Graft copolymers of microcrystalline cellulose as reinforcing agent for elastomers based on natural rubber

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ABSTRACT: In the present study, free radical graft copolymerization of acrylic monomers and microcrystalline cellulose (MCC) was applied to develop a biopolymer for natural rubber reinforcements. The copolymerization was carried out in aqueous media. Cerium ammonium nitrate was employed as the initiator in the presence of nitric acid. Acrylic monomers used in the copolymer synthesis were ethyl acrylate (EA) and butyl acrylate (BA). Effects of monomer concentration, initiator concentration, polymerization time, and polymerization temperature on the obtained graft copolymers were investigated. The graft parameters were obtained by thermal gravimetric analysis method. The obtained copolymers (MCC-g-PEA, MCC-g-PBA) were characterized by attenuated total reflection, wide-angle X-ray diffraction, field-emission electron microscopy, and thermal gravimetric analysis. In comparison to native MCC, better thermal stability of graft copolymers were observed. In addition, the graft copolymers reinforced natural rubber composites were produced, and sulfur was used as the vulcanizing agent. Their vulcanization and mechanical properties were characterized. Comparing to the native MCC reinforced natural rubber composites, the copolymers reinforced natural rubber composites shows improved mechanical properties, indicating the copolymer's potential application as rubber reinforcements. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43087.

INTRODUCTION

Cellulose is the most abundant biopolymer in the biosphere,[1–3] which is a linear condensation polymer composed of repeating D-glucopyranose residues linked by β-1,4-glucosidic bonds.[3] Cellulose exhibits a high degree of polymerization, the individual glucan chains can reach lengths of greater than 25,000 glucose residues. The adjacent anhydroglucose molecules are rotated 180° with respect to their neighbors, coupling with adjacent cellulose molecules by extensive hydrogen bonds[4] and van der waals forces[5] which produces a straight, stable heterogeneous supramolecular structure.[6–8] It is the main reason that cellulose shows high strength properties. Additionally, cellulose also presents biodegradability, renewability, low density, and is potential for chemical modification.[9] Thus, cellulose is potential as reinforcing biomaterial.

MCC is particles of hydrolyzed cellulose consisting of a bunch of cellulose microcrystals together with amorphous areas, which can be obtained from wood and cotton cellulose, and it is widely applied in cosmetic, food, and other industries.[10] MCC is a mesoporous material, and the specific surface area is about 2.50 m²/g.[11] However, due to the hydrophilic nature of cellulose, it cannot be uniformly dispersed in most nonpolar polymer media. Thus, cellulose modification is of interest in order to improve compatibility with a wider variety of matrices. Up to our knowledge, grafting of synthetic polymers on cellulose not only eliminates these drawbacks but also allows the acquisition of the additional properties of grafted polymers without destroying its own properties.

Up to now, there are three main approaches to synthesis graft copolymers, including grafting-on to method, grafting-from method, and grafting-through method.[12] The grafting-from method has been extensively studied since 1960s. Different techniques such as anionic grafting,[13,14] cationic grafting,[15,16] atom-transfer radical polymerization,[17,18] and free radical polymerization[19] have been used in the synthesis of graft copolymers. Additionally, free radical copolymerization initiated by ammonium cerium (IV) nitrite (CAN) in aqueous media has been

thoroughly investigated and employed for the grafting of polysaccharides,[20] such as cellulose and starch.

The synthetic polymers grafted on MCC are also an important influence factor for the copolymer's properties. In our previous work, we studied MCC grafted poly(methyl methacrylate), which showed reinforced mechanical properties of rubber composites.[21] Thus, in the present work, we studied MCC grafted polyacrylates. As we know polyacrylates and polymethacrylates are usually employed as the graft copolymers, while their properties are considerably different. Polyacrylates are much softer due to the absence of the methyl groups on alternating carbons of the polymer chains, which find applications requiring flexibility and extensibility,[22] especially work as the base material of acrylate rubber. In addition, ethyl acrylate (EA) is the ester of acrylic acid and ethanol, and butyl acrylate (BA) is the ester of acrylic acid and n-butanol. They are used as raw materials for fiber processing agents, adhesives, coatings, plastics, acrylic rubber, and emulsions. Meanwhile, polymethacrylates tend to be used as shaped objects due to the rigid structure. Therefore, polyacrylates is more suitable for the reinforcement of rubber composites. In our previous work, not only the free radical copolymerization of ethyl acrylate and butyl acrylate on to MCC was carried out and investigated, but also the rubber reinforcement effect of graft copolymers were studied.

The graft ratio is an important parameter for graft copolymer synthesis, providing information about the level of a polymer grafted onto the backbone polymer, which is a preferred parameter for thermal stability of the graft copolymer. Additionally, the copolymers with different graft ratio shows different reinforcement effects on rubber composites. As known, there are three different methods to get the graft ratio of cellulosic copolymers, including hydrolysis method,[23–25] TGA method[26] and NMR method.[27] Among them TGA method is the most effective and convenient method, due to the simple and fast processing, easy control, and accurate results.[21]

In our present work, the graft copolymers were prepared by CAN initiated free radical polymerization in aqueous media. The effects of monomer ratio, reaction time, reaction temperature and initiator concentration on copolymerization were studied. TGA method was used to investigate graft ratio and thermal stability of the copolymers. The obtained copolymers with different content of grafted polymers were used for the preparation of elastomeric materials based on natural rubber by sulfur crosslinking. Their vulcanization and mechanical properties were investigated.

EXPERIMENTAL

Materials
Microcrystalline cellulose was purchased from Daejung Chemicals and Metals Cooperation and the particle size was in the range of 20–100 μm. Ethyl acrylate and butyl acrylate monomer were provided by Duksan Pure Chemical Cooperation. Ammonium Cerium (IV) Nitrate was applied by Daejung Chemicals and Metals Cooperation. Hydrochloric acid (35%), nitric acid (60%), and perchloric acid (60–62%) were purchased from Duksan Pure Chemicals (South Korea). Acetone was provided by Samchun Pure Chemical Cooperation. Tetrahydrofuran

(THF) was purchased from Avantor Performance Material. Natural rubber (NR) latex was provided by Korea Kumho Petrochemical Company (KKPC). Stearic acid (above 95.0%), zinc oxide (above 99.0%), and sulfur (purity above 99.0%) were supplied by Daejung Chem. Dibenzothiazole disulfide (DD) and N-cyclohexyl-2-benzothiazolysulfenamide (CBS) were purchased from T.C.I. All the chemicals and rubber additives were used as received without further purification.

