



Compatibilization of poly(vinylidene fluoride)/natural rubber blend by poly(methyl methacrylate) modified natural rubber

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ABSTRACT

Natural rubber-grafted-poly(methyl methacrylate) (NR-g-PMMA) was successfully synthesized using emulsion polymerization technique. NR-g-PMMA with various PMMA levels was further blended with poly(vinylidene fluoride) (PVDF) at the fixed 50/50 wt% blend ratio, as simple blend or as dynamically cured blend. The compatibilization efficiency in the blend improved significantly with PMMA level. The morphological evaluation indicated that grafting PMMA onto NR reduced the domain size in the blend, resulting in improved mechanical and rheological properties. The enhanced properties were attributed to strong interactions between PVDF and NR-g-PMMA. Furthermore, the mechanical properties improved with PVDF content, consistent with the blend morphology. In addition, thermal analysis revealed low crystallinity in the blend, which corresponds to the molecular interactions of PVDF and grafted PMMA in NR-g-PMMA.

1. Introduction

In the past decade, thermoplastic elastomers (TPEs) produced by blending a thermoplastic with an elastomer have been proven as an alternative type of elastomeric materials, which has been widely adopted in many applications. The major characteristic of TPE is its behavior characteristics between thermoplastic and thermoset rubber. Therefore, TPEs exhibit rubber-like properties (i.e., good elastic recovery and high elongation at break) at room temperature, while at melting temperature TPE can be melt-processed like a thermoplastic. A thermoplastic-elastomer blend produced by dynamic vulcanization is known as a Thermoplastic Vulcanizate or TPV, in which the elastomer phase is selectively crosslinked under intensive mixing. This process provides TPE with superior mechanical properties and elasticity. Various binary thermoplastic-elastomer blend systems have been studied extensively over the last few years. However, a non-polar elastomer and a polyolefin are generally selected to prepare a TPV. Polypropylene (PP)/ethylene propylene diene rubber (EPDM) blend is the most conventional commercialized TPV because of the good compatibility between PP and EPDM phases without need for a compatibilizer. A disadvantage of polyolefin based TPE or TPV is poor resistance to oil and heat. Therefore, to improve upon such conventional

TPV, a variety of engineering-thermoplastics have been employed/ tested for TPV, such as polyamide-12 (PA12) [1–3], poly(ethylene terephthalate) (PET) [4] and poly(vinylidene fluoride) [5,6]. Chatterjee et al. have investigated Super-TPV based on carboxylated acrylonitrile butadiene rubber (XNBR) and PA12 blend. They found that cross-linked XNBR was dispersed in the PA12 matrix after dynamic vulcanization with a rubber domain size of 0.5–2.0 μm. Moreover, the XNBR/PA12 TPV showed superior mechanical properties and oil resistance when compared to a not crosslinked blend [3].

Poly(vinylidene fluoride) or PVDF is a homopolymer produced by polymerization of vinylidene fluoride monomers. The simple repeating unit in PVDF (i.e., $-(CH_2-CF_2)_n-$) is intermediate between that in polyethylene (PE) and poly(tetrafluoroethylene) (PTFE). PVDF belongs to the class of highly crystalline thermoplastics, with typical 50–70% crystallinity, and depending on preparation method can contain at least four distinct crystal polymorphs named α , β , γ and δ . Since PVDF has excellent mechanical properties and good resistance to chemicals, UV radiation and weathering, it is classified as an engineering thermoplastic [7]. Moreover, the β -crystalline phase in PVDF has piezo-, pyro- and ferroelectric properties, which is unique among polymeric materials. Due to its unique properties, PVDF has been widely studied in polymer composites and blends for many applications, especially as an

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advanced material for sensors and actuators [8], energy harvesting [9], giant permittivity composites [10,11], and polymer electrolytes [12]. Some studies on TPV based on PVDF-elastomer blend have been reported, and have been of considerable interest in recent years [6,13,14], making a new type of TPV. Li and co-workers succeeded in developing oil resistant TPV based on PVDF/acrylic rubber (ACM) blend. A unique morphology was observed in this blend, in which PVDF chains crystallize and segregate out as crystal lamellae in ACM particles. For that reason, PVDF/ACM TPV showed excellent physical properties, strain recovery and oil resistance [6]. However, blends of natural rubber (NR) and PVDF for TPV have rarely been studied. Blends of these two different polarity polymers have phase separation due to incompatibility, which is responsible for the poor mechanical properties. From our previous studies, it was clear that PVDF is compatible with epoxidized natural rubber (ENR), and PVDF/ENR blend showed excellent mechanical properties [15–17]. Indeed, it is well known that PVDF/poly(methyl methacrylate) (PVDF/PMMA) blend has been a popular system for decades because PVDF is miscible with PMMA, due to dipole-dipole interactions [18]. Such strong interactions between PVDF and PMMA could also enhance the compatibility of PVDF and NR when using natural rubber-grafted-PMMA. Graft copolymerization of NR with PMMA has been widely studied and successfully performed. After grafting, polarity, oil resistance and heat resistance of NR are improved. Moreover, the presence of grafted PMMA on NR backbone chains is expected to significantly enhance the compatibility with PVDF, resulting blends with superior mechanical properties. TianKhoon et al. studied polymer electrolytes based on PVDF/NR-g-PMMA doped with lithium trifluoromethanesulfonate (LiCF_3SO_3) [19]. They found that PVDF/NR-g-PMMA blend exhibited good electrical properties with the addition of LiCF_3SO_3 , making it suitable for electrochemical devices. However, until now there is no report on morphology and mechanical properties of PVDF/NR-g-PMMA blend prepared via simple blend or via dynamic vulcanization. The novelty in this work was primarily the aim to achieve significantly enhanced compatibility between PVDF and NR by using a graft copolymer of natural rubber, and to thereby extend the use of that graft copolymer of natural rubber to a new family of high-performance TPV.

