

SYNTHESIS OF POLYACRYLAMIDE WITH PENDANT POLY(BUTYL ACRYLATE) CHAINS USING THE MACROMER TECHNIQUE AND STUDIES ON THEIR PROPERTIES

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Abstract An amphiphilic graft polymer, (PAM-g-PBA), polyacrylamide (PAM) having poly(*n*-butyl acrylate) (PBA) side chains, was obtained by radical copolymerization of acrylamide with PBA macromer in solution. The macromer was synthesized by free radical polymerization of butyl acrylate in the presence of different amounts of thioglycolic acid as the chain transfer agent, followed by termination with glycidyl methacrylate. The reactivity ratio and effects of copolymerization conditions on the conversion of macromer or grafting efficiency were studied. The crude products were purified by extraction with toluene and water successively. The purified graft copolymer was characterized by IR, DSC and TEM. PAM-g-PBA can bring about microphase separation and exhibits good emulsifying properties and water absorbency. PAM-g-PBA exhibits a very good compatibilizing effect on the acrylic rubber/poly(vinyl chloride) blends. 2%–3% of the graft copolymer is enough for enhancing the tensile strength of the blends. The tensile strength of the blends is more than twice that without the compatibilizer. DSC and SEM demonstrated the enhancement of compatibility in the presence of the graft copolymer.

Keywords Graft copolymerization, Macromer, Amphiphilic polymer, Blend, Compatibilizer

INTRODUCTION

Since Milkovich and Chiang^[1] developed a method of preparing copolymers with uniform side chains by using the macromer technique, the synthesis of copolymers with uniform side chains from different macromers has been studied extensively. Milkovich *et al.* reported the synthesis of polystyrene macromer through termination of living polystyrene anions with methacryloyl chloride and its copolymerization with butyl acrylate to form thermoplastic elastomer^[2]. Rempp^[3] obtained polyoxyethylene macromer by using potassium alcoholate as initiator and studied its copolymerization. Later Xie *et al.* reported a new synthesis method^[4] and the copolymerization^[5, 6] of polyoxyethylene macromer, which was prepared in dimethyl sulfoxide (DMSO) solution by using potassium naphthalene in tetrahydrofuran as initiator. The synthesis of poly(methyl methacrylate) (PMMA) macromer was reported by Ito^[7] and by Bonardi *et al.*^[8] independently through free radical polymerization using thioglycolic acid or thioglycol as chain transfer agent, followed by the reaction of the carboxylic acid end groups with glycidyl methacrylate or by the reaction of hydroxyl groups with methacryloyl chloride, respectively. Yamashita *et al.*^[9] studied the copolymerization of PS macromer with 2-hydroxyethyl methacrylate. Albrecht and Wunderlich^[10] synthesized amphiphilic graft copolymers through copolymerization of PMMA macromer with methacrylic acid (MAA). We have used PMMA macromer to prepare graft copolymers with *n*-butyl acrylate (BA)^[11] as thermoplastic elastomers and also used PS macromer to prepare amphiphilic graft copolymers with MAA^[12] and others.

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Received November 29, 2002; Revised January 6, 2003; Accepted January 10, 2003

This paper deals with the synthesis, characterization and properties of a new amphiphilic polymer containing polyacrylamide (PAM) as the backbone and PBA as the side chains. Since PAM is hydrophilic and PBA is hydrophobic, therefore the emulsifying properties and water absorbency of the copolymer were studied. An attempt was made to use the graft copolymers of PAM with PBA side chains as compatibilizer for polymer blends of acrylic rubber with poly(vinyl chloride).

EXPERIMENTAL

Materials

Acrylic rubber AR-200 with ML 40 was produced by Qing-Long Acrylic Rubber Factory, Sichuan. Polyvinyl chloride 1300 with an intrinsic viscosity of 128 mL/g was purchased from Gehua Chemical Technology Co., Wuhan. *n*-Butyl acrylate (C.P. grade) was purified by washing with 10% NaOH solution and water successively, followed by drying with anhydrous Na_2SO_4 and distillation under reduced pressure. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Solvent used for polymerization, such as dimethyl sulfoxide, was dried over 4 Å molecular sieve overnight. Other reagents were chemically pure.

