



Layered silicate-polymer nanocomposite coatings via radiation curing process for flame retardant applications



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ABSTRACT

Polymer-clay nanocomposite (PCN) films were fabricated by uniformly dispersing organically modified montmorillonite clay (Cloisite 20A and 30B) in varying concentrations of 2%, 5%, 10% and 15% (w/w) in an optimized composition of aliphatic urethane acrylate (AUA)-Trimethylolpropane triacrylate (TMPTA) mixture by ultra-sonication followed by ⁶⁰Co-gamma radiation induced curing. Radiation doses were optimized to obtain non-tacky, homogeneous thin films, which were subsequently characterized by UV-vis spectrophotometry, X-ray diffraction (XRD), small angle X-ray scattering (SAXS), Fourier transform infrared spectrometry (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques. Gloss of the PCN films decreased, and fracture toughness and hardness of PCN films improved with the incorporation of the clay in the PCN coatings. Limiting Oxygen Indices (LOIs) of the samples were calculated from the thermogravimetric analyses data to ascertain the efficacy of the PCN films as potential flame retardant materials.

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1. Introduction

Inorganic-organic hybrid nanocomposite materials have received great attention from the industrial community because of their wide range of novel physical properties. Relative to virgin polymer or conventional composites, polymer-clay nanocomposites show significant improvement in certain material properties, such as barrier property, enhanced mechanical property. In particular, these hybrid nanocomposite materials find wide application as flame retardant materials. Early flame retardants including halogenated compounds are currently being phased out because of environmental concerns [1,2]. For this reason, metal hydroxides [3–5] and intumescent flame retardant (IFR) [6,7] additives, as main halogen-free flame retardants (HFFR), have attracted considerable attention. However, large loadings of IFR additives and metal hydroxides are usually needed (>60 wt%) in the polymer matrix to get high flame retardancy, which leads to significant loss in the mechanical properties of the polymer. Hence, layered

silicates (clay)-polymer nanocomposites containing modified organophilic clay as nano fillers have been the focus of research over the past few years owing to their unique flame retardant properties [8–11].

Polyurethanes are the most widely used polymers in the field of polymer nanocomposites. The overwhelming popularity of polyurethane as the base matrix is due to its unique properties and wide range of applications, including in the field of adhesives, foams, textiles, membranes, elastomers and rubber adhesion promoters, besides in coatings [12]. Inclusion of nanofillers into these polyurethane matrices leads to further enhancement in their thermal and mechanical properties, thereby expanding the scope of their application into more diverse fields.

The addition of clay to organic polymers viz. polyurethanes differs from conventional blending of non-swellable inorganic fillers into polymers, as the clay nanofiller interacts with the organic matrix at a nano-scale level, and the final structure depends largely on the extent of intermixing and compatibility between the organic and the inorganic phases. Clay is identified as an inexpensive, environmentally benign nanofiller material with unique, mechanical, barrier and rheological properties. On adding just a tiny amount of clay to the polymer matrix, these new-generation composite materials exhibit significant decrease in the peak heat release rate

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(PHRR), change in the char structure, and decrease in the mass loss rate during combustion in the cone calorimeter [13–27]. It does not have the usual drawbacks associated with other fire retardant additives. Moreover, these PCN materials exhibit increased physical, thermal and mechanical properties [28–32].

Mechanical noncovalent blending, including melt blending and solution blending, is usually used for the fabrication of polymer composites, which, however, generally leads to poor interaction between fillers and polymer matrices. Compared to these conventional techniques, the major advantages of using high energy radiation, including electron beam or gamma irradiation, for curing, are that these are pollution-free, high efficiency techniques that impart long service life, uniform cross-linking degree, and excellent heat-resistance and cold-resistance properties to the materials [33,34]. Moreover, inorganic/organic nanocomposites containing inorganic nanofillers fabricated using radiation curing method were found to exhibit distinctly enhanced properties compared to conventionally prepared materials [35]. In this work, modified montmorillonite clay has been utilized as a nanofiller in an attempt to introduce flame retardant properties in radiation cured polymer coating films. Aliphatic urethane acrylate was used as the matrix owing to its unique properties, including excellent abrasion resistance, flexibility, hardness, chemical resistance, solvent resistance, light stability and weatherability [36]. A ^{60}Co Gamma chamber was used to achieve curing of the coating formulations by subjecting the samples to an optimized radiation dose. The polymer coating samples were characterized in detail and tested for their flame retardant properties.

2. Experimental

2.1. Materials

Modified montmorillonite clay (Cloisite 20A, Cloisite 30B, Southern Clay Ltd.), Aliphatic urethane acrylate (AUA, Cognis) as oligomer and Trimethylolpropanetriacrylate (TMPTA, Aldrich) as reactive diluent, were used as received. Radiation curing of coating formulations was carried out using ^{60}Co -gamma radiation in a gamma chamber (GC-5000, BRIT, Mumbai) having dose rate of 2.0 kGy h^{-1} . Radiation curing dose of 150 kGy , under aerated condition, was optimized to achieve curing of the composite formulations with non-tacky coating surfaces. The absorbed radiation dose was determined by using Fricke dosimetry [37]. The total dose was calculated by multiplying the dose rate with the time of exposure.

