by using either EPDM or EPDM-g-MAH as adhesive and Cu powder as pigment.^[26] EPDM-g-SAN with SAN resin, called the engineering plastics AES, has excellent properties.^[27]

In the present work, we have synthesized EPDM-g-MAA-BA multi-polymers using benzoyl peroxide as a redox initiator in toluene. The optimum reaction conditions for grafting were evaluated by varying the concentrations of monomer and the ratio of EPDM/MAA-BA. Finally, the copolymers were systematically analyzed.

Experimental

Materials and Synthesis

EPDM (4770, ratio of E/P = 2.8) was supplied by Guangzhou Chemical Industrial Co., Ltd., China. The content of ethylidene norbornene (ENB), the third monomer of EPDM, was 4.9wt%. Methacrylic acid (MAA) and butyl acrylate (BA) were purchased from Wulian Chemical Factory, China. The initiator, benzoyl peroxide (BPO, analytically pure grade), was recrystallized three times from methanol and vacuum dried. All other chemicals and solvents, such as toluene, ethanol, acetone, and carbon tetrachloride were used without further purification.

EPDM-g-MAA-BA grafting polymers were obtained by solution polymerization using BPO as the initiator.^[28,29] The reaction was carried out in a 250 ml four-necked round bottom flask equipped with a reflux condenser, Teflon-coated magnetic stirring bar, thermometer inlet and nitrogen inlet. EPDM was dissolved in toluene until completely dissolved, and then BPO and MAA and/or BA solutions were slowly added with nitrogen. The reactions were carried out with various compositions (Table 1) at 90°C for 3 h. After the completion of the reaction, the solutions were allowed to cool to room temperature naturally. The products were precipitated with acetone, filtered and dried in a vacuum at 60°C to constant weight. Finally, the grafted polymers were obtained.

After the synthesis, the products obtained may consist of EPDM, MAA, and BA homopolymers or copolymers, and the grafted EPDM multi-polymer. The ungrafted MAA and BA homopolymers and copolymers were removed by filtration and extraction using a Soxhlet extraction with boiling acetone for 24 h. Finally, the residue was dried in a vacuum oven for 24 h at 60°C to constant weight. The grafting ratio (GR) of the

Table 1
Grafting polymerization feed compositions

Sample	EPDM/MAA+BA ^a	MAA/BA ^b	BPO(wt%) ^c
P1	30/50	30/50	0.5
P2	40/40	30/50	0.5
P3	50/30	30/50	0.5
P4	55/25	30/50	0.5
P5	60/20	30/50	0.5
P6	50/30	10/70	0.5
P7	50/30	15/65	0.5
P8	50/30	25/55	0.5
P9	50/30	40/40	0.5
P10	50/30	50/30	0.5
P11	50/30	60/20	0.5

^aWeight ratio of EPDM/(MMA+BA).

^bWeight ratio of MMA/BA.

^cThe initiator dosage was based on EPDM and monomers.

grafting reaction was calculated using the following equation (1):^[30]

$$GR(\%) = (W_g - W_0 \times 100/W_0) \quad (1)$$

where W_g and W_0 are the weights of grafted and original ungrafted EPDM, respectively.

Characterization of Products

The products were characterized by Fourier-transform infrared (FTIR) spectroscopy, using a FTIR Spectrometer Nicolet NEXUS-870 (USA) from 4000 to 1000 cm^{-1} with a 0.2 cm^{-1} resolution. KBr tablets of 50–60 μm thickness were obtained by using a laboratory press; the KBr tablets were then coated with pure and grafted EPDM which had been dissolved in carbon tetrachloride. The films were dried under an infrared lamp to remove the solvents.

Differential scanning calorimetry (DSC) of EPDM and EPDM-g-MAA-BA was carried out in a Q2000 DSC (TA Instruments Co., USA). Heating runs of the extracted residues were obtained in a temperature range of -80 to 250°C at a rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere. The weight of the samples was maintained at 9 mg.

The contact angle of different liquids on EPDM and modified EPDM surfaces were measured using a DSA100 Goniometer (Kruss Co., Germany). Bidistilled water and ethylene glycol were used as probe liquids for the contact angle measurements. Each contact angle value quoted was the mean of at least three measurements.

