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Synthesis, Characterization and Application of Amphiphilic Copolymer Poly(vinyl alcohol)-g-Poly(butyl acrylate)

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An amphiphilic graft copolymer poly(vinyl alcohol)-g-poly(butyl acrylate) (PVA-g-PBA) was synthesized by grafting butyl acrylate (BA) onto poly(vinyl alcohol) (PVA) with potassium persulfate (KPS) as free radical initiator in N₂ atmosphere and aqueous medium. The formation of graft copolymer was confirmed by means of infrared spectroscopy (IR). The influences of initiator, monomer concentration and reaction time on the percentage of monomer conversion (C_M), graft degree (G_d) and graft efficiency (G_e) have been discussed in detail. PVA-g-PBA was used as compatibilizer in blends of chlorinated polyethylene (CPE)/ poly(acrylic acid-co-acrylamide)[P(AA-AM)], and the compatibility between CPE and P(AA-AM) was also investigated.

Keywords: Poly(vinyl alcohol), butyl acrylate, potassium persulfate, graft copolymerization

1 Introduction

Amphiphilic copolymers have been used for versatile applications in recent decades, such as the delivery and release of drugs, agrochemistry, personal care, and food products. As a result, the design, synthesis, and characterization of amphiphilic copolymers have become one of the most significant research areas in the polymer sciences (1,2). Especially in the field of polymer alloys, amphiphilic graft copolymers modify interfacial properties and dramatically enhance compatibilities of immiscible polymers (3–7).

Poly(vinyl alcohol) (PVA) is a well-known biomedical polymer and biocompatible. It is also a water-soluble and good film-forming polymer, which contains plenty of hydroxyl groups. Grafting vinyl monomers onto poly(vinyl alcohol) (PVA) can be traced back to the 1950's (8), and plenty of work has been done in this field. Chiang et al. (9–15), did a series of studies about graft copolymers prepared with PVA, such as grafting maleic anhydride, acrylonitrile, methyl methacrylate-co-maleic anhydride and methyl methacrylate-co-imide, etc. Several different methods were adopted in these studies. The graft copolymerizations were carried out in a dimethyl sulfoxide (DMSO) solution with different initiation systems, for example, potassium persulfate (KPS), azodiisobutyronitrile (AIBN).

It is a universally accepted opinion that Ce⁴⁺ is an effective initiator for graft copolymerization of polymer containing hydroxyl group. R. Silberman et al. (16) synthesized new graft copolymers by grafting benzyloxyethyl methacrylate, the benzyl ether of HEMA, on high-molecular weight PVA in DMSO solution with Ce⁴⁺ as initiator. S. Mishra et al. (17) grafted methyl methacrylate and acrylic acid monomers onto PVA using a Ce(IV)–glucose redox system at different temperatures, and more than 80% grafting could be achieved in the process. Ce⁴⁺ is used as high-grade catalyst in similar polymerizations, but it is an expensive reagent which would limit its applications in polymer synthesis.

In recent years, some novel methods or catalysts were employed in PVA modifications. The graft reaction of succinic anhydride onto poly(vinyl alcohol) (PVA) was catalyzed by p-toluenesulfonic acid monohydrate in solid state, and the solid-state graft reaction was carried out using a two roll mills (18). N. Guerrouani et al. (19) investigated the grafting of poly(ϵ -caprolactone) and poly(lactide) chains onto PVA backbone using MgH₂ environmental catalyst and melt-grown ring-opening polymerization (ROP) of ϵ -caprolactone and L-lactide, that avoiding undesirable toxic catalyst and solvent. Another article (20) described a process for esterifying PVA with L-lactide (LLA) and D,L-lactic acid (LA), using ethyl acetate and N,N'-dimethyl formamide at temperatures varying from 120 to 150°C. There are many novel aspects in these new reports, but some problems are also existent, such as complicated graft process, lower graft level etc.

