



Self-formation of elastomer network assisted by nano-silicon dioxide particles: A simple and efficient route toward polymer nanocomposites with simultaneous improved toughness and stiffness



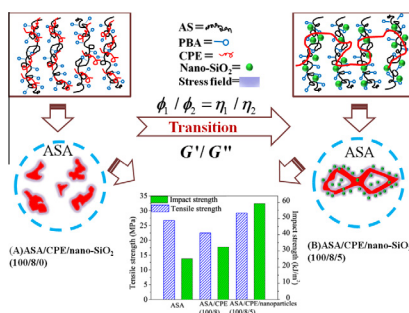
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HIGHLIGHTS

- An easy route toward polymers with simultaneous improved toughness and stiffness was proposed.
- A self-formed CPE network assisted by nano-SiO₂ was observed and verified.
- The self-formed CPE network was responsible for the improved mechanical performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Adding nano-fillers into plastic matrix have been proved to be a possible way to reinforce polymeric materials. However, it is difficult to simultaneously improve the toughness and stiffness. To fix this, we herein provide a simple and efficient method—adding 8 phr elastomer—chlorinated polyethylene (CPE) and 5 phr nano-silicon dioxide (nano-SiO₂) particles into poly(acrylonitrile–styrene–acrylic) (ASA) matrix. By such a simple combination, the impact strength, tensile and flexural strength were enhanced by 82.7%, 22.7%, and 30.7%, respectively. It was demonstrated that the self-formation of CPE network assisted by nano-SiO₂ was responsible for the improved mechanical performance. Four issues are considered to be responsible for the self-formation of network: the increase in the viscosity, the decrease in the elasticity of nano-SiO₂-localized ASA phase, the effect of nano-SiO₂ on distracting the molecular interactions between CPE and ASA, and the interfacial adhesion. Our present study provides an easy and effective route toward polymeric materials with simultaneous improved toughness and stiffness.

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1. Introduction

Recently, incorporating nanofillers as a reinforcement into polymeric matrix has received a great deal of interest, because it provides a simple way to improve the strength of polymer at a quite

low fraction, together with other benefits such as excellent electrical properties and thermal conductivity [1–4]. Typical nanofillers, including carbon nanotubes [5], graphene oxide [6], nanoclay [7], cellulose nanomaterials [8–10], have been investigated extensively. However, one drawback of this strategy is that the reinforcing effect is usually accompanied with the loss in toughness, especially for the nanofillers without surface-modification [11]. This embrittles the polymers and therefore restricts their applications in some harsh conditions.

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To fix this issue, incorporating a third rubbery/elastomeric component seems plausible, since it can increase the toughness and therefore balance the reinforcing and embrittling effects [12]. More importantly, the high rigid nature of the nanofillers might help to offset the loss in stiffness, which is the main drawback of rubber-toughened plastic [13–17]. Therefore, these two benefits make this technique to be the optimal one. However, whether the stiffness and toughness can be balanced strongly depended upon the phase morphology in the prepared nanocomposite system. Different phase morphology usually results in different mechanical performance. There are four possible localizations for the fillers in the plastic/elastomer/nanofiller ternary system: the fillers localize randomly within the matrix, or selectively localize within the plastic or the elastomer phase, or the interface between the plastic and elastomer. The localization of nanofillers is a crucial factor, and it can be adjusted by the thermodynamic and kinetic parameters between different polymeric components [18–22], such as interfacial tension, melt viscosity ratio, and melt elasticity ratio.

Some studies have already investigated the relationship between the phase morphology and mechanical performance in plastic/elastomer/fillers system. In polypropylene (PP)/ethylene propylene diene monomer (EPDM)/nano-silicon dioxide (nano-SiO₂) ternary composites system [23,24], the formation of nanofiller-elastomer network structure was observed and a considerable improvement in impact toughness was achieved. Xiu et al. [25,26] successfully used titanium dioxide (TiO₂), nano-SiO₂ and carbon black to toughen polylactide (PLA)/poly(ether) urethane (PU) blend, and find that TiO₂ selectively localized at the interface between PLA and PU, while the other two fillers were located within PU phase. In our previous study [13], it was found that nano-SiO₂ particles selectively localize within poly(vinyl chloride)/ α -methylstyrene-acrylonitrile copolymer matrix rather than within chlorinated polyethylene (CPE) phase, based on which the impact toughness was greatly improved. In general, it is suggested that the formation of network structure is more beneficial to achieve an impressive toughening effect. However, the appreciable toughening effect was not combined with reinforcing effect in the aforementioned papers. To the best of our knowledge, simultaneous reinforcing and toughening effects in plastic/elastomer/nanofillers ternary system were not reported. Therefore, the simultaneous improved stiffness and toughness reported in this work is of great interest.