The surface energies of the pure EPDM and grafted polymers were calculated by the Owens and Wendt equation through contact angle measurements:^[13,31,34]

$$\gamma_L(1 + \cos\theta) = 2(\gamma_s^d\gamma_L^d)^{1/2} + 2(\gamma_s^p\gamma_L^p)^{1/2} \quad (2)$$

where

$$\gamma_L = \gamma_L^p + \gamma_L^d$$

γ_L is the free surface energy of the liquid. γ_S^p , γ_S^d and γ_L^p , γ_L^d the polar and dispersion components of the free surface energies of solid and liquid, respectively (S for solid and L for liquid). The surface parameters of these liquids were obtained from the literature^[13] (Table 2).

Inherent viscosities were measured in toluene using an Ubbelohde viscometer at 30°C.

The morphology of free surfaces of the pure EPDM and grafted polymers solvent cast films (thickness \approx 200 nm) was measured by atomic force microscopy (AFM) (CSPM5500, BenYuan Ltd., China). The experiments were carried out in air at 25°C and 72% RH. Topographic phase images were recorded in the tapping mode (TMAFM) with a set point ratio of 0.8 using a rotating tapping etched silicon probe (RTESP) tip having a spring constant of 40 N/m. The cantilever was oscillated at a resonance frequency of 300 kHz. The average roughness (R_a) and root-mean-square roughness (R_{rms}) of the polymer surface were calculated directly from the AFM images.

Results and Discussion

Effect of Ingredient Ratios on the Grafting Reaction

Figure 1 shows the effect of EPDM/MAA-BA ratio on GR of the grafted polymers. The EPDM-g-MAA-BA was synthesized in toluene at 90°C for 3 h, with initiator dosage of 0.5 wt%, and the MAA/BA ratio of 30/50. The GR increased with increasing EPDM/MAA-BA ratio up to 50/30 then rapidly decreased. With an initially higher concentrations of EPDM, more active centers were present which increased the grafting ratio. On the other hand, when the EPDM concentration was high enough, the viscosity of the reaction medium increased, so the diffusion and mobility of the MAA and BA radicals to the EPDM molecule became difficult and they tended to homopolymerize or copolymerize; therefore, the grafting ratio reduced.

Figure 2 shows the effect of MAA/BA ratio on GR of EPDM-g-MAA-BA. The grafted polymer was synthesized in toluene at 90°C for 3 h, with BPO concentration of 0.5 wt%, and the EPDM/monomer ratio of 50/30. The grafting ratio increased slightly with increasing ratio of MAA/BA to 25/55, more than doubled at 30/50, then decreased slightly to 50/30, and then decreased rapidly to 60/20. This effect, we suggest, can be explained by the difference in reactivity between MAA and BA. Because the carboxyl groups of methacrylic acid possess electron-withdrawing effects, the reactivity of the MAA radical is higher than BA; therefore, the GR of EPDM-g-MAA-BA increased

Table 2
Parameters of the surface energy (mJ/m²) of the liquids used

Used liquid	γ_L	γ_L^p	γ_L^d	Reference
Water	72.8	21.8	51.0	[33]
Ethylene glycol	48.0	29.0	19.0	[32]

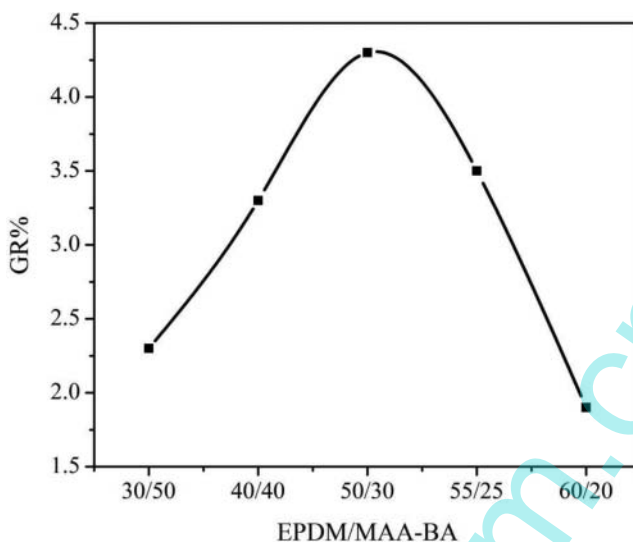


Figure 1. Effect of the EPDM/MAA-BA ratio on the GR of EPDM-g-MAA-BA (MAA/BA, 30/50; BPO, 0.5 wt%; solvent, toluene; reaction temperature, 90°C; reaction time, 3 h.).

initially with increasing dosage of MAA. When the weight ratio of MAA/BA was 30/50, the GR of EPDM/MAA-BA was the maximum, probably because the probability of contact between the active radicals with EPDM could be the largest. With the further increase of MAA dosage, the probability of contact between the monomer increased, thus leading to increasing the homopolymerization or copolymerization of the monomers, since much of the product would have been removed during the Soxhlet extraction.

