Composites: Part A 56 (2014) 290–299

Contents lists available at ScienceDirect

Composites: Part A

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

Layered double hydroxide/multiwalled carbon nanotube hybrids as reinforcing filler in silicone rubber

B. Pradhan, S.K. Srivastava *

Inorganic Materials and Nanocomposite Laboratory, Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

ARTICLE INFO

Article history:
Received 12 March 2013
Received in revised form 29 August 2013
Accepted 14 October 2013
Available online 24 October 2013

Keywords:
Hybrid
Nano-structures
Thermal properties
Mechanical properties

ABSTRACT

The dispersion of filler and filler–matrix interfacial interaction are crucial factors to improve the properties of nanocomposites. In the present work, the dry grinding of 1D multiwalled carbon nanotube (MWCNT) and 2D layered double hydroxides (Li–Al-LDH, Mg–Al-LDH and Co–Al-LDH) have been used to prepare the corresponding 3D Li–Al-LDH/MWCNT, Mg–Al-LDH/MWCNT and Co–Al-LDH/MWCNT hybrids and characterized. Subsequently, these 3D hybrids are used as nanofiller in the development of silicone rubber (SR) nanocomposites. Tensile strength is found to be significantly improved by 134%, 100% and 125% compared to neat SR in 1 wt.% Mg–Al-LDH/MWCNT, Li–Al-LDH/MWCNT and Co–Al-LDH/MWCNT hybrids filled SR nanocomposites respectively. It is also noted that Mg–Al-LDH/MWCNT/SR nanocomposites exhibit superior thermal stability and swelling behavior. The best effect of Mg–Al-LDH/MWCNT on SR compared to other hybrids is related to the highest surface area which contributes to nanolevel dispersion and strong interfacial interaction between Mg–Al-LDH/MWCNT and SR matrix.

1. Introduction

In recent years, polymer nanocomposites have received a considerable amount of attention due to their enhanced mechanical, electrical, thermal, flame retardant and other functional properties for better applications compared to the neat polymer [1–3]. Such improvements in properties strongly depend on the nature and properties of filler, dimension, aspect ratio, dispersion of the filler and interfacial interaction between matrix and the filler. Silicone rubber (SR) is one of most important functional polymers with its flexible silicone–oxygen backbones. Though, it exhibits excellent physical, chemical and thermal properties, the low thermal/electrical conductivity and poor mechanical strength remains one of the bigger challenges for many multifaceted applications. In this regard, one-dimensional (1D) carbon nanotubes (CNT) have been considered as most exciting nanofillers in the development of polymer nanocomposites [4–6] due to their excellent mechanical strength and high electrical and thermal conductivity. Compared with 1D CNT, layered double hydroxides (LDH) are one kind of two-dimensional (2D) nanomaterials which have been also used as nanofiller for fabrication of polymer nanocomposites [7,8]. For both 1D and 2D nanofillers, homogeneous dispersion and strong interactions with the matrices maintaining the intrinsic properties of nanofillers are the most important issue. Many studies have been conducted on modification and dispersion of CNT [9–11] and LDH [7,8] in polymeric matrices.

However, considering special structure and properties of CNT and LDH, it is very interesting to prepare 3D LDH/CNT by the hybridization of 1D CNT and 2D LDH for their promising applications in the field of hydrogen storage device [12], electro catalyst [13], photo degradation of dye etc [14]. Recently, this kind of hybrids have been prepared by in-situ growth of CNTs on LDH [12,15–17], co-precipitation method [13,14], hydrothermal method [18,19], wet mixing [20] and dry grinding of CNT and LDH [21]. Huang et al. [20] reported the synergistic effect of Co–Al-LDH/CNT hybrid filler on the mechanical properties of polyamide 6. Motivated by this, we focused our work on the preparation of 3D hybrids by dry grinding of CNT and three different LDH viz. Li-Al-LDH, Mg-Al-LDH and Co–Al-LDH and their characterization. Subsequently, these 3D hybrid fillers have been used as reinforcing fillers in the development of SR nanocomposites.