Graft Copolymerization
The graft copolymerization procedure was based on the method of Li's work.[28] Firstly 300 mL distilled water and a certain amount of MCC power were mixed with 10 min stirring, then purged with dry nitrogen for 30 min to exclude the oxygen. Subsequently CAN, which was dissolved in 0.1 mol/L nitric acid, and acrylic monomers were dropwise added for 30 min. The copolymerization took three hours under nitrogen atmosphere. After reaction, the suspension was filtered and dried in the oven at 70°C for 12 h. The products were extracted using acetone in a Soxhlet apparatus for 72 h to remove homopolymers. Finally the extracted products were dried and weighted.

Isolation of Graft Chains
In order to achieve the graft side chains, hydrolysis method was used. Firstly, 5 g copolymers were hydrolyzed in 200 mL 10 wt % HCl solution at the boiling point for 5 h. Then 10 mL perchloric acid (60–62%) was added into the solution with 30 min stirring. The hydrolyzed products were filtered and dried at 70°C until a constant weight.

The gravimetric parameters include graft ratio, graft efficiency, polymer weight fraction, and monomer conversion were calculated with the following equations.

$$\text{Graft ratio} \ (G_R) = \frac{m_G}{m_C} \times 100\% \qquad (1)$$

$$\text{Graft efficiency} \ (G_E) = \frac{m_G}{m_P + m_G} \times 100\% \qquad (2)$$

$$\text{Polymer weight fraction} \ (W_G) = \frac{m_G}{m_C + m_G} \times 100\% \qquad (3)$$

$$\text{Conversion} \ (C) = \frac{m_G + m_P}{m_F} \times 100\% \qquad (4)$$

where m_G is the mass of grafted polymer; m_C is the mass of cellulose; m_P is the mass of homopolymer, and m_F is the mass of fed monomer.

Characterization of Graft Copolymers
Determination of Molecular Weights. The molecular weight of the obtained grafted materials after hydrolysis were determined by gel permeation chromatography (GPC, 1200 series, Agilent Technologies), which equipped with Refractive Index Detector, isocratic pump, PLgel GPC columns (5 μm MIXED-C, 300 × 7.5 mm) and thermostatted column compartment. ASTM method E-1303-95 was used for testing. The optics temperature was 35°C, response time was 4 s, and flow rate was 1.0 mL/min. THF was used as an eluent, and the calibration curve was obtained with polystyrene standards.

Chemical Structural Characterization. Infrared spectra of the starting material and all products were recorded on a
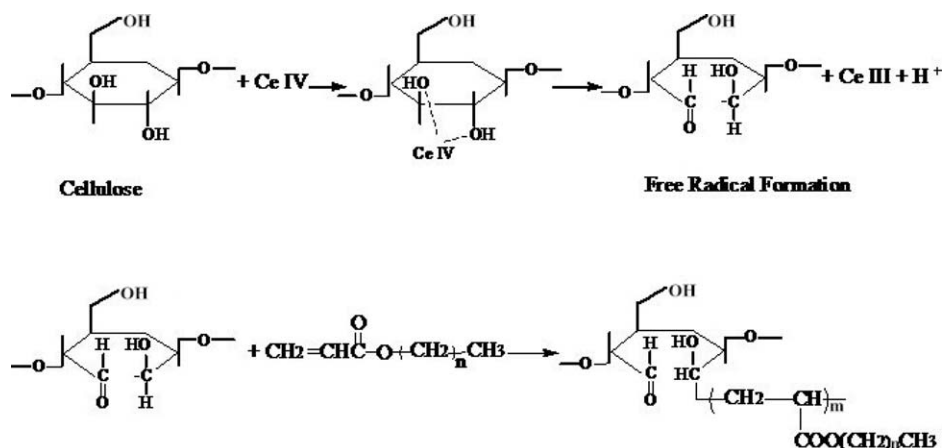
Scheme 1. Mechanism of cerium initiated graft copolymerization.

PerkinElmer spectrum 1000 as an attenuated total reflection (ATR) measurement to verify the presence of new function groups after modification. The frequency range of Infrared spectra was 400–4000 cm^{-1} with a resolution of 4.0 cm^{-1}.

Wide-Angle X-ray Diffraction (WXRD). WXRD patterns of the samples were measured using Empyrean (manufactures by PANalytical) X-ray diffractometer at 25°C. The WXRD data were generated by a diffractometer with Cu Kα radiation ($\lambda = 1.542$ Å) at 40 kV and 30 mA over the angular range $2\theta = 5°$–50°, a step size of 2°min^{-1}. The degree of crystalline index (CI %) for each sample was evaluated using eq. (5).

$$CI = (A_c/A_a) \times 100\% \qquad (5)$$

where A_c is the area of the crystalline reflection and A_a is the area subtending the whole diffraction profile.

Surface Morphology of the Copolymer. The surface morphology of the MCC and copolymers was investigated using the field emission scanning electron microscopy (FE-SEM, JSM-7500, JEOL). All the samples were sputter-coated with gold before the test.

Thermal Gravimetric Analysis (TGA). The graft parameters of copolymer were investigated using thermal gravimetric analysis (PerkinElmer TGA 4000), in nitrogen atmosphere at a flow rate of 20 cm^3/min. The temperature range investigated was from ambient temperature to 600°C at a heating rate of 20°C/min.