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Poly(butyl acrylate) (PBA) could form long pliable side chains, which could improve the elasticity of copolymers. Grafting BA onto PVA can modify properties of PVA, and the graft copolymer PVA-g-PBA is an amphiphilic copolymer containing hydrophilic backbone and hydrophobic branched chains. In this research, BA grafting onto PVA was performed with potassium persulfate (KPS) as free radical initiator under N₂ atmosphere in aqueous medium, in which a familiar and cheap initiator was used compared with a redox initiator (21). Besides, the preparation adopted a facile and typical polymerization method. The influences of reaction factors, such as initiator concentration, monomer concentration and reaction time on grafting were discussed in detail. Blending type water-swallowable rubber (WSR) is a sort of elastic caulking material involving rubber matrix, super-absorbent resin (SAR) and certain additives (such as compatibilizers, reinforcing agent, vulcanizer and so on), which is prepared by mechanical blending. PVA-g-PBA was used as compatibilizer in blends of chlorinated polyethylene (CPE)/poly(acrylic acid-co-acrylamide) [P(AA-AM), a sort of SAR] for preparing WSR, and the compatibility between hydrophilic P(AA-AM) and hydrophobic CPE was also investigated.

2 Experimental

2.1 Materials

PVA (analytical reagent) with an average degree of polymerization 1750 ± 50 and molecular weight 8×10^4 was purchased from Bodi Chemical Co. Ltd., Tianjin, China. BA was distilled under reduced pressure to remove the inhibitor and KPS was recrystallized from methanol before use (analytical reagent, Sinopharm Chemical Reagent Co., Ltd). CPE (135A, Cl-35%) powder used in this work was obtained from Weifang Yaxing Chemical Co. Ltd. (Shandong, China), dried in oven at 50°C before use. SAR, P(AA-AM) was synthesized in our laboratory in advance according to previous publications (22, 23), and all the reagents were used as received (chemical purity and special grade for analysis).

2.2 Synthesis of PVA-g-PBA

2.2.1. Synthesis procedure

The graft reactions were carried out in a four-necked, round-bottom flask of 250 mL capacity, fitted with a mechanical stirrer, a N₂ gas inlet, thermometer and a reflux condenser. The reaction temperature was controlled by a constant-temperature water bath. A known amount of PVA was dissolved in 80 ml distilled water in the flask. Before a required amount of KPS solution in 10 ml H₂O was added into the flask, the solution was stirred, flushed slowly with N₂ for 30 min and adjusted to reaction temperature under N₂; BA was then added slowly by a drop funnel. The re-

action temperature was raised and kept at 70°C for several hours to the end in N₂ atmosphere. Acetone was added in excess to precipitate the polymer. The crude products were filtered and dried under vacuum. The dried products were extracted with acetone by means of a Soxhlet extractor for 48 h to remove the homopolymer of BA and then the remaining products, pure graft copolymers, were dried under vacuum and recorded weights.

2.2.2. C_M, G_d and G_e

Percentage of monomer conversion (C_M), graft degree (G_d) and graft efficiency (G_e) were calculated by the following equations:

$$C_M = (W_3 - W_1) / W_2 \times 100\%$$

$$G_d = (W_4 - W_1) / W_1 \times 100\%$$

$$G_e = (W_4 - W_1) / (W_3 - W_1) \times 100\%$$

W₁, W₂, W₃ and W₄ are the weight of used PVA, weight of used BA, dry weight of crude products and dry weight of pure grafted products, respectively.

2.3 Blending

CPE, P(AA-AM), and the compatibilizer, PVA-g-PBA, were fed to an open mill (Φ160 mm, linear rate of front roll 10.97 m/min, linear rate ratio of front roll to rear roll 1/1.35) in a lump and masticated at 140°C for 15 min. The compound was put in an 150 mm × 150 mm × 1 mm mold, preheated for 5 min, and cured for 30 min at 150°C in a 15 MPa press vulcanizer. After that, the mold was taken out and cooled to room temperature. Thus, the sheets of water-swallowable rubber were obtained.

