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Catalyst driven preferential growth of in-situ generated nanosilica particles in the phases of incompatible polymer blend and its effect on physico-mechanical properties

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HIGHLIGHTS

- Preferentially growing in-situ nanosilica in the phases of rubber blend.
- Nanosilica precursor and catalyst are used for the generation of in-situ nanosilica.
- Using different types catalyst to preferentially grow in-situ nanosilica.
- In-situ nanosilica in dispersed phase significantly improves the properties.
- In-situ nanosilica in continuous phase does not significantly improve the properties.

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ABSTRACT

Selectively localizing nanofillers in a particular phase of polymer blend to achieve required properties are hardly possible. Herein, an approach to solve the above mentioned problem is reported by exploring the effect of catalyst in preferentially growing in-situ generated nanosilica particles in the phases of incompatible natural rubber (NR): carboxylated nitrile rubber (XNBR) (50:50) blend. In-situ generated nanosilica particles prepared using tetraethylorthosilane (TEOS) as silica precursor and *n*-butylamine (nBA) as catalyst preferentially grow in the dispersed non polar NR phase (due to the hydrophobic nature of the silica particles) and ultimately leads to significant enhancement in the blend properties. On the other hand, in-situ generated nanosilica particles prepared using TEOS as silica precursor and hydrochloric acid (HCl) as catalyst preferentially grow in the continuous polar XNBR phase (due to the hydrophilic nature of the silica particles) and ultimately does not increase the blend properties to a greater extent.

1. Introduction

In-situ generation of nanosilica particles into polymer matrix by sol-gel process has attracted attention in recent past in order to achieve better filler dispersion and improved composite properties [1]. In this method, the nanosilica particles have been generated by exploring the sol-gel chemistry which primarily consists of hydrolysis and condensation of a precursor in the sol-gel solution [2]. The properties of the composites prepared by this method depend on several factors like polymer type, nature of catalyst, silica precursor, reaction conditions etc [3]. The literature reveals that the in-situ formation of nanosilica particles results in formation of hybrid organic-inorganic materials with improved properties for many advanced applications, such as photochromatic materials, optical biosensors, and lasers [3].

Although conventional silica offers a number of advantages in the rubber compounds, its capability to provide same level of reinforcement, with reference to carbon black is limited due to strong filler-filler interaction [4–6]. This leads to high aggregation of silica particles in the rubber matrix which does not favor significant reinforcement because of poor polymer-filler interaction [7,8]. Hence, excellent polymer-filler interaction through homogeneous dispersion of fillers in polymer matrix is mandatory for significant reinforcement effect. Therefore, incorporation of nanosilica into rubber matrix by in-situ method has emerged to be very efficient technique in the past few years [9–12]. Numerous studies have been dedicated to investigate the potential of in-situ generated nanosilica particles for improving different

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properties of various rubber matrices such as natural rubber (NR) [13], epoxidised natural rubber (ENR) [14], nitrile rubber (NBR) [15,16], isoprene rubber (IR) [17,18], styrene butadiene rubber (SBR) [19], chloroprene rubber (CR) [20,21], acrylic rubber (ACM) [22,23] and polydimethylsiloxane rubber (PDMS) [24–27]. These improvements can include increased reinforcement and mechanical properties [13–23,25–27], increased storage modulus [14,15,18,19,21,22,24–27], increased thermal stability [26,27], increased tear resistance [21] and increased hardness [22,23].

There are relatively few papers in literature which examine the effect of in-situ generated nanosilica particles in rubber-rubber blends [28–31]. Kapgate et al. have studied the effect of sol–gel derived in-situ generated nanosilica particles on the mechanical behavior of NR/NBR blend [28]. In-situ generated nanosilica particles have been found to grow in the NR phase of the NR/NBR blend [28]. The in-situ generated nanosilica particles enhance the compatibility between the blend components and significantly improve the mechanical properties of NR/NBR blend in comparison to those of the unfilled and precipitated silica (ex-situ addition) filled NR/NBR blend [28]. Kapgate et al. have investigated the reinforcing efficiency and compatibilizing effect of sol-gel derived in-situ nanosilica for NR/CR blends [29]. In-situ generated nanosilica particles are preferentially located at the interface of the blend components [29]. The in-situ generated nanosilica particles enhance the compatibility between NR and CR which in turn significantly improve the physical properties of the blend when compared to the unfilled and externally silica filled NR/CR blend [29]. Bansod et al. have reported the controlled growth of in-situ silica in NR/CR blend prepared by sol–gel method [30]. In-situ generated nanosilica particles are homogeneously dispersed throughout the blend matrix [30]. The thermal and mechanical properties of the composites increases owing to the uniform distribution of in-situ generated nanosilica particles and improvement in the compatibility between the blend components [30]. It has been shown that addition of silane coupling agent during the in-situ generation of silica can lead to further increase in the properties [30]. Bansod et al. have studied the compatibilization of NR/NBR blend by sol-gel nanosilica generated by in-situ method [31]. In-situ generated nanosilica particles are mostly found in the NR phase [31]. It has also been shown that the in-situ generated nanosilica particles grow at the interface when silane coupling agent is used during sol–gel silica generation [31]. The growth of in-situ generated nanosilica particles at the interface enhances the compatibility of NR and NBR and leads to improvement in the mechanical properties of the composites [31].