Application of Copolymers as NR Reinforcements
Compounding. Copolymers/NR compounds were prepared by directly mixing copolymers with NR latex. The mixtures were vigorously stirred for 30 min at 1000 rpm, and then dried at 70°C until a constant weight. Compounding was conducted on a two-roll mixing mill. The dried compounds were compounded using the conventional elastomeric additives, such as sulfur, zinc oxide, stearic acid, accelerator *n*-cyclohexyl-2-benzothiazole sulfenamide (CBS), and accelerator dibenzothiazole disulfide (DD). The compounding formulation is as follows: NR, 100 phr; copolymers, 5 phr; sulfur, 2 phr; zinc oxide, 3 phr; stearic acid, 1 phr; CBS, 2 phr; DD, 0.5 phr. Sulfur and accelerators were mixed in the final step to avoid prevulcanization. The vulcanization characteristics of compounds were determined using a MDR

2020 Reometer (Myung Ji Tech, South Korea) at 140°C. Finally, the compounds were vulcanized under 10 MPa for the optimum cure time at 140°C in a hot-pressing machine. The thickness of the specimens were about 1 mm. For the purpose of comparison, neat NR and MCC/NR were also prepared.

Characterization of Copolymers/NR. Vulcanization characteristics of compounds, including minimum torque (M_L), maximum torque (M_H), scorch time (t_{S2}), and optimum cure time (t_{90}) were determined. Curing rate index (CRI) was employed to evaluate the cure rate of rubber compounds, which was calculated by the following equation:

$$CRI = \frac{100}{t_{90} - t_{s2}} \qquad (6)$$

Tensile tests were performed on a Tinius Oisen H5KT-0401 testing machine at a speed of 500 mm/min according to ASTM D412. Tear strength was measured on the same machine at a speed of 50 mm/min according to ASTM D642. Shore A hardness of the specimens was obtained with Shore Durometer Type A according to ASTM D2240. Five different specimens were measured to obtain an average value.

RESULTS AND DISCUSSION

Effect of Reaction Parameters on the Graft

The mechanism for acrylate monomers graft copolymerization onto cellulose using CAN as initiator has been reported as shown in Scheme 1.[21,29] Different reaction parameters on the graft were studied. The products were characterized by FTIR, XRD, SEM, and TGA. Furthermore, the application of copolymers as NR reinforcements has also been studied.

Effect of the Cellulose-to-Monomer Ratio on Graft Copolymerization. The effect of cellulose to monomer ratio on graft copolymerization was shown in Table I. The results show that G_R and W_G of microcrystalline cellulose-graft-poly(ethyl acrylate) (MCC-g-PEA) and microcrystalline cellulose-graft-poly(butyl acrylalte) (MCC-g-PBA) were increased with the increase in acrylic monomers, however G_E and C were decreased. The same trend of molecular weight with G_R was achieved. So it can be concluded that with more acrylic monomers the graft chains will be longer and graft ratio will be higher.

Table I. Effect of the Cellulose-to-Monomer Ratio on Graft Copolymerization

	MCC-*g*-PEA					MCC-*g*-PBA				
Cellulose:monomer	3/1	2/1	1/1	1/2	1/3	3/1	2/1	1/1	1/2	1/3
G_R (%)	41.6	48.2	86.7	153.6	215.8	34.1	61.7	76.1	139.7	190.9
G_E (%)	87.2	82.7	74.0	70.1	65.6	78.3	80.1	74.4	68.0	71.7
W_G (%)	29.4	32.5	46.4	60.6	68.3	25.4	38.1	43.2	58.3	65.6
C (%)	99.6	99.1	98.9	96.2	95.5	97.9	98.9	93.0	92.5	91.6
$\overline{Mn}$(e^5·g/mol)	0.8491	0.9863	2.3242	3.8836	4.7053	2.4880	2.6743	3.0547	3.6023	3.9789
$\overline{Mw}$(e^5·g/mol)	3.0965	5.5885	5.7033	7.6192	10.108	8.3080	10.191	12.045	13.898	15.615
$\overline{D}$	3.6470	5.6661	5.4539	1.9619	2.1482	3.3393	3.8105	3.9431	3.8580	3.9245

CAN, 0.5 wt %, 45°C, 3 h.

Compared to the G_R of MCC-*g*-PBA, the G_R of MCC-*g*-PEA was higher, which was attributed to the longer alkyl length of BA, preventing the graft copolymerization from conducting. It has been reported that the hydrophilic properties decreases with the increase in alkyl length.[23] The trend of W_G was similar with that of G_R. However the $\overline{M_w}$ of grafted PBA was much higher than PEA. The possible reason was that when the grafted PEA and PBA had the same polymerization degree, the longer alkyl length of BA would result in higher molecular weight. The G_E and C of MCC-*g*-PEA were also a little higher than MCC-*g*-

PBA, which was due to the better hydrophilic properties of EA. In comparison with our previous work,[21] higher G_R, G_E, W_G, and C were observed, which was due to the better hydrophilic properties of acrylate monomer. In conclusion, MCC-*g*-PEA shows the highest graft parameters.

Effect of Reaction Time on Graft Copolymerization. The effect of reaction time on graft copolymerization was shown in Table II. When the reaction time was 0.5 h, the C of MCC-*g*-PEA and MCC-*g*-PBA were 91.0 and 85.6% respectively,

Table II. Effect of Reaction Time on Graft Copolymerization

	MCC-*g*-PEA (h)				MCC-*g*-PBA (h)			
Reaction time	0.5	1	3	5	0.5	1	3	5
G_R (%)	70.1	83.3	86.7	89.4	64.3	75.1	76.1	83.3
G_E (%)	74.0	74.4	74.4	76.0	72.0	73.4	74.0	74.5
W_G (%)	41.2	45.5	46.4	47.2	39.1	42.9	43.2	45.5
C (%)	91.0	94.4	98.9	99.0	85.6	93.6	93.0	97.5
$\overline{Mn}$(e^5·g/mol)	1.4658	1.6902	2.3242	3.1712	0.9450	1.5579	3.0547	3.3282
$\overline{Mw}$(e^5·g/mol)	3.9757	4.5999	5.7033	7.0120	6.0884	6.2285	12.045	12.208
$\overline{D}$	2.7124	2.7216	2.4539	2.2111	6.4429	3.9981	3.9431	3.6680

Cellulose-to-monomer ratio: 1:1, CAN 0.5 wt %, 45°C.

