Colloids and Surfaces A 540 (2018) 11–22

Contents lists available at ScienceDirect

Colloids and Surfaces A

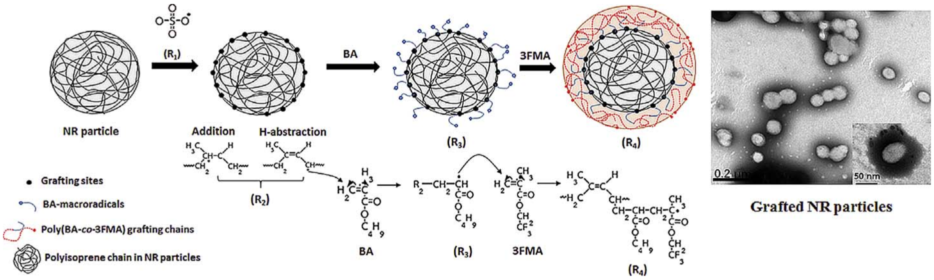
journal homepage: www.elsevier.com/locate/colsurfa

Poly(butyl acrylate-*co*-fluorinated acrylate)-*graft*-natural rubber: Synthesis and application as compatibilizer for natural rubber/poly(butyl acrylate-*co*-fluorinated acrylate) films

Kotchamon Yimmut[a], Kritiya Homchoo[a], Napida Hinchiranan[b,c,*]

[a] *Program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*
[b] *Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*
[c] *Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok 10330, Thailand*

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Fluorinated acrylate
Butyl acrylate
Natural rubber latex
Graft copolymerization
Mechanical properties
Surface properties

ABSTRACT

Poly(butyl acrylate-*co*-fluorinated acrylate)-*graft*-natural rubber was successfully prepared via emulsion graft copolymerization and applied as a compatibilizer for improving phase compatibility and toughness of natural rubber/poly(butyl acrylate-*co*-fluorinated acrylate) films. From graft copolymerization step, butyl acrylate (BA) acted as a co-monomer to be initially grafted onto the natural rubber (NR) and then copolymerized with 2,2,2–trifluoroethyl methacrylate (3FMA) to form a grafting poly(BA-*co*-3FMA) chain onto the NR backbone. The appropriated BA/3FMA ratio at 30/70 (w/w) provided the highest graft copolymer fraction of 72.8 wt% with 25.3 mol% grafted 3FMA and 68.5% grafting efficiency under center reaction condition. Transmission electron microscopy analysis indicated that the graft product had core-shell morphology, which NR was a core and covered by poly(BA-*co*-3FMA) shell. The results from Molau test and atomic force microscopy showed that the addition of 5–10 wt% graft product could enhance the compatibility between NR and poly(BA-*co*-3FMA) phases in the NR/poly(BA-*co*-3FMA) films (20/80 (w/w)) and provided the obtained films with a greater elongation at break to 266% than that of poly(BA-*co*-3FMA) film (27%). The compatibilized films also exhibited a high hydrophobicity (water contact angle = 109°) and oleophobicity (hexadecane contact angle = 54°) with a low surface energy (8.04 mN/m), which can be further applied as self-sealing films for moisture and oil protection.

---

* Corresponding author at: Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.
E-mail address: napida.h@chula.ac.th (N. Hinchiranan).

https://doi.org/10.1016/j.colsurfa.2017.12.062
Received 31 October 2017; Received in revised form 25 December 2017; Accepted 26 December 2017

1. Introduction

Fluorinated polymers have been applied in various applications owing to their superior performance, such as a high thermal stability, chemical inertness, excellent resistance to weather attack and superb water and oil repellence. These properties result from the strong electronegativity of the fluorine atoms in the fluorine-containing groups in these polymers, which provide a low surface energy. Thus, they are normally applied as the non-wettable coating on many substrates such as textile, paper or glass including silicon wafer [1–3]. Moreover, they can be used as the protective films for outdoor applications such as the solar cell backplane [4].

The fluorinated polyacrylates are a kind of fluorinated polymers. They do not only provide such above properties, but their acrylic group can provide these polymers to adhere well various substrates [2]. Poly (2,2,2-trifloroethyl methacrylate (P3FMA), a member of fluorinated polyacrylates, can easily be polymerized via a free radical mechanism of 2,2,2-trifloroethyl methacrylate (3FMA) monomer with 34% fluorine content in bulk, solution or emulsion processes to form P3FMA or its copolymers [5,6]. Although P3FMA has a high performance in coating applications, the disadvantage of this polymer is its high glass transition temperature (T_g) at ca. 77–82 °C that results in a poor elasticity with inferior film-foaming properties [6,7]. Moreover, it is expensive, which limits its use in large scale applications [6]. To solve these problems, the introduction of $-CH_2CH_2O-$ functional group into the fluorinated side chain to form 2-(2,2,2-trifluoroethoxy)ethyl methacrylate (FEMA) significantly decreased the T_g from 81.2 °C for P3FMA to 13.0 °C for PFEMA while retaining a good hydrophobicity (water contact angle = 99.9°) [7]. The copolymerization of 3FMA with other monomers, such as methyl methacrylate (MMA) and butyl acrylate (BA), could also reduce the cost and improve the mechanical properties of the obtained copolymer products [8]. However, MMA is also classified as a rigid polymer due to its high T_g (ca. 94 °C) [9]. Thus, MMA should not be used alone for copolymerization with 3FMA. Rather, BA has been suggested as another co-monomer since the T_g of poly(BA) (PBA) is in the range of −55 to −42°C [10] and so it is expected to decrease the T_g of the final copolymer and allow flexible copolymer film formation.