2.4 Characterization

2.4.1. Amphiphilicity

The hydrophilicity and hydrophobicity of PVA-g-PBA were investigated by being immersed in distilled water and toluene, respectively. The samples of different G_d, about 0.5 g wt, were soaked in liquid for several hours. After reaching the equilibrium state, they were removed, and weighed after gently absorbing the excess liquid on the surface with tissue paper. The weight of samples in equilibrium state were recorded. The amphiphilicity was described by Q_e in different liquid as the following equation:

$$Q_e(\text{g/g}) = (M_e - M_0) / M_0$$

M_e and M₀ are mass of reaching equilibrium state and before soaking liquids of samples, respectively.

2.4.2. IR spectra

IR spectra of the pure PVA and the graft copolymer in KBr pellet specimen were recorded on a Perkin-Elmer Spectrum One spectrometer.

2.4.3. Mechanical properties tests

The sheets of WSR were cut into standard specimens using dumbbell die cut. Following the Chinese standard GB/T 1040-92, tensile testing of dumbbell shaped specimens was performed by using an AG-10KNA electronic universal tester (Shimadzu Corporation, Japan) at a tensile rate of 20 mm/min before water swelling and after water swelling for 12 h. The reported results of tensile strength (σ , MPa) and breaking elongation rate (ε , %) are the average of 10 tests.

2.4.4. Atomic force microscope measurement

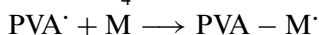
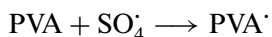
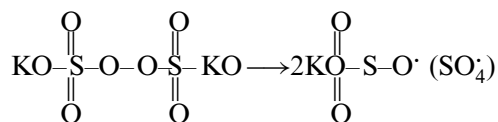
The surfaces of the WSR samples were observed by atomic force microscopy (AFM) in the tapping mode (NanoScope IIIa, Digital Instruments Inc.).

3 Results and Discussion

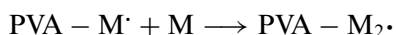
3.1 Reaction Mechanism

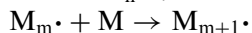
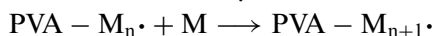
The graft copolymerization of BA onto PVA with potassium persulfate as an initiator is proposed to occur according to following mechanism:

1. Initiation



2. Propagation



$$\vdots$$


3. Termination

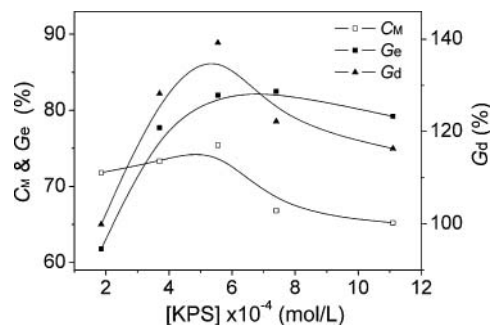
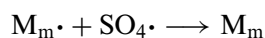
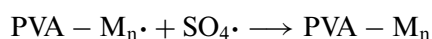
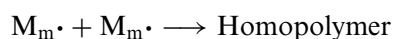
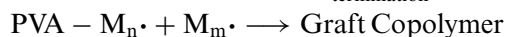
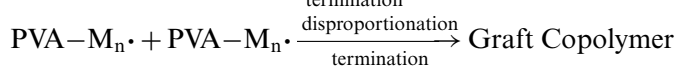
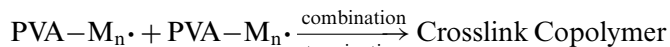


Fig. 1. Effect of [KPS] on C_M , G_d and G_e ; [PVA] = 2.5×10^{-4} mol/L, [BA] = 0.35 mol/L, 70°C, 4 h.

3.2 Influences of Reaction Factors

3.2.1. Effect of initiator concentration

The influence of KPS concentration ([KPS]) on grafting is shown in Figure 1. C_M , G_d and G_e increase initially and then decrease with a further increase in initiator concentration. This is a typical behavior shown by a grafting reaction occurring via chain transfer. The initial increase is due to an increase in the concentration of radicals formed through the decomposition of KPS. Thus, the higher [KPS], the higher the chain transfer to the polymer, and the higher C_M , G_d and G_e will be. However, with a further increase in [KPS], the decrease of C_M , G_d and G_e may be determined by the increased mutual termination reactions. These two opposite tendencies result in the appearance of the maximum.

