

Synthesis and characterization of flame retardant vermiculite polystyrene composites

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Received: 31 March 2016, Revised: 04 October 2016 and Accepted: 15 December 2016

DOI: 10.5185/amp.2017/406

www.vbripress.com/amp

Abstract

Presently, polymer-clay composites (PCC) have shown promising advancements in different properties of polymers due to presence of layered silicate structure and also extend its multi fold advanced applications. In the present work, vermiculite (VT) was organically modified by cetylpyridinium chloride (CPC). Thus obtained organo vermiculite (OVT) was used to prepare its composite film with polystyrene (PS-OVMT) with varying amounts of OVT by the solution blending and casting method on a glass substrate. The prepared films were characterized by scanning electron microscope (SEM), x-ray diffraction (XRD), infrared (FT-IR) spectroscopy and thermal analytical (TG-DTA) techniques. X-ray diffraction pattern of the composite shows peaks of VT and PS along with decrease in the intensity of the PS peaks present between $2\theta = 12.5^\circ$ to 24.5° . Decreases in the intensity of peaks suggest dispersion of clay within the polymer matrix and lowering of crystallinity. The dispersion of clay and interaction with PS is also evident from the FTIR and microscopic data. Further, hardness test (shore-D), TG-DTA and flammability(UL-94) results of the composite indicate the improvement in hardness, thermal stability and inhibition in burning behaviour of the PS due to the presence of OVT in the PS matrix. Copyright © 2017 VBRI Press.

Keywords: Organo vermiculite, polystyrene, PS-OVMT composites, thermal stability, hardness, flammability.

Introduction

PCC are an important class of composite and it offer tremendous improvement in different physical, chemical and mechanical properties of polymers [1-3]. Thus, it finds versatile applications in transportation vehicles, construction materials, electronics and sporting goods and consumer products due to their advanced properties. The properties of PCC depend on the dimensions and microstructure of clay, which act like dispersed phase or filler in polymeric matrix [4]. The improvements in properties are depend on the dispersion, structural orientation and interfacial bonding between the clay particles and the polymer [5-6]. The other factors that control the properties are the mineralogical composition of clay minerals and, particle size distributions, electrolyte content of exchangeable cations and soluble salts, the nature and content of organic and textural characteristics of the clay [7]. In this regards vermiculite clay has good plasticity because it contains divalent cations between the clay inter layers to balance the negative charge on the clay surface. However, its hydrophilic nature prevents the homogenous dispersion in the polymer matrix, so it's essential to modify the clay by exchanging ions into organophilic. [8-11] The organophilic clay surface allowed the polymer to wet the

surface of the clay and disperse the clay into the polymer [12-13].

Polystyrene is a thermoplastic material with outstanding optical properties and favourable mechanical along with excellent processing behaviour. But its several properties like flammability, stability, gas permeability need to be improved for its effective use in different fields like coating and food packaging materials [10]. Polystyrene containing organically modified clay particles as additives are the promising new generation of packaging materials with specific barrier functionality to actually hit the market [14]. Due to its favourable properties, it can replace inorganic glass and packing materials in many applications [15-16]. The PCC can be prepared by several methods like situ polymerization, solution and melt intercalation, solvent blending, melt blending and roller mills but preparation of composite by solvent methods is simple and cost effective method since it occurs at low temperature and with better dispersion of clay. In this paper, the properties of PS and vermiculite clay have been modified by making their composite using solvent casting method. The mechanism of preparation, intercalation, and their structural, thermal flame retarding properties are discussed to explore their use in flame retardant coating materials.

Experimental

Materials

Vermiculite (high purity) was procured from Sigma Aldrich Germany. Polystyrene (M.W. 280 000) granules was purchased from local market of Delhi and was used as such. The analytical grade tetrahydrofuran (THF) and cetylpyridinium chloride (CPC) were procured from MERCK- India and used without any further purification.

Preparation of composite films

Vermiculite clay was modified by the reported procedure [17]. The modified clay was recovered by centrifugation and then dried in an oven at 80°C. The sample was then grinded and sieved to obtained fine particles.

