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Development of sustainable elastomeric engineering nanocomposites from linseed oil with improved mechanical stability and thermally induced shape memory properties

Rakesh Das [a], Sovan Lal Banerjee [a], Rajesh Kumar [b], P.P. Kundu [a,*]

[a] Department of Polymer Science and Technology, University of Calcutta, 92, A.P.C. Road, Kolkata 700009, India
[b] Precision Metrology Laboratory, Department of Mechanical Engineering, Sant Longowal Institute of Engineering & Technology, Sangrur, Punjab 148106, India

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ABSTRACT

The elastomeric nanocomposites having high mechanical stability and shape memory property were fabricated via in situ cationic polymerization of vegetable oil (linseed oil) in the presence of nano fly ash (NFA). The enhanced dynamic moduli and Young's modulus of nanocomposites with respect to matrix elastomers were witnessed. The vibration damping behavior of nanocomposites in wide frequency region, observed under a laboratory fabricated machine reveals their effectiveness to attenuate hazardous vibration in broad application regions. Under thermally stimulated shape memory test, the nanocomposites exhibit 100% shape recovery, and the shape recovery time improves when the content of NFA filler increases.

Introduction

In recent years, bio-based materials from natural resources replace petroleum based raw materials in plastic, rubber and composite industries to develop sustainable end products because they are renewable, inexpensive, universally available and biodegradable in nature [1]. Among all renewable resources, vegetable oils are exceptional building block elements for generating functional polymeric materials. This is because of their easy availability, low cost, and wide possibilities of chemical transformation [2]. Reinforcing polymers with fillers has come a long way to improve some important properties like thermal stability, flame retardancy, mechanical stability, barrier properties and lowering of production cost [3–5]. In different engineering applications, polymeric nanocomposite proves its potentiality compare with the conventional non-polymeric composites due to their light weight, durability, recyclability, etc. [6–9]. As the nano fillers have high surface to volume ratio, the polymer filler interaction improves tremendously. For this reason even low amount of filler loading can improve the composite properties significantly [10].

The vegetable oils have a lot of functional groups, which can be utilized through different routes during the chemical reaction to develop varieties of polymeric materials [11–13]. The well-established mechanism are direct polymerization of native vegetable oil through cationic or free radical polymerization, condensation polymerization of chemically modified oils and some other newly invented polymerization techniques like ring-opening metathesis polymerization (ROMP), acyclic diene metathesis polymerization (ADMET). Depending on specific applications, different fillers or fibers are incorporated into the vegetable oil based polymer matrix to get suitable polymeric composites or nanocomposites [14]. These types of polymeric composite materials have found promising applications in aircraft, automobile, packaging, defense, etc. Filler like clay [15], glass fiber [16] or natural fibers [17–19] have attracted major attention for the fabrication of potential nanocomposites based on vegetable oil.

Fly ash is basically an inorganic residue of thermal power station which mainly comprise of high amount of silica (SiO_2) along with small proportion of Al_2O_3, Fe_2O_3, MgO, K_2O and Na_2O, etc. [20,21]. It is produced by the combustion of pulverized coal and it pollutes air and groundwater through leaching of its toxic constituents like lead, arsenic, cobalt and chromium especially from unused fly ash [22,23]. Thus, for scientific community, it is a

* Corresponding author. Tel.: +91 3323525106; fax: +91 3323525106.
E-mail address: ppk923@yahoo.com (P.P. Kundu).

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major concern to develop beneficial applications of fly ash to keep environment alive. Extensive research has been carried out for utilization of fly ash as a reinforcing filler of different polymer matrix like elastomers [24], high density polyethylene (HDPE) [25], epoxy [26], rubbers [27], etc. These establish the fly ash as excellent and cost effective filler. Sometimes, the incompatibility between polymer matrix and fly ash has been overcome through surface treatment of fly ash or using coupling agent [28,29].

Among different engineering applications, elastomers or rubbers are most widely used as vibration damping materials to reduce harmful consequences of unwanted vibration and noise in machinery, civil structures, transportation vehicles, aerospace and naval vessels, etc. The loss factor, which evaluates the performance of any damping materials generally determined through dynamic mechanical analysis (DMA) in a wide range of temperature and frequency [30].

Shape memory polymer (SMP) is a class of special materials with ability to store a temporary shape and to recover a permanent shape under external stimuli of temperature, light, pH, moisture, and electric or magnetic field [31–34]. The thermally stimulated SMP are most commonly used. Over the conventional shape memory metals (alloys), the SMP have advantage because of their low cost, easy processability, low density and high shape recoverability. In vibration damping applications, the damping materials support the vibrating structures and they undergo cyclic deformation during operation. The shape recovery test is required to enrich the knowledge about its deformability and recoverability after operation. The Larock group performed extensive research on thermally stimulate shape memory behavior of cationically cured soybean oil based polymers [35], which exhibited 100% shape recovery. Also polymers based on tung oil and epoxydized soybean oil exhibited good shape memory behavior [36–38]. The polyurethane and polyurethane nanocomposites derived from different vegetable oils also exhibited good shape memory properties [39–41].