Table III. Effect of Reaction Temperature on Graft Copolymerization

	MCC-*g*-PEA (°C)				MCC-*g*-PBA (°C)			
Reaction temperature	35	45	55	65	35	45	55	65
G_R (%)	88.2	86.7	81.4	76.6	87.7	76.1	69.3	68.5
G_E (%)	75.5	74.0	73.6	73.5	76.6	74.4	73.8	69.6
W_G (%)	46.9	46.4	44.9	43.4	46.7	43.2	40.9	40.7
C (%)	99.1	98.9	96.3	94.6	97.3	93.0	91.4	91.3
$\overline{Mn}$(e^5·g/mol)	2.3906	2.3242	2.2913	1.7547	3.1498	3.0547	2.6958	2.1474
$\overline{Mw}$(e^5·g/mol)	6.4725	5.7033	5.4414	4.7452	10.819	12.045	9.2527	7.7438
$\overline{D}$	2.7075	2.4539	2.3747	2.7034	3.4349	3.9431	3.4323	3.6062

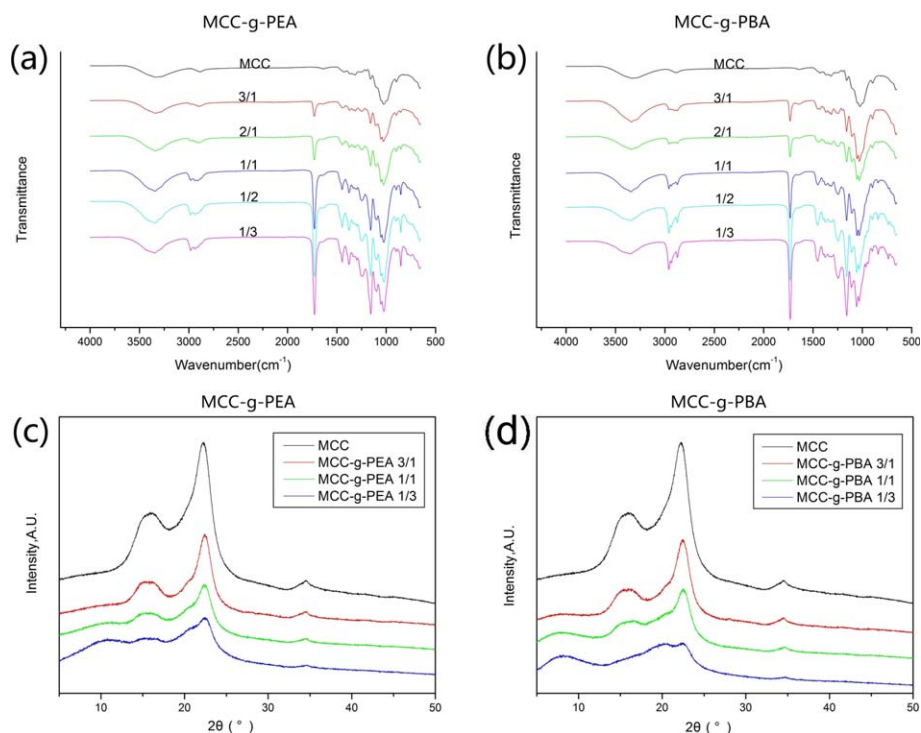Cellulose-to-monomer ratio 1:1, CAN 0.5 wt %, 3 h.

Figure 1. Characterization of copolymers, FTIR spectroscopy of (a) MCC-*g*-PEA, (b) MCC-*g*-PBA; X-ray diffraction patterns of (c) MCC-*g*-PEA, (d) MCC-*g*-PBA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicating that most of the graft copolymerization was completed within 0.5 h. As the reaction time increased, the C of MCC-*g*-PEA and MCC-*g*-PBA were increased accordingly. The G_R of MCC-*g*-PEA and MCC-*g*-PBA were also increased along with the reaction time, thus more graft chains formed while less homopolymers produced. Additionally, the G_R and W_G of MCC-*g*-PEA and MCC-*g*-PBA were all increased with the same trend with molecular weights of graft chains. Meanwhile, the $\overline{D}$ of grafted PEA and PBA were all decreased with time increase, so improved dispersion state of graft chains were achieved.

The effect of reaction time on graft copolymerization were different for MCC-*g*-PEA and MCC-*g*-PBA. As we can see the graft parameters of MCC-*g*-PEA were higher than MCC-*g*-PBA,

due to the better hydrophilicity of EA. In comparison with our previous work,[21] higher graft parameters were achieved due to the better hydrophilicity of acrylate monomers. In conclusion, MCC-*g*-PEA shows the highest graft parameters.

Effect of Reaction Temperature on Graft Copolymerization. The effect of reaction temperature on graft copolymerization was shown in Table III. The decreased C of MCC-*g*-PEA and MCC-*g*-PBA was attributed to the instability of CAN at elevated temperature.[30] The G_E of MCC-*g*-PEA and MCC-*g*-PBA were also decreased, so more homopolymers formed as the temperature increased. Additionally, G_R and W_G were all decreased, accordingly with the molecular weight of graft chains.

Table IV. Effect of Initiator Concentration on Graft Copolymerization

Initiator concentration	MCC-*g*-PEA				MCC-*g*-PBA			
	0.20%	0.50%	0.80%	2.00%	0.20%	0.50%	0.80%	2.00%
G_R (%)	96.4	86.7	81.3	78.8	76.6	76.1	75.5	70.9
G_E (%)	77.5	74.0	71.6	68.0	69.8	74.4	71.8	65.0
W_G (%)	49.1	46.4	44.8	44.1	43.4	43.2	43.0	41.5
C (%)	92.8	98.9	98.5	99.8	78.0	93.0	97.2	99.3
$\overline{Mn}(e^5 \cdot g/mol)$	4.3328	2.3242	2.1133	1.4530	4.6578	3.0547	2.1212	1.0002
$\overline{Mw}(e^5 \cdot g/mol)$	12.311	5.7033	5.6248	4.0149	14.863	12.045	9.0018	5.0842
$\overline{D}$	2.8413	2.4539	2.6616	2.7631	3.1909	3.9431	4.2438	5.0832