Synthesis of PBA Macromer

Radical polymerization of BA was carried out in benzene under a nitrogen atmosphere by using AIBN as the initiator and different amounts of thioglycolic acid as the chain transfer agent at 65°C for 12 h, in order to obtain prepolymers with different molecular weights. The prepolymers were then purified by precipitation in toluene with methyl alcohol. The yield was about 60%. Carboxyl end group of the prepolymer was determined by titration in acetone with absolute alcoholic KOH solution, using a methanolic solution of phenolphthalein as the indicator. The purified prepolymer was then reacted in xylene with glycidyl methacrylate (GMA) at a molar ratio of GMA/COOH = 2 by using *N,N*-dimethyl benzylamine as the catalyst at 139°C under nitrogen atmosphere for 8 h. The macromer thus obtained was purified by precipitation in benzene with methanol. The conversion of carboxyl groups into methacrylate group was nearly 100%, determined by titration of the remaining carboxyl end groups in the macromer.

Copolymerization of PBA Macromer with Acrylamide

Calculated amounts of PBA macromer, AM and AIBN were mixed in DMSO with stirring. After purging with nitrogen, the mixture was heated to 65°C and the reaction was carried out at 65°C for 8 h with stirring. After precipitation with acetone, the solvent was evaporated under an infrared lamp and the crude product was vacuum dried to constant weight.

The crude product was extracted with toluene three times to remove the unreacted PBA macromer. The dried residue was then extracted with water three times to remove the homopolymer of AM.

The conversion of the macromer (P_1) or the grafting efficiency ($G.E.$) and the conversion of the monomer (P_2) can be calculated from the following equations:

$$G.E. \text{ or } P_1 (\%) = (\text{Macromer charged} - \text{Macromer extracted}) \times 100 / \text{Macromer charged}$$

$$\text{Conversion of AM or } P_2 (\%) = (\text{Weight of crude product} - \text{Macromer charged}) \times 100 / \text{Monomer charged}$$

$$\text{Content of the side chains in the graft copolymer } (\%) = \text{Macromer charged} \times G.E. \times 100 / \text{Weight of purified graft copolymer}$$

Determination of Reactivity Ratio

At the different stages of copolymerization, aliquot portions of the copolymerizing solution were taken out and terminated with *p*-hydroxyphenol solution, followed by drying and purification procedure as above, in order to calculate P_1 and P_2 .

Since the steric hindrance of the macromer is higher and the molar ratio of the macromer to monomer is much lower, the reactivity ratio r_2 of the monomer can be calculated according to the Kennedy equation^[13]:

$$r_2 = \ln(1 - P_2)/\ln(1 - P_1)$$

where P_2 and P_1 are the conversions of the monomer and the macromer at the same stage of copolymerization, respectively.

Characterization and Testing

The molecular weight of PBA macromer was determined by titration of the COOH groups of the prepolymer before termination with glycidyl methacrylate for forming the PBA macromer.

IR spectra of the purified graft copolymers were obtained with an Equinox 55 FT-IR spectrometer, using a KBr disc, coated with a solution of the sample, followed by drying. Glass transition temperature was determined with differential scanning calorimeter made by Mettler Toledo Co. with a heating rate of 20 K/min under nitrogen. The morphology of graft copolymer was observed with a JEMCX-100 transmission electron microscope after coating the sample on the carbon grate and treatment with 1% hydrazine solution at 50°C for 72 h, followed by staining with OsO₄. Hydrazine reacts with the acrylate ester groups to form the hydrazide^[14] which can be stained with OsO₄.

The blends were compression molded at 150–160°C under a hot press for 10 min, and the mechanical properties of the blends were determined on a DL-250 tensile tester with a stretching rate of 250 mm/min at room temperature. Permanent set was measured as percent elongation 3 min after the specimen was broken and united.

Morphology of the fracture surface of the blend sample obtained after tensile testing was observed with a JSM-35C scanning electron microscope. The broken section of the specimen surface was coated with thin gold layer.

Emulsifying Properties and Water Absorbency of PAM-g-PBA

Emulsifying properties of the amphiphilic PAM-g-PBA are characterized by emulsifying volume^[12]. The copolymer was dissolved in 30 mL toluene and then 70 mL water was added. The mixture was shaken thoroughly for several minutes and allowed to stand overnight, whereupon the system separated into two layers. The emulsifying volume is taken as the total volume of the toluene solution plus water minus the volume of the lower water layer after separation.