The alternative way to increase the toughness of rigid polymers is to blend them with elastomeric materials. Among the engineering elastomers, natural rubber (NR), one of bio-based elastomers with excellent mechanical performance and a low T_g (ca. −61 °C) [11], is most widely studied for this purpose. However, the polarity difference between NR and polymers normally induces phase separation and causes inferior properties of the finished products. To reduce the interfacial tension between constituents in the rubber-polymer blends, NR is modified via graft copolymerization with vinyl monomers, which are compatible to the polymer phase in the blends. The obtained graft NR (GNR) can be then applied as the compatibilizer or impact modifier for NR/brittle polymers, such as poly(lactic acid) [11,12], polypropylene [13] and poly(vinyl chloride) [14], or NR/polar fillers, such as silica and nanoclay [15].

Graft copolymers of NR can be normally prepared via melt mixing, solution and emulsion processes. In the case of grafting of fluorinated acrylate monomers onto the NR structure, it has been reported that the graft copolymer could be prepared via argon plasma treatment followed by UV-induced graft copolymerization of 2,2,3,3,4,4,4-heptaflurobutyl acrylate onto the NR film for increasing its water contact angle to 109° [16]. Moreover, Hinchiranan et al. [17] synthesized P3FMA-*graft*-NR via solid-state graft copolymerization without the assistance of co-monomer for using as a compatibilizer for NR/fluoroelastomer vulcanizates. Although this technique was easy for commercialization, a high reaction temperature was required (> 80 °C) and this severe condition could promote a high level of gel formation (ca. 20–90%) in the obtained graft product with only a 1.34% maximum grafting efficiency (GE). To overcome these problems, this current study focused on the graft copolymerization of P3FMA onto the NR backbone in the latex state due to the availability of NR latex being cheaper than the solid form. Besides, this process provides a good heat transfer control to promote a fast polymerization rate in the presence of a lower reaction temperature (50–80 °C, depending on the initiator type). Because the polarity difference between NR and the 3FMA monomer would obstruct the direct grafting of P3FMA onto the NR structure, BA was selected as a co-monomer to enhance the GE of this system since BA can be grafted onto the NR backbone [11] and copolymerized with 3FMA [8]. The effects of the BA/3FMA wt ratio, potassium persulfate (KPS) initiator concentration, reaction temperature and reaction time on the monomer conversion, grafting properties and GE of the graft product were investigated. The morphology of the NR latex before and after graft copolymerization was comparatively observed. The obtained GNR was then applied as the compatibilizer for NR/poly(BA-*co*-3FMA) films. The compatibility, mechanical performance, thermal and surface properties of the film products were also examined.

2. Experimental

2.1. Materials

High ammonia preserved NR latex with 60% dry rubber content (DRC) was purchased from the Rubber Research Institute (Bangkok, Thailand). The 3FMA monomer with 99% purity was obtained from Sigma-Aldrich (USA) and used as received, while BA monomer (99% purity, Merck, USA) was purified with 10% (w/v) sodium hydroxide (NaOH; QREC, New Zealand) to remove inhibitors. Sodium dodecyl sulfate (SDS) and isopropanol (IPA) were purchased from QREC (New Zealand). Potassium hydroxide (KOH) and KPS, used as the buffer and initiator, respectively for graft copolymerization, were received from Ajax Finechem (Australia). Toluene, acetone and light petroleum ether were obtained from Fisher Scientific (Leicestershire, UK). All chemicals used in this research were analytical grade. Nitrogen (N_2) gas (commercial grade with 95% purity) was manufactured by Praxair, Inc. (Thailand).

2.2. Graft copolymerization of poly(BA-co-3FMA) onto NR latex

Graft copolymerization of NR with poly(BA-*co*-3FMA) in the latex stage was performed in a 100-mL three-necked round-bottle flask. The NR latex was diluted with distilled water to 30% DRC and then mixed with 0.25 parts per hundred of rubber (phr) KOH and 0.1 phr SDS. The mixture was stirred under N_2 atmosphere at room temperature for 15 min, whereupon 10 phr IPA was added as the stabilizer and left with stirring for 30 min. Then, 100 phr BA/3FMA monomer mixture at various wt ratios (0/100 – 100/0) was charged into the system under stirring followed by heating the system to the desired reaction temperature (50–80 °C). The graft copolymerization was initiated by introducing KPS at given concentrations (0.5–2.0 phr) and the reaction proceeded for 4–10 h. After completion of grafting, the graft NR (GNR) in the latex form was directly casted on a glass mold (10 × 10 × 0.3 cm), dried in a vacuum oven at 40 °C and then washed with distilled water to remove the unreacted monomers and dried at 40 °C in a vacuum oven to a constant weight. The components of the dry casted product, such as free NR, free copolymer and NR grafted with poly(BA-*co*-3FMA) (NR-*g*-poly(BA-*co*-3FMA)) called as graft copolymer fractions were distinguished using sequential soxhlet extraction. The free NR and free copolymer portions were removed using light petroleum ether and acetone, respectively, for 24 h and then dried at 40 °C in a vacuum oven for each extraction step to a constant weight. The final residual matter was the graft copolymer product. After soxhlet extraction, the degrees of monomer conversion and GE were calculated following Eqs. (1) and (2), respectively:

$$\text{Conversion}(\%) = \frac{\text{Weight of total polymer formed}}{\text{Weight of monomer charged}} \times 100 \qquad (1)$$