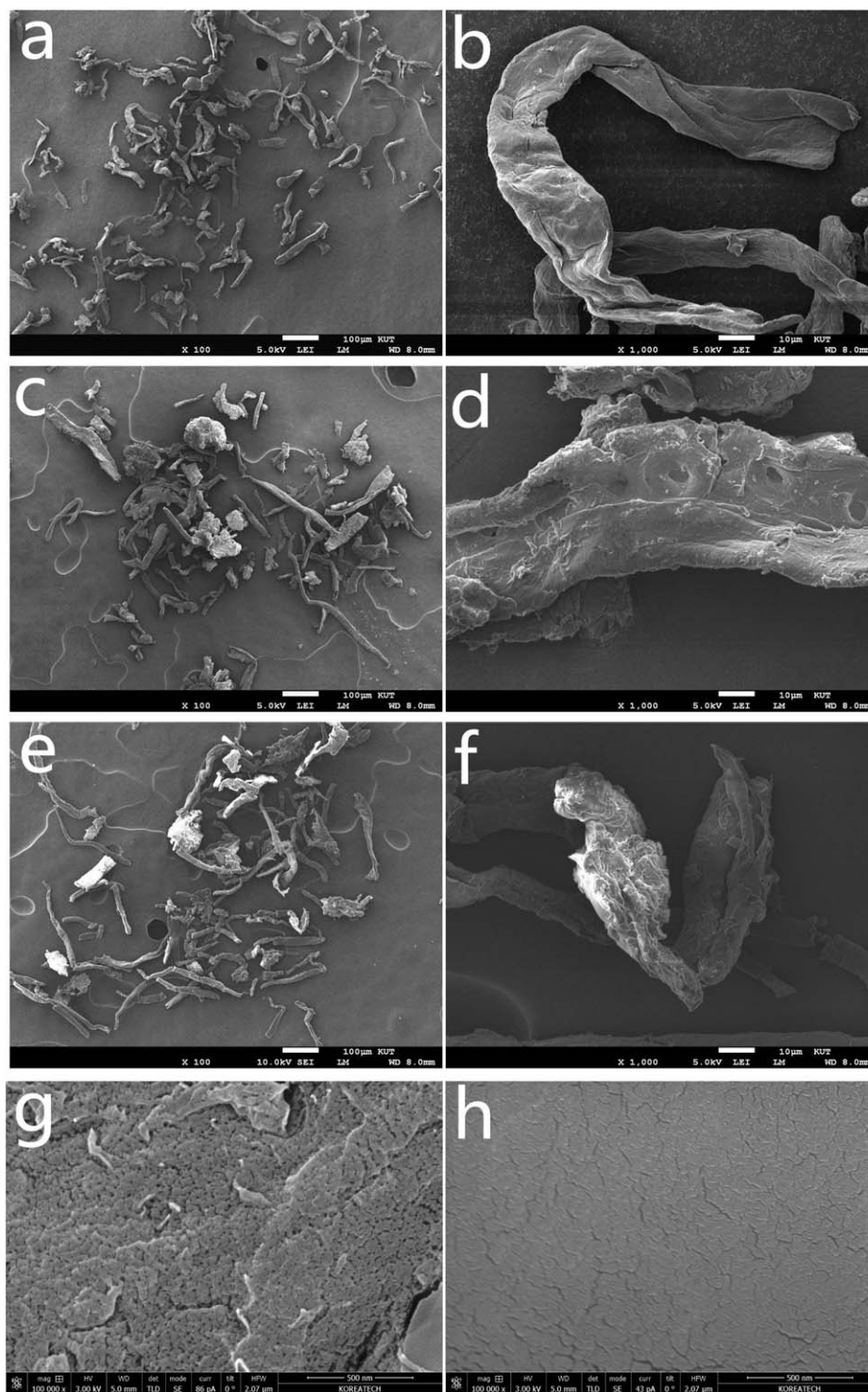Cellulose-to-monomer ratio 1:1, 45°C, 3 h.

Figure 2. SEM photographs of (a) MCC, 100 μm, (b) MCC, 10 μm, (c) MCC-g-PEA 1/1 (after extraction), 100 μm, (d) MCC-g-PEA 1/1 (after extraction), 10 μm, (e) MCC-g-PBA 1/1 (after extraction), 100 μm, (f) MCC-g-PBA 1/1 (after extraction), 10 μm, (g) MCC, 500 nm, (h) MCC-g-PEA 1/1 (after extraction), 500 nm.

Compared to G_R of MCC-g-PEA, the G_R of MCC-g-PBA decreased more drastically. The same phenomenon was shown in G_E, W_G, and C. The ΔH of grafted PBA was higher than PEA as shown in Figure 1, owing to the longer alkyl length of BA. So with the same G_R of MCC-g-PEA and MCC-g-PBA, more graft chains formed on

MCC-g-PEA. We can conclude that the temperature has prominent influence on the graft copolymerization of MCC-g-PBA. In comparison to our previous work,[21] higher graft parameters were achieved due to the better hydrophilicity of acrylate monomers. In conclusion, MCC-g-PEA shows the highest graft parameters.

Table V. Absorbance of C═O Bond and CI Values of MCC-*g*-PEA and MCC-*g*-PBA

	Absorbance		CI values	
	MCC-g-PEA	MCC-g-PBA	MCC-g-PEA	MCC-g-PBA
MCC	0	0	41.87%	41.87%
3/1	13.17	17.52	40.17%	39.91%
2/1	20.55	18.01	–	–
1/1	51.62	40.07	30.55%	30.52%
1/2	65.05	63.21	–	–
1/3	68.01	66.77	21.03%	10.80%

Effect of Initiator Concentration on Graft Copolymerization. The effect of initiator concentration on graft copolymerization was shown in Table IV. The G_R and W_G of MCC-*g*-PEA and MCC-*g*-PBA were all decreased with the increase of initiator concentration. The G_E also decreased, however C increased, resulting in more homopolymers. The molecular weights of grafted PEA and PBA also decreased with the initiator concentration increase, so the graft chains became shorter with the initiator concentration increase. Additionally, the $\overline{D}$ of grafted PEA and PBA were increased, proving that poor dispersion states of graft chains were achieved.