Water absorbency was measured by the following procedure. A sample of about 1 mm thickness was weighed and immersed in water at constant temperature for 24 h. After removing water from the surface with filter paper, the sample was weighed. The water absorbency is given by:

$$\text{Water absorbency (\%)} = (W_a - W_b) \times 100/W_b$$

where W_b is the weight of sample before absorption and W_a is the weight of sample after water absorption.

Blending of Polymers using Graft Copolymer as the Compatibilizer

Blending of acrylic rubber (ACR) with poly(vinyl chloride) (PVC) was performed in the presence of 0.5% antioxidant 264, 2% lead stearate with or without different amounts of PAM-g-PBA on a hot mill at 160°C for 10 min and then hot pressed at 150°C for 20 min.

RESULTS AND DISCUSSION

Reactivity Ratios

Dimethyl sulfoxide can be used as a solvent in the copolymerization of PBA macromer with acrylamide so as to keep the copolymerization solution homogeneous up to high conversion. Table 1 shows the relationship between reactivity ratio r_2 of AM in its copolymerization with PBA macromer and time. Below $P_2 = 23\%$ and $P_1 = 34\%$, r_2 remained almost unchanged and was equal to 0.62.

Table 1 also illustrates that the conversion of macromer is faster than that of the monomer in the earlier stages of the copolymerization. This is apparently due to the higher reactivity of the double bonds of methacryloyl groups of the macromers than those of acryloyl groups of the monomers in the copolymerization. However, when the viscosity of copolymerization system becomes higher at higher conversions of both

macromer and monomer, it seems easier for the monomer than the macromer to diffuse and react with the active centers. Thus the conversion of monomer exceeds that of the macromer.

Table 1. Reactivity ratio of acrylamide during its copolymerization with PBA macromer at 65°C

Time (h)	P_1 (%)	P_2 (%)	r_2
0.5	20.0	13.0	0.62
0.75	28.0	18.4	0.62
1	34.2	23.2	0.63

Factors Affecting Grafting Efficiency in the Copolymerization

Figure 1 indicates that in the copolymerization of AM with PBA macromer, the grafting efficiency (*G.E.*) or conversion of the macromer increases with the amount of initiator (AIBN). This is because the active centers increase with the increase of initiator, resulting in a decrease of the average length of propagating active centers and a decrease of the viscosity of the polymerization system. Lower viscosity is favorable for increasing *G.E.*, since it is easier for the macromer to diffuse and react with the active centers (in the solution with lower viscosity). However, when the amount of initiator exceeds 0.4%, *G.E.* increases slightly, probably due to the increase of the chain transfer probability.

Figure 1 also illustrates that *G.E.* decreases with increasing charging weight % of the macromer. This result may probably be due to an increase of viscosity of the polymerization system containing more macromers, and also due to the fact that the macromer is very difficult to homopolymerize.

G.E. decreases with increasing molecular weight of the PBA macromer, as shown in Fig. 2. This result may be attributed to the increase of difficulty in diffusion and the increase of steric hindrance of the macromer associated with higher molecular weight, which affects the reaction between the active centers and the macromer.

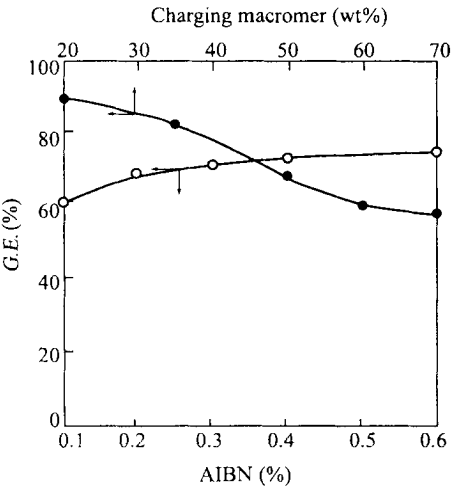


Fig. 1 Effects of amount of initiator and charging wt% of PBA macromer on the grafting efficiency in the copolymerization of PBA macromer with AM at 65°C for 8 h