3.2.2. Effect of monomer concentration

Figure 2 shows the effect of BA concentration ([BA]) on grafting. C_M , G_d and G_e all increase initially and then decrease. This is a possibility because, when [BA] is at a lower level, the polymerizing probability of each radical site on PVA promotes with increasing [BA]. On the other hand, with a further increasing of [BA], the viscosity of the solution increases, decreasing the diffusion rate of radicals attacking the PVA backbone, resulting in more homopolymerization and termination reactions.

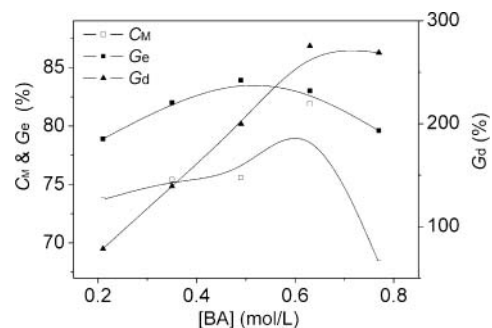


Fig. 2. Effect of [BA] on C_M , G_d and G_e . [PVA] = 2.5×10^{-4} mol/L, [KPS] = 5.55×10^{-4} mol/L, 70°C, 4 h.

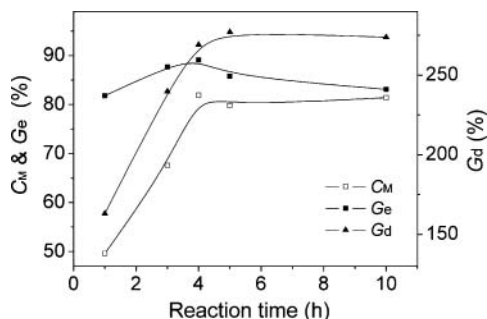


Fig. 3. Effect of reaction time on C_M , G_d and G_e . [PVA] = 2.5×10^{-4} mol/L, [BA] = 0.63 mol/L, [KPS] = 5.55×10^{-4} mol/L, 70°C.

3.2.3. Effect of reaction time

C_M , G_d and G_e increase with reaction time as shown in Figure 3. As reaction time was prolonged, more monomers could graft onto PVA backbone, and 4–5 h is long enough for this polymerization.

3.3 Characterization

3.3.1. Amphiphilicity

Figure 4 exhibits the influence of G_d on Q_e in distilled water and toluene. The higher G_d of PVA-g-PBA, the lower Q_e in water, and the higher Q_e in toluene. It is obviously caused by the fact that PBA is a hydrophobic segment, and the absorbing ability in toluene increases with increasing BA mass fraction.

3.3.2. IR spectra

IR spectra of (a) pure PVA and (b) PVA-g-PBA (extracted with acetone) are shown in Figure 5. The IR spectrum of PVA shows absorption bands at 3000–3600 cm^{-1} (strong, very broad, –OH stretching), caused by intermolecular hydrogen bonds among the hydroxyl groups. The curve of PVA-g-PBA reveals a weakened and narrowed absorption band at 3350 cm^{-1} (attributed by –OH of PVA), and a strong absorbency at 1733 cm^{-1} which is characteristic of –C=O

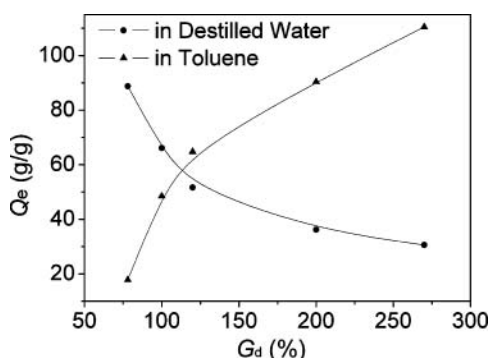


Fig. 4. Influence of G_d on Q_e in distilled water and toluene.