From thorough literature search it is evident that there are many papers which discuss the effect of in-situ generated nanosilica particles on the physico-mechanical properties of the various rubber matrices. In addition, there are few reports in literature which address the effect of in-situ generated nanosilica particles on the compatibility and physical properties of rubber blends. However, there are no reports in literature which attempt to preferentially grow the in-situ generated nanosilica particles either in the continuous phase or in the dispersed phase of rubber blend and subsequently to decipher the effect of the selective localization of the nanosilica particles on the overall blend properties. Projected for the first time in literature, this work reports the catalyst driven preferential growth of in-situ generated nanosilica particles in the in the dispersed NR phase or in the continuous carboxylated nitrile rubber (XNBR) phase of the incompatible XNBR:NR (50:50) blend and its effect on the overall blend properties. Tetraethylorthosilane (TEOS) has been used as the precursor for generating in-situ nanosilica particles. N-butylamine (n-BA) or hydrochloric acid (HCl) has been used as the catalyst for generating nanosilica particles. Base catalyzed reactions generate higher percentage of in-situ hydrophobic nanosilica particles in the NR phase. On the other hand, acid catalyzed reactions generate higher percentage of in-situ hydrophilic nanosilica particles in the XNBR phase. It has been shown that the presence of higher percentage of in-situ generated hydrophobic nanosilica particles in the NR phase significantly improves the overall blend properties. However, the presence of higher percentage of in-situ generated hydrophilic nanosilica particles in the XNBR phase does not significantly improve the overall blend properties.

2. Experimental

2.1. Materials

Carboxylated acrylonitrile butadiene rubber (XNBR, Krynac X 750, acid content = 7.0%, acrylonitrile content = 27.0 ± 1.5%, specific gravity = 0.99, Mooney Viscosity, ML_{1+4} at 100 °C = 47 ± 5) was procured from Lanxess, Germany. Natural rubber, (NR, ISNR 3CV, Mooney Viscosity, ML_{1+4} at 100 °C = 63 ± 5) was procured from Rubber board, Kottayam, India. Tetraethylorthosilane (TEOS, density = 0.933 g/ml, boiling point = 168 °C), *n*-butylamine and concentrated hydrochloric acid (laboratory grade) were purchased from Acros Organics, USA. Toluene was purchased from Sigma-Aldrich, India. The vulcanizing agent for the rubbers, dicumyl peroxide (DCP, 99% pure), was procured from Sigma-Aldrich, India.

2.2. Synthesis of pristine nanosilica particles

A given amount of TEOS, water, ethanol (TEOS: water: ethanol = 1: 2: 4 mol) was taken in a clean glass beaker and *n*-butylamine or HCl (2 wt% or 8 wt% relative to the amount of TEOS, as catalyst for the sol process) is added to the mixture. The mixture was stirred for 10 min by a magnetic stirrer (1000 rpm at 25 °C). After completion of stirring, the mixture was poured into a flat glass petridish and dried in room temperature. The samples prepared are shown in Table 1.

2.3. Synthesis of pristine rubber films and rubber nanocomposite films

4 g of NR or 4 g of XNBR was dissolved in 80 ml of toluene and stirred thoroughly by a magnetic stirrer at 25 °C for 10 h at a speed of 1000 rpm. After completion of stirring, the rubber solution was poured on a glass petridish and dried for 4 days at room temperature. For preparing rubber nanocomposite films, the pristine rubber solutions (NR or XNBR) were prepared as per the procedure explained above. A given amount of TEOS, water, ethanol (TEOS: water: ethanol = 1: 2: 4 mol) and *n*-butylamine or HCl (2 wt% or 8 wt% relative to the amount of TEOS, as a catalyst for the sol process) were added to the rubber solutions (NR or XNBR). 30 wt% of TEOS was added to achieve 30 wt% of nanosilica content in rubber matrix. The mixture was stirred further using a magnetic stirrer for 9 h (1000 rpm at 25 °C). Once the stirring is completed, the rubber nanocomposite solution was poured into a glass petridish and dried in room temperature. The samples prepared are shown in Table 1.

2.4. Synthesis of pristine rubber-rubber blend film and rubber-rubber blend nanocomposite film

2 g of NR and 2 g of XNBR were dissolved in 80 ml of toluene and stirred thoroughly by a magnetic stirrer for 10 h (1000 rpm at 25 °C). Once the stirring is completed, the rubber-rubber blend solution was poured into a glass petridish and dried for 4 days. For preparing rubber-rubber blend nanocomposite films, the pristine rubber-rubber blend solutions were prepared as per the procedure explained above. A given amount of TEOS, water, ethanol (TEOS: water: ethanol = 1: 2: 4 mol) and *n*-butylamine or HCl (2 wt% or 8 wt% relative to the amount of TEOS, as a catalyst for the sol process) were added to the rubber-rubber blend solution. TEOS was added in various quantities (0, 10, 20, 30 and 40 wt %) to achieve 0 to 40 wt% of nanosilica content in NR/XNBR blend matrix. The mixture was stirred further using a magnetic stirrer for 9 h (1000 rpm at 25 °C). After completion of stirring, the rubber-rubber blend nanocomposite solution was poured into a glass petridish and dried in room temperature. In order to understand the effect of