In current research work, elastomeric nanocomposites have been fabricated by using linseed oil, which is very cheap and most abundant oil in India and nano fly ash which is a thermal power waste product. The objective of this research work is to develop value added engineering elastomeric nanocomposites with improved mechanical stability and shape memory properties from renewable and waste resources. From the best of our knowledge, there is no reported research work available on the development of engineering nanocomposites from regular linseed oil and fly ash and we employed this nanocomposite material as a vibration damping material having shape memory property. In our regular life, some of the low frequency vibrations (<10 Hz) like wind induced vibration, earthquake, machinery vibration, etc. can cause severe damage on human being and large constructions. To determine the efficiency of our prepared material in the reduction of such low frequency vibrations, we performed an extensive dynamic mechanical analysis of these nanocomposites in a wide range of frequency and temperature. We also performed a vibration damping test of these nanocomposites under a laboratory fabricated vibration damping machine to determine its practicality in real vibration damping applications. Also, polymers are employed in high frequency vibration damping applications such as automotive noise and vibrations, railway noise and vibrations, spacecraft vibration, etc. Thus, high frequency (up to 1.5 kHz) vibration analysis of elastomers has been performed through another laboratory fabricated testing system following the procedure of ASTM E756-05 [42]. Also, the shape memory property of the nanocomposites has been performed utilizing thermal stimulus.

Experimental

Materials

The fly ash having density of 2.17 gm/cm^3 and total moisture content of 2% was collected from CESC thermal power station, Kolkata. Linseed oil used in our study was obtained from the local market of Kolkata. Styrene (ST), divinylbenzene (DVB) (55 mole% DVB and 45 mole% ethylvinylbenzene) and boron trifluoride diethyl etherate complex were purchased from Sigma–Aldrich, USA. Methanol, concentrated sulphuric acid, acetone and hydrogen peroxide were purchased from Merck, India.

Preparation of nano fly ash (NFA)

The particle size of fly ash (FA) was reduced mechanically from micron to nano level using a planetary ball mill. In a stainless steel chamber, the fly ash was loaded in 1:10 volume ratio with the tungsten carbide balls of 10 mm diameter. The total duration of milling was 30 h in a rotational speed of 300 rpm. The surface of the fly ash was cleaned by acetone to remove dirt or foreign objects [28]. The Fly ash was then dried in vacuum oven for 24 h at 80 °C before use. The particle size of fly ash after milling was determined by dynamic light scattering analysis (DLS).

Nanocomposites preparation

In linseed oil, required amount of DVB and ST were added and predetermined amount of NFA was dispersed into it by maintaining a constant magnetic stirring at 800 rpm for 6 h followed by strong ultrasonication for 30 min. After obtaining a stable dispersion of NFA in linseed oil matrix, initiator was purged into the system in cold condition and under vigorous magnetic stirring. The 5 wt% BFE initiator was modified with 10 wt% methyl ester of linseed oil before purging into the system to confirm a homogeneous polymerization. Methyl ester was prepared by previously utilized method after slight modification [43]. For uniform distribution of the initiator into the reaction system, this methyl esterification was performed. After homogeneous mixing, the whole mixture was shifted into a glass mold and it was properly sealed with silicon adhesives. Then the whole system was kept at room temperature for 2 h and then it was heated sequentially at 60 °C for 2 h, 110 °C for 24 h and finally post cured at 120 °C for 3 h. To get different elastomeric nanocomposites, a fixed predetermined amount of matrix composition (linseed oil 40 wt%, ST 27 wt%, DVB 18 wt% and initiator 15 wt%) was used for composite preparation with a varying NFA content of 0–5 wt%. The reaction scheme of cationic polymerization of linseed oil, ST and DVB to form the crosslinked elastomer is illustrated in Fig. 1.

Characterization

Dynamic light scattering (DLS)

To determine the average particle size of NFA and its distribution into the dispersing medium (deionized (DI) water), DLS technique was employed. For this NFA sample was dispersed in DI water followed by ultra-sonication for. The DLS measurement was performed at 25 °C on a Zetasizer Nano ZS 90 (Malvern Instrument, UK) instrument at a scattering angle of 90°.

X-ray diffraction (XRD) analysis

X-ray diffraction spectrometry was employed to determine the crystalline or amorphous nature of the NFA, pure elastomer and nanocomposites. The wide angle X-ray scattering (WAXS) diffractometer (Panalytical X-Ray Diffractometer, model: X'pert Powder)