2. Experimental

2.1. Materials

Commercially available silicone rubber (Baysilone U10, vinyl content 0.05 mmol/g), vinyl terminated, linear polydimethylsiloxane base polymer and Baysilone U crosslinking agent 430, polysiloxane,

* Corresponding author. Tel.: +91 03222 283334; fax: +91 3222 255303.
E-mail address: sunit@chem.iitkgp.ernet.in (S.K. Srivastava).

1359-835X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compositesa.2013.10.011

and Pt catalyst complex were supplied by Momentive Performance Materials, Bangalore, India. Ethynyl cyclohexanol (Inhibitor) and carbon nanotube, multiwalled 724769 (carbon > 95%, O.D × L 6–9 nm × 6 μm) were purchased from Sigma-Aldrich. Magnesium nitrate [$Mg(NO_3)_2{\cdot}6H_2O$], aluminum nitrate [$Al(NO_3)_3{\cdot}9H_2O$], cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$] and tetrahydrofuran (THF) were purchased from E. Merck, India. Lithium nitrate ($LiNO_3$) and sodium hydroxide (NaOH) was obtained from Loba Chemie Pvt. ltd., Mumbai and Quest Chemicals (Kolkata, India) respectively.

2.2. Synthesis of Li–Al-LDH, Mg–Al-LDH, Co–Al LDH

Li–Al-LDH, Mg–Al-LDH and Co–Al-LDH were prepared according to the co-precipitation method [22]. In this method, $Mg(NO_3)_2{\cdot}6H_2O$ (0.025 mol, 19.65 g) and $Al(NO_3)_3{\cdot}9H_2O$ (0.075 mol, 9.25 g) were first dissolved completely in 100 mL of H_2O and then added drop wise to aqueous NaOH solution (pH ~ 8–9) and stirred time to time. The resulting product was subsequently aged at 80 °C for 16 h followed by filtration and washing with distilled water and dried under vacuum at 80 °C/24 h. The similar methodology was adopted for the preparation of Li–Al-LDH and Co–Al-LDH.

2.3. Preparation of LDH/MWCNT hybrid

LDH/MWCNT hybrids were prepared by simple dry grinding of pristine LDH (Li–Al-LDH, Mg–Al-LDH and Co–Al-LDH) and MWCNT with various weight ratios (6:1, 3:1, 2:1, 1:1, 1:2) in a mortar-pestle for half an hour [21]. The sides of the mortar were also occasionally scraped down with the pestle during grinding in order to ensure the through mixing.

2.4. Preparation of LDH/MWCNT/Silicone rubber composites

LDH/MWCNT/silicone rubber composites were prepared by solution intercalation method. A desired amount (0.5, 0.75, 1.0 and 1.5 wt.%, as the case it may be) of different LDH/MWCNT hybrids (1:1) were dispersed separately in THF and mixed with vinyl terminated, linear polydimethylsiloxane base polymer solution by ultrasonication for 1 hour. Then, the appropriate amounts of crosslinker (V430) with a 3:1 mole ratio of hydride (crosslinker) to the vinyl group of base polymer, catalyst and inhibitor were added to the above mixture at room temperature. Finally, the resultant mixture was cast on a Teflon Petri dish for solvent evaporation and then cured at 165 °C for 15 min followed by post curing at 200 °C for 4 h in a hot air oven. This same methodology was adopted for neat SR, MWCNT/SR, Li–Al-LDH/SR, Mg–Al-LDH/SR, and Co–Al-LDH/SR composites.

2.5. Characterization

Wide angle X-ray diffraction (WAXD) patterns were conducted at room temperature on a PANalytical (PW3040/60), model 'X' pert pro with Cu Kα radiation (λ = 0.1542 nm) in the range of diffraction angle 2θ = 10–70 and 5–60° at a scanning rate of 3°/min. The average crystallite size of LDH and LDH/MWCNT hybrids was calculated using the Scherrer equation [23,24]:

$$L_{hkl} = \frac{K\lambda}{\beta \cos\theta}$$

where k is 0.9 (constant), L_{hkl} is the crystallite size, λ is the wavelength of the radiation (λ = 0.15418 nm), β is the width of the (hkl) peak at half maximum intensity, and θ is the Bragg angle.