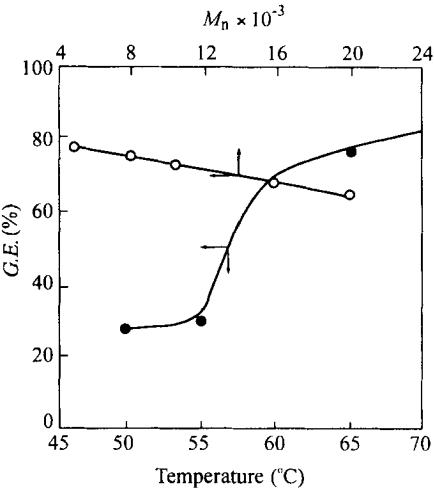


Fig. 2 Effect of molecular weight of PBA macromer and copolymerization temperature on the grafting efficiency in the copolymerization of PBA macromer with AM using 0.2% AIBN for 8 h

Figure 2 also shows that *G.E.* increases with increasing copolymerization temperature. This fact can be interpreted as indicating that on the one hand the viscosity of copolymerization system reduces with increasing temperature, thus favoring the diffusion of the macromer and the reaction between the active centers and the macromer; on the other hand the decomposition of the initiator to form free radicals increases with copolymerization temperature and the excess radicals produced cause more chain transfer.

Characterization of the Purified Graft Copolymers

The crude products obtained from the copolymerization were purified by extractions. The efficiency of purifications was ascertained by extractions of a mixture of PBA macromer and PAM with toluene and water successively.

The IR spectrum of the purified PAM-g-PBA (Fig. 3) exhibits absorption peaks of the NH_2 group at 3450 cm^{-1} , that of the carbonyl group of amide at 1650 cm^{-1} , that of the $\text{C}-\text{N}$ group at 1450 cm^{-1} and that of the carbonyl group of ester at 1735 cm^{-1} , as well as that of the $\text{C}-\text{O}$ bond at 1167 cm^{-1} and that of the butyl group at 950 cm^{-1} . These absorption peaks indicate that the purified product contains both PAM and PBA segments.

Figure 4 is the DSC curve of PAM-g-PBA, which also exhibits two T_g s, the one at -45.3°C corresponds to T_g of PBA and the other at 77.0°C corresponds to that of PAM. Since T_g for pure PBA is 54°C and that for PAM is 150°C , the inward shift of T_g s demonstrated the occurrence of phase separation and partial compatibility of the two components.

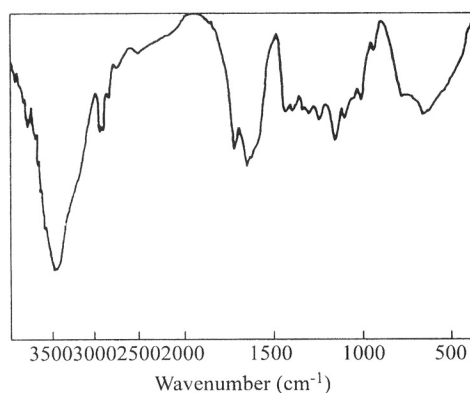


Fig. 3 IR spectrum of the purified PAM-g-PBA containing 47.2 wt% PBA

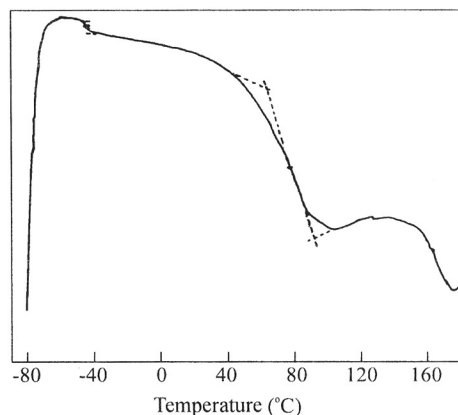


Fig. 4 DSC curve for the purified PAM-g-PBA containing 19.8 wt% PBA

Figure 5 is the TEM micrograph of the purified PAM-g-PBA containing 19.8 wt% or 11.7 mol% PBA. The PBA segments can react with hydrazine to form hydrazide^[14], which can be stained with OsO_4 , whereas PAM cannot. Thus the dark part in the picture represents the PBA domains while the bright continuous part is the PAM phase.