In this work, poly(acrylonitrile–styrene–acrylic) (ASA), a kind of engineering plastic that is composed of poly(butyl acrylate) (PBA) and poly(acrylonitrile–styrene) (AS) components, was selected as the polymeric matrix. Due to its good weatherability, ASA has been recently developed as a good substitute for acrylonitrile–buta diene–styrene (ABS) resin for outdoor applications [27]. However, as an excellent candidate for outdoor application, it must exhibit high impact resistance, especially under the severe condition such as high wind load. In our previous work [28], CPE was used to toughen ASA. The results showed that the toughening efficiency of CPE was not drastic, and there was considerable loss in stiffness. As an ongoing work, nano-SiO₂ particles were further added in ASA/CPE blends. To better clarify the role of nano-SiO₂ in the mechanical performance, two polymeric matrices, including ASA/CPE (100/8) and ASA/CPE (100/15), were selected. By a simple combination of 8 phr CPE and 5 phr nano-SiO₂, a CPE network structure was self-formed. As a result, the prepared nanocomposite exhibited higher stiffness and considerable increase in the impact toughness in comparison with those of pure ASA. The reason for the self-formation of network and the mechanisms for the simultaneous improvement in stiffness and toughness were systematically investigated and fully elucidated.

2. Experimental

2.1. Materials

ASA (Luran 776 SE, BASF Co., Ltd., Korea) was extrusion grade and its melt volume rate is 4 cc/10 min measured under the condition of 220 °C and 10 kg load. CPE (135 A), with 36 wt% chloride, was provided by Weifang Yaxing Chemical Co., Ltd. Nano-SiO₂ (TS-530, Shanghai Cabot Chemical Co., Ltd., China) was pre-coated with hexamethyldisilazane and its BET value is 226.9 m²/g.

2.2. Sample preparation

ASA, CPE and nano-SiO₂ were compounded at 180 °C in a two-roll mill for 10 min and were then compression-molded into sheets. The testing samples with both dumbbell and rectangular shape were prepared via further machining. The specific details can be seen in our previous paper [14]. The weighting ratio of ASA/CPE/nano-SiO₂ was 100/x/y ($x = 0, 8, 15, y = 0, 5$). The samples were designated as ACxSi_y, where x, y is the dosage of CPE and nano-SiO₂, respectively. Neat CPE was also melt compounded in the same way for the purpose of measuring its rheological properties.

2.3. Characterizations

2.3.1. Mechanical properties

Notched Izod impact strength was measured using an Izod impact tester (UJ-4, Chengde Machine Factory, China) at room temperature referring ISO 180. The tensile and flexural tests were conducted using a universal machine (CMT 5254, Shenzhen SANS Testing Machine, Co., Ltd, China) with a testing rate of 5 mm/min and 2 mm/min following ISO 527 and ISO 178, respectively.

2.3.2. Thermal stability

Thermogravimetric analysis (Q50, TA, USA) was used to evaluate the thermal properties. The tests were carried out under a nitrogen flow rate (50 mL/min) and the testing temperature ranged from room temperature to 600 °C. The heating rate was 20 °C/min.

2.3.3. Morphology observations

Cryo-fractured (using liquid nitrogen) surfaces were observed by scanning electron microscopy (SEM, JSM-5900, JEOL, Japan) at 15 kV. Transmission electron microscopy (TEM, JSM-1400, JEOL, Japan) was used to investigate the particle size of nano-silicon dioxide. A droplet of diluted suspension of nano-SiO₂ (ethanol worked as the solvent) was allowed to dry on a carbon coated copper grid. To enhance the contrast, the staining technique was used. Both chlorosulfonic acid and osmium tetroxide were used as the staining agents [13].

2.3.4. Selective extraction tests

Each specimen with the dimension of 10 × 10 × 1 mm³ was immersed with tetrahydrofuran (THF) for different time at room temperature. No stirring process was used so that a static process was guaranteed. THF was selected for the reason that it can dissolve ASA, but partly dissolve CPE.

2.3.5. Fourier transform infrared spectra (FTIR) analysis

FTIR spectra of specimens were characterized by FTIR spectrometer (Tensor-27, Bruker Optics, USA). The attenuated total reflection (ATR) technique was utilized at a resolution of 4 cm⁻¹ with 32 scans. The tested range of wave number was 4000–500 cm⁻¹.

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