2.2. Sample preparation

Modified montmorillonite clay samples in different concentrations (% w/w) were added to an optimized mixture (4:1) of AUA and TMPTA. To achieve uniform dispersion of the filler in the coating formulation, each of the samples was subjected to probe ultrasonication (Q700, Qsonica, USA) for 30 min. The formulations obtained were coated onto glass substrates and subjected to γ -radiation for a total absorbed dose of 150 kGy to obtain non-tacky, homogeneous PCN thin films under aerated condition. The thickness of the γ -radiation cured coatings was found to be $\sim 100\ \mu\text{m}$ as estimated by a thickness gauge 'coat measure M12' (Yuyutsu, Japan).

2.3. UV-vis spectroscopy

The transmittance of the control polymer and PCN films was determined using a UV-vis spectrophotometer (Evolution 300, Thermoelectron, UK) operated in the transmittance mode in the wavelength region of 250–1000 nm with resolution of 1 nm.

2.4. Thermogravimetric analysis (TGA)

The non-isothermal thermogravimetric measurements were carried out with TGA/DSC1 system with gas controller system (GC100) from Mettler Toledo, Switzerland, to determine the thermal degradation behavior of Gamma radiation cured PCN films. For TG experiments $\sim 10\text{ mg}$ of the powder sample was taken in alumina crucible and heated in temperature range of $35\text{--}850\text{ }^\circ\text{C}$ at heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under inert dynamic high purity nitrogen atmosphere at a flow rate of 50 ml min^{-1} .

2.5. Differential scanning calorimetry (DSC)

Glass transition temperatures (T_g) of the samples was determined by a differential scanning calorimetry (DSC) using DSC 823e system from Mettler-Toledo, Switzerland. For all experiments $\sim 10\text{ mg}$ of the sample was taken in standard aluminum pan and heated to $250\text{ }^\circ\text{C}$ at heating rate of $20\text{ }^\circ\text{C min}^{-1}$ followed by cooling to $-50\text{ }^\circ\text{C}$ at cooling rate of $20\text{ }^\circ\text{C min}^{-1}$, and then again heated to $250\text{ }^\circ\text{C}$ at heating rate of $20\text{ }^\circ\text{C min}^{-1}$. All the cooling and heating cycles were carried out under inert dynamic high purity nitrogen atmosphere at a flow rate of 50 ml min^{-1} . The T_g values of PCN samples were estimated from the second heating cycle.

2.6. Small angle X-ray scattering (SAXS) and X-ray diffraction (XRD)

SAXS measurements were performed on the clay powder samples and PCN samples using a laboratory based SAXS facility using $\text{CuK}\alpha$ source. The diameter of the incident photon beam on the sample was 0.4 mm . The SAXS detector was mounted at a sample-to-detector distance of 1.07 m , corresponding to a 2θ range of $0.1\text{--}3.5^\circ$. The magnitude of the scattering wave vector, $s = 2 \sin \theta / \lambda = q / 2\pi$, where 2θ is the scattering angle and the used wavelength $\lambda = 0.154\text{ nm}$. In order to access further higher scattering angles above 3.5° , X-ray diffraction (XRD) experiments were performed using a diffractometer using $\text{CuK}\alpha$ source in $\theta\text{--}\theta$ geometry with $2^\circ/\text{min}$ scanning speed.

2.7. Fourier transform infrared spectrometry (FTIR)

The FTIR spectra of the γ -radiation cured PCN samples were recorded in ATR mode using diamond single reflectance ATR assembly in FTIR spectrometer (Affinity-1, Shimadzu, Japan) using resolution of 4 cm^{-1} and with data acquisition run of 25 scans for each sample.

2.8. Scanning electron microscopy (SEM)

The bulk morphologies of the Gamma radiation cured polymer coatings were investigated by SEM analysis using VEGA MV2300T/40 (TS 5130 MM) microscope (TESCAN) at acceleration voltage of 5 kV . SEM images of the cross-section of the nanocomposite coatings were taken at $10\text{ k}\times$ magnification, after the gold coated fractured coating films were fixed vertically on to a conducting steel stub surface using conducting carbon paste.

2.9. Transmission electron microscopy (TEM)

TEM images of the PCN samples were carried out using a bench top Transmission Electron Microscope (LVEM5, Cordouan Technologies, France) operated at 5 kV in electron scattering mode for higher contrast. Prior to analysis, samples were sliced into ultrathin sections of 30 nm thickness using an ultramicrotome and collected on to 400 mesh Cu grids.

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