The difference of MCC-*g*-PEA and MCC-*g*-PBA on the initiator concentration was shown in Table IV, the graft parameters of MCC-*g*-PEA were higher than MCC-*g*-PBA at the same initiator concentration. The $\overline{D}$ of grafted PEA was smaller than PBA, shown better dispersion state of grafted PEA. Additionally, the G_R of MCC-*g*-PEA decreased from 96.4 to 78.8% with the increase of initiator concentration, while the G_R of MCC-*g*-PBA decreased from 76.6 to 70.9% with the increase of initiator concentration, so it can be concluded that the G_R of MCC-*g*-PEA decreased much more than MCC-*g*-PBA. The same phenomenon were shown in G_E and W_G. Therefore, the initiator concentration has bigger influence on the graft copolymerization of MCC-*g*-PEA. However, the $\overline{M_W}$ of grafted PBA was higher than PEA at the same initiator concentration, owing to the longer alkyl length of BA. In comparison with our previous work,[21] higher graft parameters were achieved due to the better hydrophilicity of acrylate monomers. In conclusion, the best initiator concentration of our present work is 0.20%, and MCC-*g*-PEA shows the highest graft parameters.

Evidence of Graft Polymerization

Characterization of the Functional Group of the Copolymers by FTIR Spectroscopy. Chemical structures of the graft copolymers were characterized by ATR. The ATR spectra of MCC, MCC-*g*-PEA, and MCC-*g*-PBA were presented in Figure 1(a,b). MCC displays the O–H stretching absorption in the region of 3650–3000 cm^{-1} (broad, s), the C–H stretching at 2900 cm^{-1} (m), and the wave number of 1025 (s) for the C–O stretching. The ATR spectra of MCC-*g*-PEA and MCC-*g*-PBA exhibited all the characteristic absorption peaks of MCC.

Additionally, the peak at 1728 cm^{-1} indicates the C═O stretching, which are characteristics of the ─COO group contained in PEA and PBA. The presence of new absorption band at 1728 cm^{-1} provided evidence for grafting of ethyl acrylate and butyl acrylate onto the cellulose backbone. And the peak at 1165 cm^{-1} indicates the C─O stretch of ester, which is also the evidence for grafting of ethyl acrylate and butyl acrylate onto cellulose.

Furthermore, the peak intensities of C─H stretching at 2900 cm^{-1}, C═O stretching at 1728 cm^{-1}, C─O stretching at 1025 and 1165 cm^{-1} increased with the increasing of graft ratio. Especially the C═O stretching shown in Table V, the absorbance of MCC-*g*-PEA increased from 13.07 to 68.01 with the increase of graft ratio, and the absorbance of MCC-*g*-PBA increased from 17.52 to 66.77 with the increase of graft ratio.

XRD Analysis. The WXRD profiles of MCC, MCC-*g*-PEA and MCC-*g*-PBA were presented in Figure 1(c,d). The MCC exhibited three diffraction peaks at 15.8°, 22.5°, and 34.5°. The peak at 15.8° was two overlapped weaker diffraction peaks at 15.1° and 16.6°.[31] The grafted cellulose with different monomer ratio all presented the peak of 15.8°, 22.5° and 34.5°. The crystalline index values were presented in Table V, with the increase of graft ratio, the CI values of MCC-*g*-PEA and MCC-*g*-PBA both decreased, resulting to more amorphous areas of copolymers. Furthermore, the CI values of MCC-*g*-PEA 1/3 and MCC-*g*-PBA 1/3 were 21.03 and 10.80%, respectively. The possible reason was that the longer alkyl length of BA results in the increase of amorphous areas.

Surface Morphology. The surface appearances of MCC, MCC-*g*-PEA 1/1 and MCC-*g*-PBA 1/1 were observed by scanning electron microscopy as shown in Figure 2. The length of MCC was about 20–100 μm as shown in Figure 2(a). The surface of MCC was smooth as shown in Figure 2(b). However, there were many aggregations of modified cellulose after polymerization as shown in Figure 2(c,e). Additionally, the surfaces of MCC-*g*-PEA and MCC-*g*-PBA looked like fish scale shown in Figure 2(d,f), which was due to microphase separation. The pore structure of MCC was shown in Figure 2(g), there were many irregular pores on the surface, and the diameter of the pores range from several nanometers to dozens of nanometers. However, after copolymerization, the pores disappeared, left irregular stripe as shown in Figure 2(h). The pores on MCC increased the specific surface area to 2.5 m^2/g, resulting in high graft ratio. And the modified MCC has a crosslinking structure.

Thermal Properties of the Graft Copolymers

The thermogravimetric analysis (TGA) technique was employed to calculate the graft parameters. The TGA thermograms of copolymers were from 100 to 600°C for the purpose of excluding water content as shown in Figure 3(a,b). There were two main decomposition stages, the first stage was the decomposition of MCC, and the second stage was the decomposition of graft chains, including PEA and PBA. Then, the weight loss of different stages were used to calculate the graft parameters such as the graft ratio and polymer weight fraction, presented in Tables I–IV.