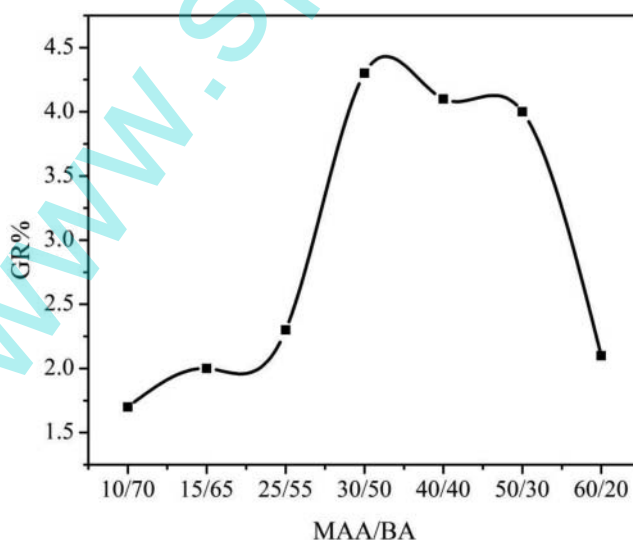


Figure 2. Effect of the MAA/BA ratio on GR of EPDM-g-MMA-BA (EPDM/MAA-BA, 50/30; BPO, 0.5 wt%; solvent, toluene; reaction temperature, 90°C; reaction time, 3 h.).

FT-IR Analysis

The FTIR spectra of pure EPDM and EPDM-g-MAA-BA are shown in Fig. 3. The FTIR spectra were recorded to characterize the structural differences between pure EPDM and EPDM-g-MAA-BA. A summary of the FTIR peak assignment is presented in Table 3. The FTIR spectrum of the pure EPDM [Figure 3(curve A)] shows the C—H stretching vibration at 2921 cm, —CH₂ rocking vibration at 1463 cm, —CH₃ symmetric bending vibration at 1376 cm due to the presence of propylene groups and the C—C stretching vibration at 2852 cm.

The FTIR spectrum of the extracted grafted polymer [Figure3 (curve B)] also has the C—H stretching vibration at 2921 cm. However, the spectrum of the extracted grafted polymer also shows an absorption band at 1733.7 cm which is a characteristic peak of C=O groups, and absorption bands at 1165 cm and 1261 cm which are characteristic peaks of C—O—C groups. In addition, the intensity of peaks at 2800–3000 cm for the C—H stretching vibration became stronger after grafting MAA and BA groups. Also, the intensity of peaks at 1464 cm for the =CH₂ scissoring vibration became weaker by grafting MAA and BA groups. The above results clearly confirmed that the MAA and BA were grafted onto the EPDM.

In order to confirm these signals originated from the MAA-BA grafted onto EPDM and not from homo-PMAA and homo-PBA mixed with EPDM, a sample was prepared by mixing pure EPDM and homo-PMAA and homo-PBA in toluene at 90° for 3 h, followed by the removal of homo-PMAA and homo-PBA by using the Soxhlet extractor with boiling acetone for 24 h. The FTIR spectrum of the extracted EPDM (Fig. 4) indicated that ungrafted homo-PMAA and homo-PBA could be completely removed by the acetone extraction. So the signals were solely contributed by the grafted MAA-BA chains.

Thermal Analysis

The DSC heating thermograms obtained for the pure EPDM and EPDM-g-MAA-BA are presented in Fig. 5. Measurements were made from -80°C to 250°C under a nitrogen

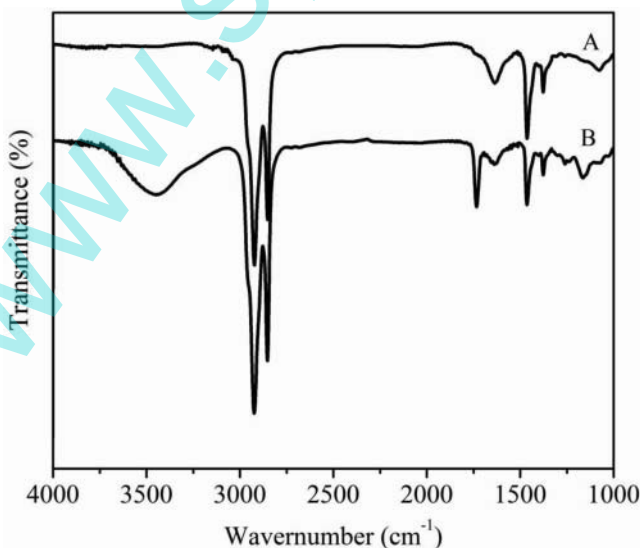


Figure 3. FTIR spectra of EPDM (A) EPDM-g-MAA-BA(B).