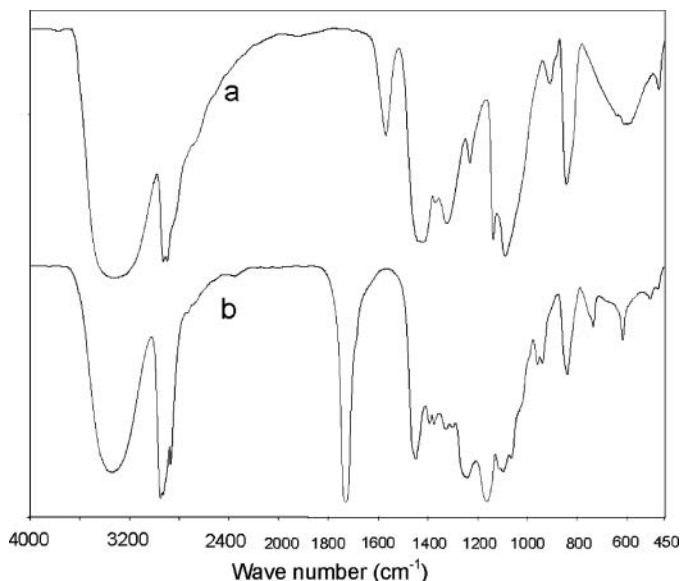


Fig. 5. IR spectra of pure PVA (a) and PVA-g-PBA (b).

stretching in BA. The formation of PVA-g-PBA copolymer could be confirmed.

3.4 Compatibilized Action of PVA-g-PBA on CPE/P(AA-AM) Blend

3.4.1. Mechanical properties tests

Table 1 shows the mechanical properties of WSR with different compatibilizers and in a different hydrous state. The tensile strength of WSR was increased after adding the compatibilizer. For example, with adding 6 phr PVA-g-PBA, tensile strength of WSR₁ in dry state was increased to 6.2 MPa compared to 3.2 MPa (without compatibilizer). This is obviously because the graft copolymer increased the cohesive force between CPE and P(AA-AM). PVA-g-PBA could improve the morphological structure and form an interaction between CPE and P(AA-AM). But when it was excessive, the mechanical properties decreased with

Table 1. Influence of compatibilizer on mechanical properties of WSR after swelling

	PVA-g-PBA/phr				
	0	3	6	9	12
*WSR1					
σ (dry)/MPa	3.2	6.0	6.2	5.5	5.5
ε (dry)/%	341	815	832	754	676
WSR2					
σ (dry)/MPa	3.2	5.0	5.6	6.1	5.1
ε (wet)/%	341	751	831	856	748

*WSR₁ and WSR₂ are compatibilized with PVA-g-PBA of 78% G_d and 270% G_d , respectively. CPE:100 phr, P(AA-AM):40 phr.