TGA technique was also used to investigate the thermal properties of the obtained graft copolymers. From the thermograms, we can see that the line shifts to right with the increase of graft ratio. And from the DTG thermograms in Figure 3(c,d), the peak intensity of graft chains increased with the increase of graft
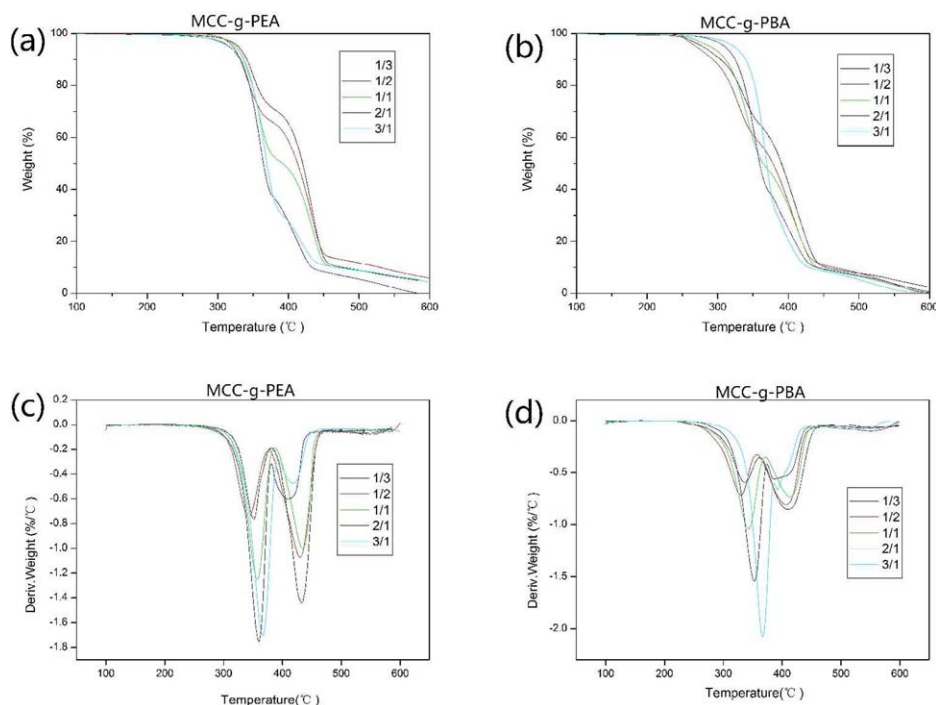
Figure 3. TGA thermograms of (a) MCC-*g*-PEA, (b) MCC-*g*-PBA; DTG thermograms of (c) MCC-*g*-PEA, (d) MCC-*g*-PBA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ratio, in which the first peak was the decomposition of MCC, and the second peak was the decomposition of graft chains. T_{max} is another important factor to investigate the thermal properties of copolymers. As shown in Figure 4(a,b), the T_{max} of MCC in MCC-*g*-PEA decreased from 367.7 to 351.7°C with the graft ratio increased from 41.6 to 215.8%, while the T_{max} of MCC in MCC-*g*-PBA decreased from 366.7 to 336.8°C with the graft ratio increased from 34.1 to 190.9%. We can see that the T_{max} of MCC in MCC-*g*-PBA decreased more sharply than that of MCC-*g*-PEA, showing better thermal stability of MCC in MCC-*g*-PEA. In addition, the T_{max} of PEA in MCC-*g*-PEA increased from 418.5 to 432.5°C with the graft ratio increased from 41.6 to 215.8%, while the T_{max} of PBA in MCC-*g*-PBA increased from 391.6 to 411.4°C with the graft ratio increased from 34.1 to 190.9%. We can see that the T_{max} of PEA in MCC-*g*-PEA was higher than PBA in MCC-*g*-PBA, showing better thermal stability of PEA in MCC-*g*-PEA.

The effect of graft ratio on the thermal decomposition kinetics of copolymer was also studied. The thermal decomposition kinetics was investigated by Broido method,[32] which is expressed as eq. (7).

$$\ln\left[\ln(1-\alpha)^{-1}\right] = -E_a/RT + \text{const} \qquad (7)$$

where α represents the decomposed reaction, E_a represents the activation energy, and T is the temperature.

Figure 4(c,d) shows the effect of graft ratio on the decomposition activation energy E_a of copolymers at the decomposition peaks of MCC and graft chains. The E_a of MCC in both MCC-*g*-PEA and MCC-*g*-PBA were decreased, owing to the surface structure changed during the graft copolymerization. However,

the E_a of PEA and PBA were both increased due to the increase of graft chains. The difference in E_a between MCC-*g*-PEA and MCC-*g*-PBA was also shown in Figure 4. The E_a of MCC in MCC-*g*-PEA decreased from 165.14 to 139.72 KJ/mol with the increase of graft ratio and the slope is −0.13074, while the E_a of MCC in MCC-*g*-PBA decreased from 194.53 to 86.88 KJ/mol with the increase of graft ratio and the slope is −0.65781. So we can conclude that the graft of BA on MCC will destroy the surface structure of cellulose drastically. In addition, the E_a of PEA increased from 57.15 to 153.69 KJ/mol and the slope is 0.51078, while the E_a of PBA increased from 64.18 to 89.44 KJ/mol and the slope is 0.21441, so the thermal stability of graft chains in MCC-*g*-PEA was better.

In summary, during the graft copolymerization, EA has less change on the surface structure of MCC and the thermal stability of PEA was better, therefore the thermal stability of MCC-*g*-PEA was better than MCC-*g*-PBA.

Characteristics of MCC-*g*-PEA/NR And MCC-*g*-PBA/NR Compounds

Vulcanization Characteristics of MCC-*g*-PEA/NR and MCC-*g*-PBA/NR. The vulcanization characteristics of NR compounds with added graft copolymers were shown in Table VI. With the incorporation of MCC, the torque values were all increased, due to the stiffness of MCC, which strongly restricted the deformation and consequently increased the stiffness of NR composites. This is also evidenced by the change in the hardness of MCC/NR composites from 53.1 to 71.8 as shown in Table VII. The scorch time and optimum curing time of MCC/NR also increased, the possible reason was that MCC increased the activation energy for vulcanization process. The curing rate index
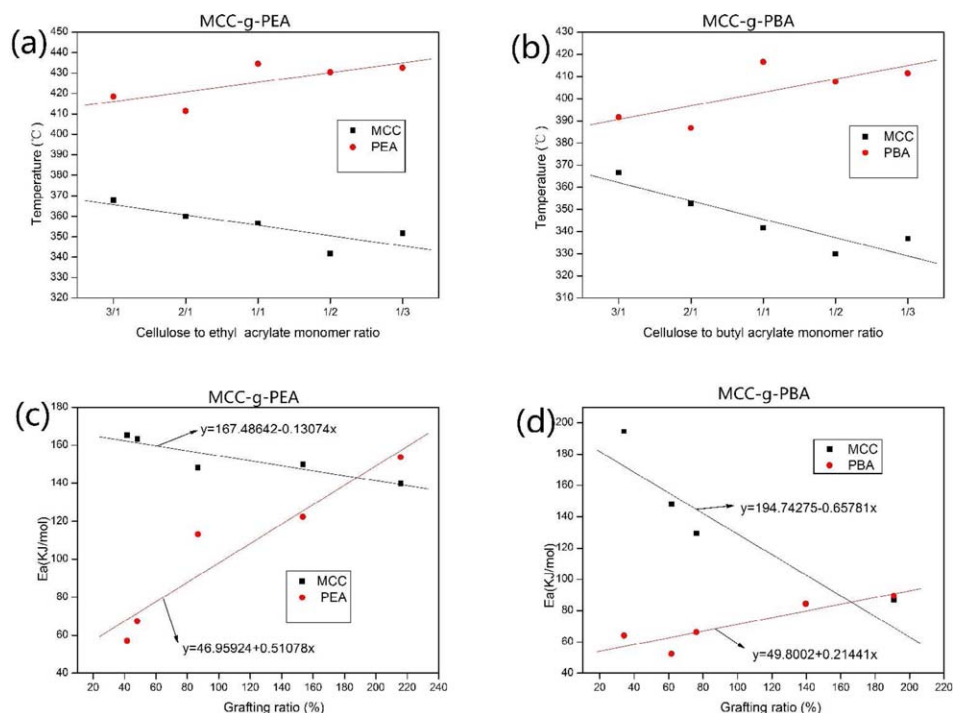
Figure 4. T_{max} of (a) MCC-*g*-PEA, (b) MCC-*g*-PBA; decomposition activation energy of (c) MCC-*g*-PEA, (b) MCC-*g*-PBA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(CRI) was applied to indicate the vulcanization rate. The CRI values of MCC/NR was decreased due to the incorporation of MCC, which reduced the vulcanization rate.