Table 3
Principal peak assignments in the spectra of EPDM-g-MAA-BA

Observed region (cm^{-1})	Peak assignment
1165	symmetric C—O—C stretching vibration
1261	asymmetric C—O—C stretching vibration
1377	symmetric C—H stretching vibration of $-\text{CH}_3$
1464	$=\text{CH}_2$ scissoring vibration
1637	$=\text{C}=\text{C}=\text{C}$ stretching vibration
1733.7	$=\text{C}=\text{O}$ stretching vibration
2852	C—C stretching vibration
2921	C—H stretching vibration
3446	—OH stretching vibration

atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$, and displayed in Table 4. The result indicated that the T_g of EPDM was shifted slightly, from -53°C to -49°C , after grafting polymerization with MAA and BA. This implied that EPDM-g-MAA-BA had slightly higher rigidity, which we attribute to the segments of the grafted units or chains restricting the motion of the EPDM main chains. Meanwhile, compared with the pure EPMA, the DSC results also showed that the grafted EPDM had three melting peaks ($\Delta H = 1.8 \text{ J/g}$, 43.1 J/g , and 25.6 J/g), whereas the ungrafted EPDM had only double peaks ($\Delta H = 2.7 \text{ J/g}$ and 152 J/g). We suggest more intermolecular hydrogen bonds of EPDM-g-MAA-BA will form through grafting polar MAA and BA chains, which had an effect on the crystalline structure of EPDM. The results illustrated that the melting temperature, melting heat and

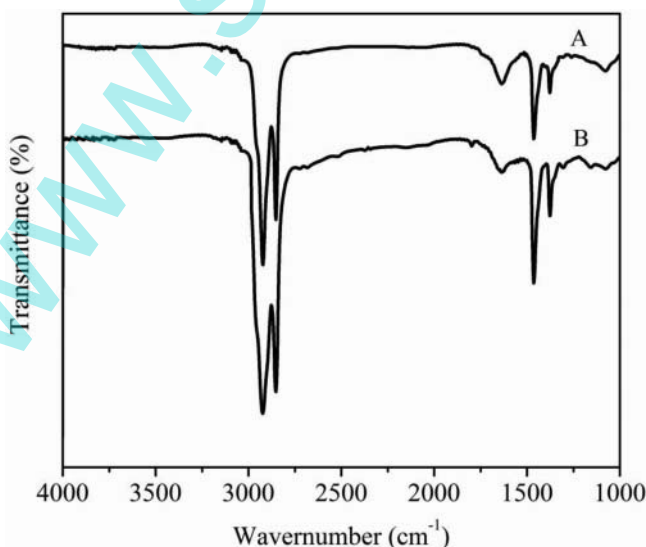


Figure 4. FTIR spectra of EPDM (A) and extracted EPDM (B).

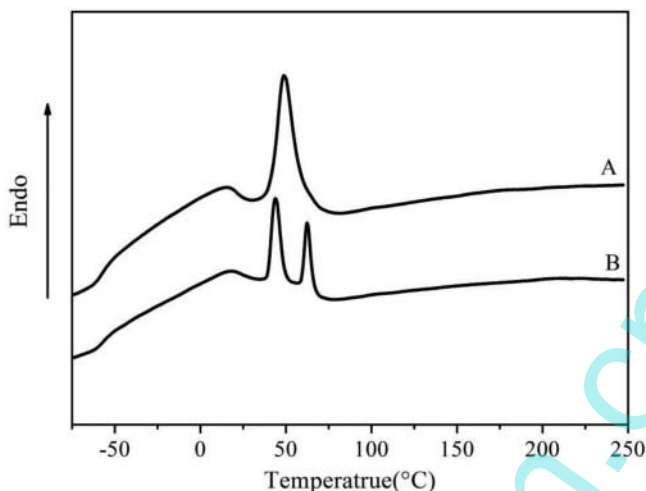


Figure 5. Typical DSC thermograms of pure EPDM (A) and EPDM-g-MAA-BA (B).

glass transition temperature of EPDM were altered by the grafted chains because the crystalline regions in EPDM could be interfered with by the grafted chains.