In recent studies, NR-g-PMMA rubber was synthesized through emulsion polymerization. The main objective of the present work was to use NR-g-PMMA rubber for the preparation of PVDF/NR-g-PMMA blend with and without dynamic vulcanization. The blending of PVDF with NR-g-PMMA having various PMMA levels was investigated. This study focused on the improvement of compatibility between PVDF and NR by PMMA grafted on NR backbones. While the PVDF/NR blend is immiscible, possibly the enhanced interfacial molecular interactions between the two phases would improve the compatibility. The phase structure of the blend was evaluated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In addition, the mechanical properties, rheology, and thermal properties of PVDF/NR-g-PMMA blends were examined to confirm the effects of grafted PMMA in NR on compatibility and phase development in the blend.

2. Experimental

2.1. Materials

High ammonia (HA) concentrated latex containing 61% dry rubber was manufactured by Yala Latex Co., Ltd. (Thailand). Methyl methacrylate (MMA) monomer used to prepare graft copolymer was manufactured by Sigma-Aldrich (USA). The MMA was purified by a standard procedure before synthesis. Cumene hydroperoxide (CHP) and tetraethylene pentamine (TEPA) used as redox initiators were manufactured by Fluka (Buchs, Switzerland). The 20% potassium laurate used to stabilize the latex was prepared by a reaction between lauric acid and potassium hydroxide. PVDF (KYNAR 740) used as blend component was purchased from Arkema, France. Phenolic resin (HRJ-10518) curing agent, was manufactured by

Table 1
The formulations used in the emulsion polymerization of NR-g-PMMA.

Chemical	NR/MMA ratio		
	95/5	90/10	80/20
61% HA latex (wt%)	95	90	80
85% TEPA (phr [*])	1	1	1
20% K-laurate (phr [*])	1	1	1
99% MMA (wt%)	5	10	20
80% CHP (phr [*])	1	1	1

* phr = part per hundred rubber.

Schenectady International Inc., New Port, USA. Wingstay L used as anti-oxidant was manufactured by Eliokem Inc., OH, USA.

2.2. Preparation of NR-g-PMMA

Graft co-polymerization of natural rubber and methyl methacrylate (NR-g-PMMA) was done in-house by emulsion polymerization. The NR/MMA ratio for this study was set at 95/5, 90/10 or 80/20 wt%. The compositions used for polymerization are given in Table 1.

The high ammonia NR latex (61% DRC) was first added into a 1-L main reactor and stirred at 120 rpm under N_2 atmosphere. TEPA and K-laurate were then added into the main reactor, followed by distilled water to adjust the total solids content (TSC) to 50%. The reaction was carried out by stirring the latex for 30 min at 60 °C. After 30 min, the mixture of MMA and CHP, which was in a feeding tank, was added drop-wise into the main reactor over 1 h. The reactions were allowed to proceed for 3 h under continuous stirring. The graft copolymer latex was coagulated with methanol, washed with deionized water, and finally dried in an oven at 50 °C until constant weight. HA latex without polymerization was also coagulated and subsequently dried for comparison. The purified NR and NR-g-PMMA were examined for the presence of grafted PMMA by ^1H NMR. The synthesis route and the NMR spectra of NR-g-PMMA are shown in Fig. 1. The mole percentage of PMMA on NR was calculated from integrated peak areas at 3.5 ppm and 5.1 ppm, as reported earlier [20]. The mole percentages of PMMA in NR-g-PMMA prepared with the alternative NR/MMA ratios are listed in Table 2. The graft co-polymers of NR and PMMA are denoted by NR-g-PMMA_x, where x is mol% of PMMA in NR-g-PMMA.

2.3. Blend preparation

Influence of PMMA level: In this study, two blending techniques were applied to prepare PVDF/NR-g-PMMA blends. The first one is called simple blend (SB), in which the polymers are blended without a vulcanizing agent. The second one blends the polymers with a vulcanizing agent to form a thermoplastic vulcanizate (TPV). Phenolic resin (HRJ-10518) was used as the vulcanizing agent in this study. NR and NR-g-PMMA with three PMMA levels (3.5, 12 and 23 mol%) were first compounded in an internal mixer at 60 °C using the composition presented in Table 3.

The PVDF/NR and PVDF/NR-g-PMMA_x blends with and without vulcanizing agent were prepared by melt mixing technique at a fixed blend ratio of 50/50 wt%. Blending of PVDF and NR-g-PMMA was performed in the 50 mL mixing chamber of an internal mixer (Brabender GmbH, Germany) at 180 °C at 60 rpm rotor speed. PVDF was first introduced into the mixer and mixed for 3 min, followed by addition of compounded NR-g-PMMA. After 8 min, the blend was discharged from the internal mixer.

Influence of blend ratio: In this part of the study, NR-g-PMMA₂₃ was selected to prepare dynamically cured PVDF/NR-g-PMMA blends. The blend ratios of PVDF/NR-g-PMMA₂₃ studied were 70/30, 60/40, 50/50, 40/60 and 30/70 wt%, and the mixing procedure was as described earlier.

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