5.0 grams of polystyrene was dissolved in 50ml of THF at room temperature on a magnetic stirrer. In the resultant polystyrene solution, different amounts of OVT was dispersed in the polymer matrix after stirring for 60 minutes. The clay dispersed polystyrene solution was poured into 10 cm diameter glass petridish and solvent was allowed to evaporate. Further film was demoulded and obtained film was air dried and stored in air tight plastic bags.

Characterizations

The physico-mechanical properties i.e., solvent content, swelling and porosity of the prepared composite films were determined by the reported methods [18-19].

Solvent content and degree of swelling

The composite film was cut in dimension of 1 × 1 cm from a surgical blade and was then dipped in molar solution of sodium chloride for 24 hours. The films were taken out of the solution, blotted quickly on a whatman filter paper to remove the surface adsorbed solvent followed by drying to constant weight in a vacuum oven. The amount of solvent absorbed was calculated using the equation:

$$W_w - W_d \times 100 / W_w,$$

where, W_w is the weight of wet film; W_d is the weight of dry film.

However, the degree of swelling was measured by estimating the difference between average thickness of the dry film and the film soaked in NaCl solution for 24 hours.

Porosity

The porosity (E) was measure from the difference in the volume of solvent incorporated in the cavities per unit dimension of the film by using solvent content data;

$$E = W_s - W_d / AL\delta_w$$

where, W_s is weight of the soaked film, W_d is dry weight of the film, A is the area of the film, L is the thickness of the film, δ_w is density of water used.

Flame retardency

Burning behaviour of composite film was carried out by under writer laboratory test (UL-94). The dimension of specimen and flame were fixed as per recommended standards.

Chemical and morphological study

X-ray diffraction patterns were recorded on a Philips X' Pert-PRO PMRD (D8 Discover Bruker AXS, Germany) system using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$, generated at 40 kV and 40 mA) from 2θ in the range of 2°- 45° with step angle of 0.02° s⁻¹. The prepared films were characterized by Fourier Transform Infrared spectrometer (FT-IR), Bruker. Alpha. Spectra were recorded in the KBr phase with an accumulation of 16 scan and a resolution of 4 cm⁻¹ in the range of 4000 cm⁻¹ to 400 cm⁻¹. The microscopic pictures were taken with the help of Hitachi - 3700, Scanning Electron Microscope after coating with gold. Further thermal characterization was made on Perkin Elmer thermo analyzer (TG-DTA) at a heating rate of 10°C/min from room temperature to 800°C under a continuous N₂ flow of 200ml/min

Results and discussion

Fig. 1 indicates XRD pattern of polystyrene and VMT polystyrene composites. The basal spacing of OVT and polystyrene remained constant in the composites. But with the increase in amount of VMT in the composites the intensity of hump of polystyrene appearing between $2\theta = 12.5^\circ$ to 24.5° decreases, which indicates the amorphous nature of polymer increases with the addition of VMT. The decrease in the intensity of hump shows that clay particles are intercalated within the polystyrene matrix. The XRD data further confirmed the miscibility of polystyrene and VMT.

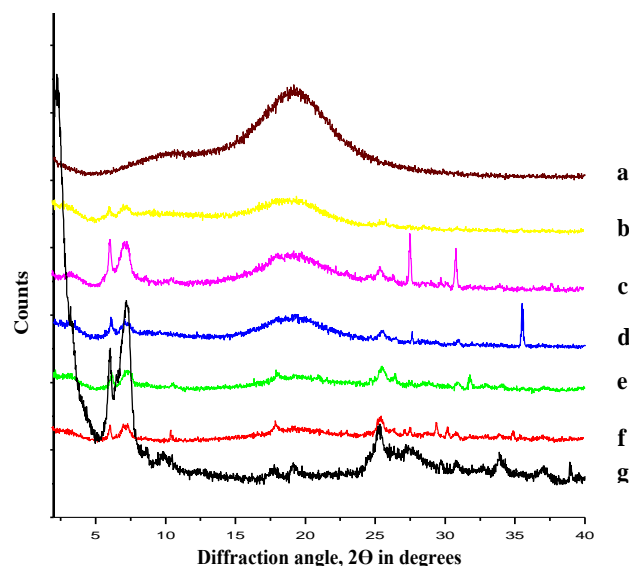


Fig. 1. XRD pattern of PS and PS-OVMT composites (a) pure PS (b) 4% wt. VMT (c) 5% wt. VMT (d) 6% wt. VMT (e) 9% wt. VMT (f) 10% wt. VMT and (g) OVMT.