Contact Angles Analysis

The surface properties of the films were investigated by contact angle measurement. Figure 6 illustrates the variation of contact angles of distilled water (DW, curve A) and ethylene glycol (ETG, curve B) on pure EPDM and EPDM-g-MAA-BA films with various grafting ratios. The contact angles decreased gradually with the increase of the grafting ratio for both liquids. The reduction of contact angles between the grafted polymers and the water or ethylene glycol molecules was a result of the polarity of the polymer's surface increasing with the increase of the polar groups in the EPDM-g-MAA-BA.

Surface Energy Analysis

Fowkes proposed that the surface energy can be decomposed into two components,^[34] $\gamma_s = \gamma_s^p + \gamma_s^d$, and the surface polar (γ_s^p) and dispersive (γ_s^d)

Table 4
DSC results of the pure EPDM and EPDM-g-MAA-BA

Samples	T_g (°C)	Melting peaks (°C)			Fusion heat (J/g)		
		T_{m1}	T_{m2}	T_{m3}	ΔH_{m1}	ΔH_{m2}	ΔH_{m3}
EPDM	-53	15	49	—	2.7	152	—
EPDM-g-MAA-BA	-49	17	44	62	1.8	43.1	25.6

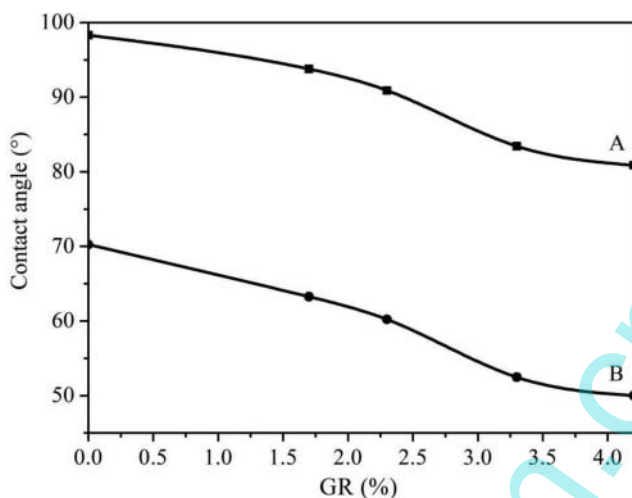


Figure 6. Contact angles of distilled water (DW, A) and ethylene glycol (ETG, B) on pure EPDM and EPDM-g-MAA-BA with various grafting ratios (P6, P8, P2, P9).

components can be calculated by the Owens and Wendt equation [equation (2)]. The surface energy (γ_s) and its polar (γ_s^p) and dispersive (γ_s^d) components for the grafted and ungrafted EPDM were calculated from the contact angles and are listed in Table 5. For pure EPDM rubber, γ_s^p was the smallest and the surface energy (27.54 mJ/m^2) was almost equal to the dispersive component of the surface energy. This indicates that the pure EPDM rubber surface was nonpolar in nature. After being grafted, the polarity of the surface of EPDM-g-MAA-BA slightly increased with increasing grafting ratio. The lowering of the contact angle of DW and ETG should be attributed to the polar groups of EPDM-g-MAA-BA. It also confirmed that the MAA and BA were grafted onto the EPDM.

Inherent Viscosity Analysis

The inherent viscosities were measured in toluene using an Ubbelohde viscometer and are shown in Table 6. The results showed that the inherent viscosity of the

Table 5
Contact angles and surface energy values of samples

Sample	GR(%)	$\theta_{\text{ethanediol}}$	θ_{water}	$\gamma_s^p \text{ (mJ/m}^2\text{)}$	$\gamma_s^d \text{ (mJ/m}^2\text{)}$	$\gamma_s \text{ (mJ/m}^2\text{)}$
EPDM	0	70.25	98.31	0.97	26.57	27.54
P2	3.3	52.47	83.43	4.45	29.80	34.25
P6	1.7	63.26	93.78	1.31	30.58	31.89
P8	2.3	60.21	90.89	1.96	30.60	32.56
P9	4.2	50	80.88	5.67	29.06	34.73