These two phenomena show that phase separation has occurred in the graft polymer.

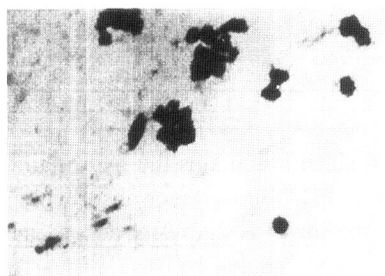


Fig. 5 TEM micrograph of the purified PAM-g-PBA containing 19.8 wt% PBA (with magnification of 72000)

Emulsifying Properties of PAM-g-PBA

Since PAM is hydrophilic and PBA is hydrophobic, the graft copolymer formed can thus emulsify the toluene/water system. The effects of the amount of the copolymer used, the content and molecular weight of the hydrophobic segments PBA on the emulsifying properties are shown in Table 2, where the emulsifying properties were measured as emulsifying volume. It can be seen that the emulsifying volume increases with the amount of

the graft copolymer used and that the graft copolymer containing about 47 wt% of the hydrophobic segments shows the largest emulsifying volume. The latter may be due to the fact that almost equal portions of the hydrophilic and hydrophobic segments benefit the formation of an emulsion.

Table 2. Emulsifying properties of PAM-g-PBA

PAM-g-PBA (g/100 mL)	PBA content (wt%)	M_n of PBA	$E.V.^*$ (mL)
0.05	47.2	15700	34.5
0.10	47.2	15700	35.2
0.20	47.2	15700	40.9
0.30	47.2	15700	45.6
0.50	47.2	15700	50.0
0.20	19.8	15700	33.5
0.20	33.5	15700	40.0
0.20	47.2	15700	40.9
0.20	54.0	15700	38.0
0.20	61.4	15700	34.6
0.20	47.2	5140	50.8
0.20	47.2	8050	49.0
0.20	47.2	10600	44.5
0.20	47.2	15700	40.9
0.20	47.2	19800	37.5

* $E.V.$ represents emulsifying volume at room temperature

Table 2 also shows that the emulsifying volume decreases with increasing molecular weight of the PBA macromer. This result is attributed to the decrease of emulsifying sites as the number of grafts decreases with increasing molecular weight of the PBA macromer.

Table 3. Water absorbency of PAM-g-PBA

PBA (%)	M_n of PBA	Water absorbency (%)
19.8	15700	258.5
33.5	15700	216.1
47.2	15700	101.6
54.0	15700	72.3
61.4	15700	48.2
47.2	5140	81.5
47.2	8050	90.1
47.2	10600	96.3
47.2	15700	101.6
47.2	19800	105.8

Water Absorbency of PAM-g-PBA

The graft copolymer can absorb water, since it contains the hydrophilic PAM backbone. Table 3 indicates the effects of content and molecular weight of PBA on its water absorbency. It can be noted that the more the PBA content or the lower the PAM content, the lower is the water absorbency. The water absorbency also increases with the molecular weight of the PBA grafts. This is because at nearly the same PBA content, the higher the molecular weight of the PBA grafts, the less is the number of the hydrophobic grafts, resulting in higher water absorbency of the graft copolymer.

Compatibilizing Properties of the Graft Copolymers

When ACR was blended with PVC alone at a weight ratio of 6/4, the mechanical properties of the blends became inferior. But if 2%–3% of PAM-g-PBA was added as a compatibilizer, the tensile strength of the blends is more than twice that without the compatibilizer and they behave like thermoplastic elastomers with ultimate elongation larger than 200% and permanent set smaller than 10% (Table 4). At a fixed amount of PAM-g-PBA used, the

behavior of the blend changes from that for thermoplastic elastomer to that for toughened plastics as the weight % of PVC in the blend increased beyond 60%. This fact can be interpreted by the change of the continuous phase from ACR to PVC.