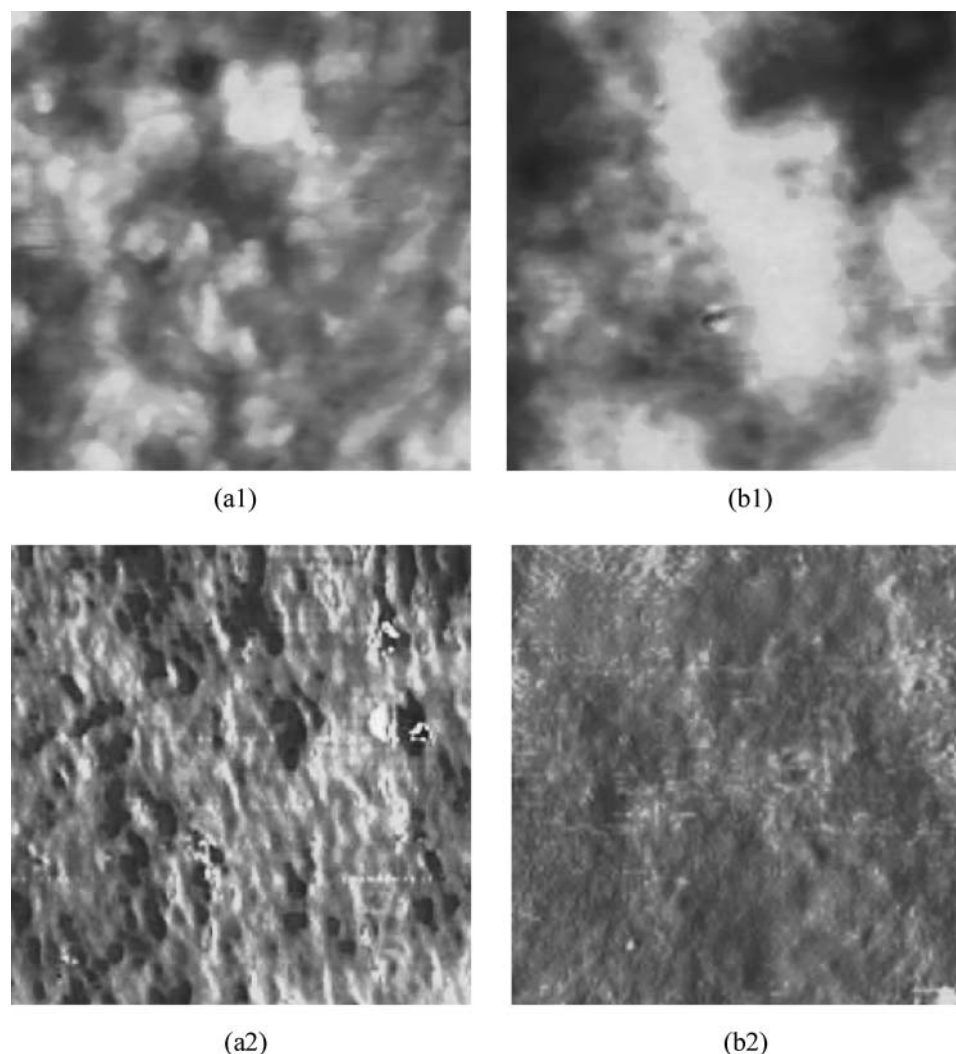


Fig. 6. AFM micrographs of WSR: (a) CPE, 100 phr; P(AA-AM), 40 phr; (b) CPE, 100 phr; P(AA-AM), 40 phr; PVA-g-PBA (78% Gd), 6phr; (1) height images; (2) phase images. Scanning scale is 5 μm .

increasing the amount of compatibilizer. This is because adding excessive PVA-g-PBA caused the interface layer to become thicker and its constitution to change. The interaction becomes lax and the delivery stress weakens, therefore, the tensile strength decreases.

PVA-g-PBA of 78% Gd performed better than that of 270% Gd in compatibilizing. It is obvious that higher Gd means a higher mass fraction of hydrophobic segments. PVA-g-PBA of 270% Gd of the same weight contained less hydrophilic PVA and -OH, which could build less interaction between the two phases, therefore, WSR₂ had poorer mechanical properties.

3.4.2. AFM

From the micrographs of AFM in Figure 6, it is obvious that there is a great difference between the morphologies of the sample with PVA-g-PBA and without PVA-g-PBA. The presence of compatibilizers improved the uniformity of

dispersed phase, P(AA-AM), and the phase size decreased dramatically.

4 Conclusions

Butyl acrylate can be easily grafted onto poly(vinyl alcohol) backbone with potassium persulfate as initiator in an aqueous medium. Weight gains and IR confirmed the formation of graft copolymer. The highest graft degree of the copolymer could reach 275% at a optimum condition, which is as follows: [PVA] = 2.5×10^{-4} mol/L, [BA] = 0.63 mol/L, [KPS] = 5.55×10^{-4} mol/L, 70°C, 5 h. Moreover, the percentage of monomer conversion and graft efficiency are also considerable, which could provide practical value in the polymer industry. PVA-g-PBA could bring significant amelioration in compatibility of a blending type WSR, which could also improve its mechanical properties.

Acknowledgments

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