$$\gamma_s \gamma_s^p + \gamma_s^d$$

Table 6.
Inherent viscosities of EPDM-g-MAA-BA in toluene

Polymer	EPDM	P6	P7	P8	P9	P10
GR (%)	0	1.7	2.0	2.3	4.2	4.0
$[\eta](\text{dl/g})$	1.52	1.85	1.92	1.98	2.29	2.25

grafted polymers increased with the increase of grafting ratio. With increasing GR of the grafted polymers, the proportion of polar groups in EPDM-g-MAA-BA increased, thus increasing the intermolecular attraction interactions between the polymer molecules. In addition, the molecular weight of the grafted polymers also increased with the increase of the grafting ratio of grafted polymers, so the inherent viscosity of EPDM-g-MAA-BA will increase.

AFM Analysis

The morphologies of pure EPDM and EPDM-g-MAA-BA were studied by tapping mode AFM. Figure 7 shows the 2D and 3D AFM images of the pure EPDM (A) and grafted EPDM (B). AFM image analysis was utilized to measure the surface roughness, and the results are listed in Table 7. Figure 7(A) shows that the surface of the ungrafted EPDM film was rough and showed a crest-like structure. However, compared with the pure EPDM surface, the surface of EPDM with grafted polar MAA and BA groups [Fig. 7(B)] was relatively smooth. It can be explained in terms of their being more intermolecular hydrogen bonds and crystalline regions in the EPDM-g-MAA-BA formed by grafting polar MAA and BA chains; therefore, the surface became more dense. The root mean square roughness (R_{rms}) and roughness average (R_a) also indicated the difference between the pure EPDM and pure EPDM. The results demonstrated that the morphology of EPDM was changed by the grafting polymerization of monomers and EPDM.

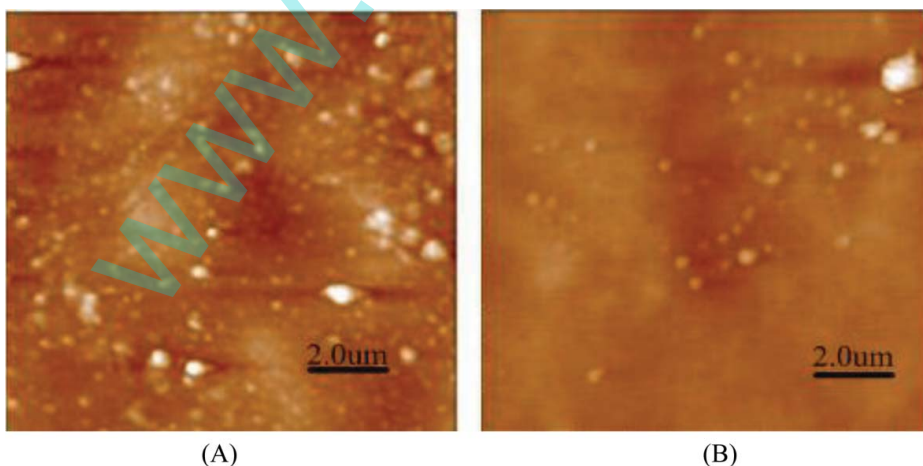


Figure 7. AFM phase two-dimensional images ($10 \mu\text{m} \times 10 \mu\text{m}$) of pure EPDM (A) and EPDM-g-MAA-BA (B).

Table 7The average roughness (R_a) and root-mean-square roughness (R_{rms}) of membranes

Membranes	R_a (nm)	R_{rms} (nm)
EPDM (A)	10.3	14
EPDM-g-MAA-BA (B)	5.75	8.36

Conclusions

EPDM-g-MAA-BA was synthesized through solution grafting polymerization of MAA and BA onto EPDM in toluene using BPO as an initiator. FTIR analysis provided evidence of the grafting of MAA and BA to the EPDM main chains. The DSC results indicated that the Tg of EPDM slightly increased by grafting the MAA and BA monomers, and the crystalline regions of EPDM were altered through grafting the P(MAA-BA) chains. The surface energy and contact angle measurements showed that the surface polarity increased with the increase of grafting ratio. The inherent viscosity of the grafted polymers also increased with the increase of grafting ratio. Finally, the AFM results showed that the grafted polymer appeared smoother than the pure EPDM. All results showed that P(MAA-BA) chains were successfully grafted onto EPDM main chains. We suggest the added EPDM-g-MAA-BA should increase the compatibility of the EPDM with polar materials, expanding the application of EPDM.

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