The incorporation of copolymers in NR matrix reduced the torque values, due to the elasticity of PEA and PBA, which worked like a soft mat between MCC and NR. The scorch time and opti-

Table VI. Vulcanization Characteristics of MCC-*g*-PEA/NR and MCC-*g*-PBA/NR Composites

Samples	NR	MCC	MCC-g-PEA			MCC-g-PBA		
			3/1	1/1	1/3	3/1	1/1	1/3
M_L (lb-in)	0.4	0.8	0.6	0.3	0.2	0.7	0.4	0.3
M_H (lb-in)	15.8	20.6	20.1	18.6	16	18.2	16.6	15.9
ΔH(lb-in)	15.4	19.8	19.5	18.3	15.8	17.5	16.2	15.6
ts_2 (min)	3.85	5.23	5.62	6.32	7.2	6.22	6.65	7.48
t_{90} (min)	8.17	9.78	10.53	10.97	11.38	10.7	10.82	11.58
CRI (min^{-1})	23.15	21.98	20.37	21.51	23.92	22.32	23.98	24.39

Table VII. Mechanical Properties of MCC-*g*-PEA/NR and MCC-*g*-PBA/NR Vulcanizates

Samples	NR	MCC	MCC-g-PEA			MCC-g-PBA		
			3/1	1/1	1/3	3/1	1/1	1/3
Tensile strength (MPa)	19.34	21.15	22.48	24.17	25.55	22.06	22.87	25.35
Elongation (%)	1320	1279	1315	1384	1427	1325	1405	1435
300% Modulus (MPa)	1.591	1.715	2.001	1.824	1.776	1.931	1.713	1.663
Tear strength (kN/m)	42.31	43.14	48.59	46.73	44.95	45.09	43.67	41.58
Hardness (Shore A)	53.1	71.8	70.9	68.5	67.5	68.7	67.8	66.5

mum curing time of copolymers/NR all increased, because with the increase of graft ratio, the copolymer's size would be larger, thus it need more time to complete the vulcanization process. However, the CRI values of copolymers/NR were all increased with the increase of graft ratio, owing to the elasticity of PEA and PBA, which were the base materials of acrylic rubber.

In addition, the different influence of MCC-*g*-PEA and MCC-*g*-PBA on NR matrix was presented in Table VI. As we can see the ΔH values of MCC-*g*-PEA were higher than MCC-*g*-PBA at the same monomer ratio, and the CRI values of MCC-*g*-PEA were lower than MCC-*g*-PBA. The possible reason was that the density of PEA is 1.12 g/cm^3 and the density of PBA is 1.08 g/cm^3, so the microstructure of PEA was stiffer, resulting to higher ΔH values and lower CRI values of MCC-*g*-PEA.

Mechanical Properties of Copolymers/NR Vulcanizates. The mechanical properties of copolymers/NR were shown in Table VII. With the incorporation of MCC, the tensile strength, 300% modulus and tear strength were slightly increased due to the weak interfacial interactions between MCC and NR, which agreed with Li's work.[33] And the elongation of MCC/NR decreased due to the stiffness of MCC. In addition, the modified cellulose with different graft ratio shows different reinforcing effect on NR matrix. The copolymers with higher graft ratio indicates higher tensile strength and elongation, which is according with Li's work,[34] while the copolymers with lower graft ratio indicates higher 300% modulus, tear strength and hardness. The possible reason was that the copolymers with higher graft ratio have thicker graft coating, which increased the elongation and improved the physical entanglement between MCC and NR; while the copolymers with lower graft ratio shows strong cellulose properties, which increase the modulus and hardness.[35,36] Comparing MCC-*g*-PEA/NR and MCC-*g*-PBA/NR, the tensile strength, 300% modulus, tear strength, and hardness of MCC-*g*-PEA/NR were all higher, owing to the stiffer microstructure of PEA. Therefore, MCC-*g*-PEA is more suitable for rubber reinforcement.

CONCLUSION

Microcrystalline cellulose grafted poly(ethyl acrylate) and poly(butyl acrylate) were successfully synthesized in aqueous media using a redox initiated free radical polymerization validated by ATR analysis. The optimum reaction conditions for both monomers EA and BA are 35°C and 0.2 wt % initiator concentration, and the reaction temperature shows more influence on the grafting of BA while the initiator concentration shows more influence on the grafting of EA. Additionally with the increase of monomer concentration the higher graft ratio was obtained, and with longer reaction time the longer graft chains were formed. The SEM graphs of copolymers provided clear evidence for microcrstalline cellulose surface modifications using acrylate monomers. XRD showed more amorphous regions were achieved with the increase of graft ratio. And the TGA technique was employed to calculate the graft ratio and validate the better thermal stability of the copolymers. The application of copolymers as rubber reinforcements was also investigated to validate the reinforcing effect of modified cellulose. And comparing to

MCC-*g*-PBA, MCC-*g*-PEA shows better thermal stability and rubber reinforcing effect.

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