Microstrain (ε) and dislocation density (ρ) were also calculated as follows [25]$\varepsilon = \frac{\beta_{2\theta}\cos\theta}{4}$, where, $\beta_{2\theta}$ is the full width at half maximum and θ is the Bragg angle.

$\rho = \frac{15\varepsilon}{aL_{hkl}}$, where the value of $a = 3.15 * 10^{-8}$ A°.

Field emission scanning electron microscopy (FESEM) images were conducted on a Carl Zeiss Supra 40 instrument at an accelerating voltage of 20 kV. The samples were coated with Au before FESEM measurements. Transmission electron microscopy (TEM) images of LDH/MWCNT hybrid and its SR composites were recorded using a JEOL 2100 200 KV transmission electron microscope. The corresponding for TEM probes of the LDH/MWCNT hybrids were prepared by mounting the THF suspension of the samples on the copper grid for about 12 h. TEM samples of LDH/MWCNT filled SR composite were prepared by ultramicrotomy using a diamond knife at −130 °C with a thickness of a section 100 nm.

AFM analysis was performed on AFM (Digital Instruments, Nanoscope III), XRD (RigakuMiniflex), by spin-coating of samples in silicon wafer. Brunauer, Emmett, and Teller (BET) analysis is the standard method for determining surface areas from nitrogen adsorption isotherms using the BET surface area analyzer (AUTOSORB−1C), supplied by Blue Star India Ltd for Quantachrome Instruments, USA. Ultaviolate–visible (UV–Vis) absorption spectra of MWCNT and LDH/MWCNT hybrids dispersion were recorded on Shimadzu UV-2450 UV–Vis spectrophotometer. For this purpose, 0.2 mg MWCNT and LDH/MWCNT hybrids were separately dispersed in 1 mL distilled water by 5 min sonication. Zeta potential has been measured using Malvern NanoZS. To check the dispersion stability, the hybrids were separately dispersed by ultrasonication in vial consisting 0.8 mg filler in 4 mL of THF and water respectively. Tensile measurements were performed according to ASTMD 412-98 using a Tinius Olsen h10KS universal testing machine at 25 °C with a crosshead speed of 300 mm/min; dumbbell shape specimens with overall length of 100 mm and width of 3 mm. Differential scanning calorimetry (DSC) of neat SR and SR nanocomposites was conducted using Perkin Elmer Pyris differential scanning calorimetric instrument at scan rate of 10 °C/min under nitrogen atmosphere over a range of temperature −150 to +150 °C. Thermo gravimetric analysis (TGA) of the neat SR and SR nanocomposites was performed using Redcroft 870 thermal analyzer, Perkin–Elmer at a heating rate of 10 °C/min over a temperature range of 50–800 °C under nitrogen atmosphere.

The volume fraction and crosslink density of polymer and polymer composite in the swollen network were estimated by following techniques. Previously weighed samples were allowed to swell in toluene to reach equilibrium swelling for 72 h at room temperature. Then the sample masses in the equilibrium swollen state were removed from toluene, blot-dryed with a tissue paper and weighed it. Finally the samples were dried to a constant weight in a vacuum oven for minimum of 24 h.

The volume fraction (V_r) of neat polymer and polymer composites were calculated using the Flory–Rehner approach [26]:

$$V_r = \frac{W_r\rho_r^{-1}}{W_r\rho_r^{-1} + W_s\rho_s^{-1}}$$

where ρ_r (W_r) and ρ_s (W_s) are the density (weight) of polymer/composite and solvent respectively. The crosslink density (n_c) and toluene uptake (mole%) of the polymer and polymer composite under equilibrium swollen conditions were also calculated from the relationship:

$$n_c = \frac{-[\ln(1-V_r) + V_r + \chi V_r^2]}{V_0\left(V_r^{\frac{1}{3}} - \frac{V_r}{2}\right)}$$

where n_c, V_0, χ, W_r and W_s are the crosslink density, molar volume of solvent (Toluene, V_0 = 106.8 cm^3/mol), Flory-Huggins polymer–solvent