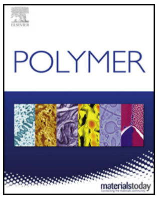
Polymer 153 (2018) 287–294

Contents lists available at ScienceDirect

Polymer

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



Synergistic reinforcing and toughening of polydicyclopentadiene nanocomposites with low loadings vinyl-functionalized multi-walled carbon nanotubes

Zhilong He, Jiacheng Sun, Li Zhang*, Yaqi Wang, Huiyan Ren, Jin-Biao Bao

Ningbo Key Laboratory of Specialty Polymers, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo, 315211, China

HIGHLIGHTS

- Excellent dispersibility of f-MWNTs in DCPD.
- Achieved synergistic reinforcing and toughening of PDCPD composites.
- Revealed the reinforcing and toughening mechanisms.

ARTICLE INFO

Keywords:
Polydicyclopentadiene
Multi-walled carbon nanotubes
Synergistic reinforcing and toughening
Mechanism

ABSTRACT

Synergistic reinforcing and toughening of polydicyclopentadiene (PDCPD) nanocomposites reinforced with multi-walled carbon nanotubes (MWNTs) were achieved and enhancing mechanism was investigated. MWNTs were functionalized with vinyl groups via chemical grafting and the vinyl groups functionalized MWNTs (f-MWNTs) were characterized by fourier transform infrared spectroscopy and field-emission scanning electron microscopy. The mechanical properties of f-MWNTs/PDCPD composites were investigated by means of universal testing, notched izod impact testing and dynamic mechanical analysis. Synergistic improvement of yield strength, tensile toughness and impact strength of composites were observed with the incorporation of 0.1–0.4 wt% f-MWNTs compared with pure PDCPD. The maximum yield strength, toughness and impact strength of the composites increased by about 48%, 94% and 97%, respectively. The simultaneous enhancement is probably ascribed to MWNTs' excellent mechanical properties and high aspect ratio, short and flexible vinyl groups onto MWNTs surface, strong covalent bonds between PDCPD and f-MWNTs.

1. Introduction

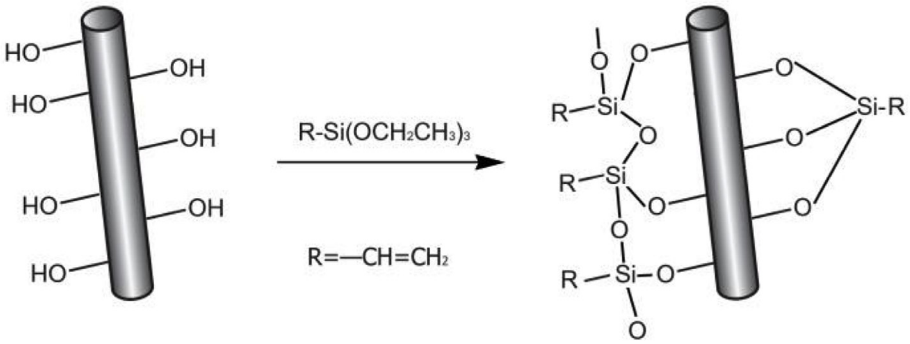
Polydicyclopentadiene (PDCPD) is one of the most promising materials [1] for applications in preparing vehicles, chemical pipes, armamentarium, and sports utilities [2] because of its excellent impact resistance, chemical corrosion resistance, and thermal stability. PDCPD was synthesized through a highly exothermic ring-opening metathesis polymerization (ROMP) [3–5], and the commercial products are manufactured by using reaction injection molding (RIM) [6] technology due to the rapid processing of PDCPD, low viscosity and simple post-treatment. With the development of various transition-metal-based metathesis catalysts [7–9], especially the invention of Grubbs catalysts [10], which have paved the way for PDCPD preparation due to their remarkable tolerance toward oxygen, moisture and extremely excellent metathesis activity. What's more, the PDCPD/Grubbs catalyst systems were extensively applied in self-healing technology because it meets the diverse demands for self-healing systems [11].

Neat PDCPD has high strength and high modulus, whereas its mechanical properties are still lower than that of metal and ceramic materials, which still cannot satisfy the requirements for many fields. Because the very low viscosity of DCPD monomer can offer fast and efficient fillers wetting within a short time [3], PDCPD composites with improved stiffness and toughness were suitably prepared by adding inorganic nonmetal or metal materials, such as clay, carbon nanotubes, mesoporous silica, graphene and fibers [12–17]. Yoonessi et al. [12] prepared exfoliated organically modified clay/PDCPD composites using Grubbs' catalyst through in situ ring-opening polymerization. The enhancement of mechanical properties occurred at the low incorporation (0.5–1 wt%) of clay. Simons et al. [13] put to use the intergallery-surface-initiated technique to aid in the exfoliation process of clay and

---

* Corresponding author.
E-mail address: zhangli2@nbu.edu.cn (L. Zhang).

https://doi.org/10.1016/j.polymer.2018.08.016
Received 6 July 2018; Received in revised form 6 August 2018; Accepted 12 August 2018



Scheme 1. Schematic illustrations of synthesis of f-MWNTs.

synthesized highly cross-linked PDCPD composites with modified clay. The improvement of compressive Young's modulus was up to 50% with 5 wt% modified clay. Jeong and Kessler [14] successfully grafted norbornene groups onto the surface of multi-walled carbon nanotubes (MWNTs), leading to the homogeneous dispersibility in DCPD monomer. Furthermore, the f-MWNTs/PDCPD nanocomposites with high toughness were fabricated by ROMP. The covalent combination between f-MWNTs and the matrix promoted the enhancement of tensile toughness by 925% with 0.4 wt% functionalized nanotubes. Peng et al. [15] modified MoS_2 and prepared PDCPD nanocomposites by means of in situ polymerization using RIM process. The friction coefficient decreased by more than 40% by incorporating 1 wt% MoS_2 nanoparticles, however, the improvement in modulus and strength was extremely limited.