Table 4. Effect of amount of PAM-g-PBA as compatibilizer and the weight ratio of ACR/PVC on the mechanical properties of the ACR/PVC blends

PAM-g-PBA (% in the blend)	ACR/PVC (weight ratio)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0	6/4	3.14	167	2
1	6/4	4.09	188	1
2	6/4	6.40	205	7
3	6/4	7.05	201	8
4	6/4	4.72	210	12
6	6/4	3.60	181	7
2	10/0	1.35	980	21
2	8/2	2.98	492	14
2	6/4	6.40	205	7
2	4/6	10.5	88	8
2	2/8	15.6	56	3
2	0/10	32.1	34	2

PBA = 47.2 wt%, $M_{n, \text{PBA}} = 15700$

The graft copolymers containing PBA side chains with molecular weight of 8,000–10,600 exhibit higher tensile strength for the ACR/PVC blend (as shown in Table 5). This fact implies that the copolymers having these molecular weight ranges show better compatibilizing effects than those with other molecular weights. This fact may be attributed to the suitable length and number of the PBA side chains which are needed to penetrate into the PVC phase and offering better adhesion between the two phases.

Table 5. Effects of PBA content and molecular weight of PBA macromer on the mechanical properties of the ACR/PVC blends

PBA (wt%)	$M_{n, \text{PBA}}$	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
19.8	15700	3.48	180	2
33.5	15700	7.26	203	10
47.2	15700	6.40	205	8
61.4*	15700*	4.15*	174*	6*
47.2	5140	5.90	188	3
47.2	8050	8.33	210	6
47.2	10600	7.92	202	7
47.2	15700	6.40	205	8
47.2	19800	4.70	163	11

* ACR/PVC = 6/4; PAM-g-PBA/blend = 2 wt%

Table 6. Glass transition temperatures of the blends with or without the addition of 2 wt% graft copolymer as compatibilizer

Blends	Amount of graft copolymer	$T_g1(^{\circ}\text{C})$	$T_g2(^{\circ}\text{C})$	$\Delta T_g(^{\circ}\text{C})$
ACR/PVC	0	-17.3	95.3	112.6
ACR/PVC	2 wt% PAM-g-PBA*	-18.6	91.0	109.6

* 47.2 wt% PBA

Table 5 also shows that when the graft copolymer contains 33.5 wt%–47.2 wt% PBA, the ACR/PVC blends have higher tensile strength and ultimate elongation than those with the other compositions.

T_g of the blend containing 2% graft copolymer, obtained by DSC curve, indicates a larger inward shift of T_g s compared with those of the blends without the graft copolymer, as shown in Table 6. Obviously, the

improvement of mechanical properties is due to the improved compatibility between the PBA side chains and the ACR phase, both containing acrylate groups, and also the hydrogen bonding interaction between PAM main chain and PVC phase.

SEM micrographs (Fig. 6) indicate that the surface of the broken section of the ACR/PVC blend with 2% PAM-g-PBA is smoother than that without PAM-g-PBA. This may probably be due to the improved adhesion between the surfaces of the two phases via the compatibilizer.

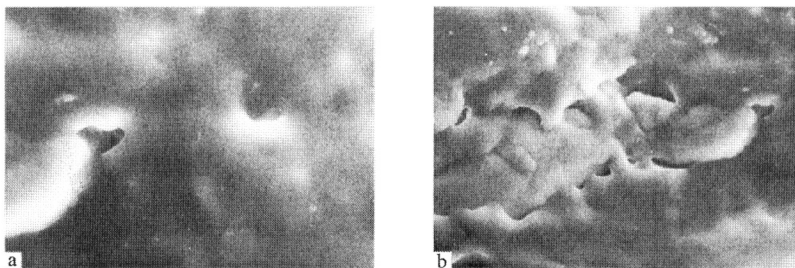


Fig. 6 SEM micrograph of ACR/PVC (6/4 W/W) blends
a) With 2% PAM-g-PBA; b) Without PAM-g-PBA (with magnification of 600)

CONCLUSION

PAM-g-PBA, obtained by copolymerization of PBA macromer with AM, is amphiphilic. It can emulsify toluene/water system and form O/W type emulsion. Its water absorbency can reach about 260%. DSC curves and TEM micrographs demonstrated the existence of two T_g s and phase separation in the graft copolymers, respectively. This kind of graft copolymer can act as a compatibilizer in polymer blending of ACR/PVC. 2%–3% of the graft copolymers based on the blend show the optimum effect on the improvement of mechanical properties of the blends. Both DSC curves and SEM micrographs demonstrated the improved compatibility between ACR and PVC by using PAM-g-PBA as the compatibilizer.

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