In our previous work [18], we prepared vinyl-functionalized SiO_2 (V-SiO_2) and V-SiO_2/PDCPD composites. Testing results showed that tensile toughness increased by a factor of 14, from 2.58 MPa to 40.96 MPa by adding 0.2 wt% V-SiO_2. However, the improvement of notched izod impact strength was limited, and the yield strength decreased slightly from 37.50 MPa to 35.22 MPa by incorporating 0.2 wt % V-SiO_2.

Although there has been a reasonable level of success achieved along these lines, there still remains significant room for improvement of the mechanical properties, especially it is very challenging to fabricate PDCPD composites with simultaneously enhancement of yield strength, tensile toughness and impact strength [19].

From the reported results abovementioned, we confirmed that the filler and the functional groups on the filler surface tended to significantly affect composite preparation process and thereby determined the reinforcing and toughening effect [20–23]. Therefore, the selection with respect to filler and the functional groups plays the key role in providing synergistic enhancement of yield strength, tensile toughness and impact strength [24]. Considering the combination of outstanding mechanical characteristics, extremely large interfacial contact area and high aspect ratio [25,26], MWNTs may be more suitable for improving yield strength and tensile toughness than other fillers [27–30], although Jeong and Kessler [14] reported only 3.6% enhancement of yield strength was achieved with the incorporation of 0.4 wt% f-MWNTs. For the reason why only 3.6% improvement was acquired, many factors should be taken into consideration [31], especially the functional groups on the surface of f-MWNTs. In contrast to other functional groups, the adopted relatively long and flexible functional groups can be very effective to improve the tensile toughness, whereas, may be not so effective to enhance yield strength. To simultaneously enhance yield strength, tensile toughness and impact strength, short flexible functional groups on MWNTs surface may be more suitable. Considering probability of covalent bonding between the MWNTs and DCPD and the nonpolarity of DCPD monomer, the nonpolar vinyl groups are attempted to introduce onto nanotube surface. The results show that introduction of the nonpolar vinyl groups onto nanotube surface not only solves the dispersion problem of the MWNTs in DCPD monomer, but also improves adhesion strength between MWNTs and PDCPD matrix through covalent bonding. The target of this investigation is to fabricate PDCPD composites with synergistic improvement of yield strength, tensile toughness and impact strength.

2. Experimental

2.1. Materials

Hydroxylated multi-walled carbon nanotubes (MWNTs-OH), with O.D. × length (8 nm × 10–30 μm, > 98%) was purchased from Chengdu Organic Chemistry Co., Ltd and Dicyclopentadiene (DCPD, 95%) was obtained from J&K Chemical Co., Ltd. Vinylmethylsilane (VTMS, 98%) was obtained from TCI Co., Ltd. Dichloro (3-methyl-2-butenylidine) bis (tricyclopentyl) phosphine ruthenium (Grubbs first-generation catalyst) was purchased from Sigma-Aldrich (USA) and dichloromethane (CH_2Cl_2, 99.9%) was obtained from Aladdin Chemical Co., Ltd. Ammonia (NH_4OH) was supplied by Sinopharm Chemical Reagent Co., Ltd. All chemicals and solvents were used without further purification.

2.2. Synthesis of f-MWNTs

Chemical grafting was used to synthesis f-MWNTs. 0.2 g pristine MWNTs and 100 mL dissolvant (50 mL distilled water + 50 mL ethanol) were placed in a 250 mL round bottom flask sonicated in a water bath for 25 min to obtain a homogeneously dispersed solution. The flask was transferred to an 80 °C oil bath, then 2 mL NH_4OH and 0.35 mL VTMS was added to the above solution, continued to react for 5 h at 80 °C. After the reaction was completed, the mixed solution was washed fully with distilled water and ethanol and centrifuged at 5000 r/min, dried under a vacuum at 60 °C for 12 h, giving vinyl-functionalized MWNTs. The reaction diagram is shown in Scheme 1.

2.3. Preparation of f-MWNTs/PDCPD composites

Considering the dramatic increase in viscosity caused by the addition of MWNTs, the effect of the f-MWNTs at low loadings (0, 0.1, 0.2, 0.3, 0.4 and 0.5 wt%) on mechanical properties of the resulting composites was investigated. Vinyl-functionalized MWNTs (f-MWNTs) was ultrasonically dispersed in DCPD by combining water bath and sonication to form a homogeneously mixed solution. Afterwards, the Grubbs catalyst was weighed in the molar ratio of Grubbs catalyst: DCPD = 1:6000 and dissolved in a small amount of CH_2Cl_2 to form much smaller crystals. The ultrasonically dispersed solution was poured into a flask equipped with the catalyst. Ultimately, the solution was stirred at 30 °C for 30 s and rapidly injected into a corresponding hot mold and cured at 70 °C for 2 h, secondarily at 110 °C for 2 h, eventually at 150 °C for 2 h. All mechanical tests were performed one day after sample preparation to minimize the effects of surface oxidation.