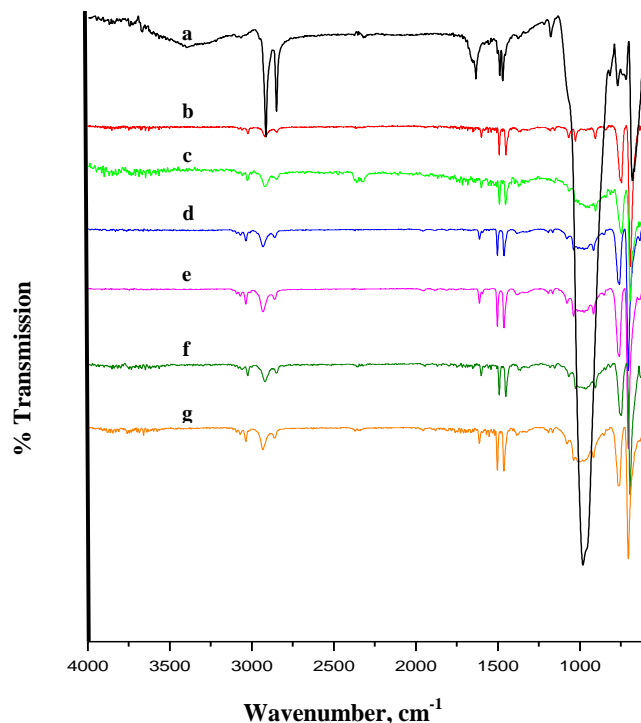


Fig. 2. FTIR spectra of PS and OVMT PS composites containing (a) OVMT (b) PS (c) 4% wt. OVMT (d) 5% wt. OVMT (e) 6% wt OVMT (f) 9% wt. OVMT (g) 10% wt. OVMT.

In **Fig. 2** bands of the FT-IR spectrum for polystyrene correspond to their functional groups, C-H aromatic tension 3081cm^{-1} - 3001cm^{-1} ; 2923 cm^{-1} and 2850 cm^{-1} CH_2 asymmetric and symmetric tension; $1943.19 - 1728.23\text{ cm}^{-1}$ aromatic ring mono substitution; 1452 cm^{-1} deformation CH_2 of the aromatic ring; 1069 cm^{-1} flexion C-H in the plane. They suggested assignments for three of the bands 758 cm^{-1} for phenyl group, 1380 cm^{-1} for CH deformation and 1460 cm^{-1} for CH_2 deformation and the band at 700 cm^{-1} is to be assigned to a CH_2 rocking mode. In the spectra of OVT polystyrene composites, most of the peak remains constant but only spectra broaden in the range $750\text{-}1200\text{ cm}^{-1}$. It may be due to the presence of clay in the composites matrix [20].

Fig. 3(a) shows the FESEM images of polystyrene which is porous in nature with various porous size [21]. The porous structures are not observable in the composite containing less than 5% wt. of OVT. The porous structure reappears when OVT contain is more than 5% indicating that the OVT particles are uniformly disperse in the polymer when OVT contain is less than 5% by wt. when further increased the OVT contained the porous structure re-appears resulting from the aggregation of OVT particles in the polymer matrix supporting the XRD pattern of the polymer and its composites. Field Emission Scanning Electron Microscopes images showed that the distribution of OVT particles in the matrix of polymer has intercalation structure [15].

Thermal study

The thermal stability of PS and its OVMT composite has been studied by TG-DTA analysis and curve is shown

in **Fig. 4**. Both the PS and its composites show a single step weight loss. However, onset temperature of thermal degradation of PS is in the range of $350\text{-}360^\circ\text{C}$, whereas in the case of PS OVMT composite is shifted in the range of $400 - 410^\circ\text{C}$. This show that the thermal stability increases with the clay contained in the polymer matrix. The increase in the thermal stability of the PS clay composite is due to the low heat release rate (HRR) due to the presence of the clay particles in the PS clay composite. Resulted from the increase in char formation, retained the heat flow in the polymer matrix. TG curve of composite is also showing lesser mass loss than four percent of PS, which again supports the improvement in stability of composite and presence of non-combustible clay component.

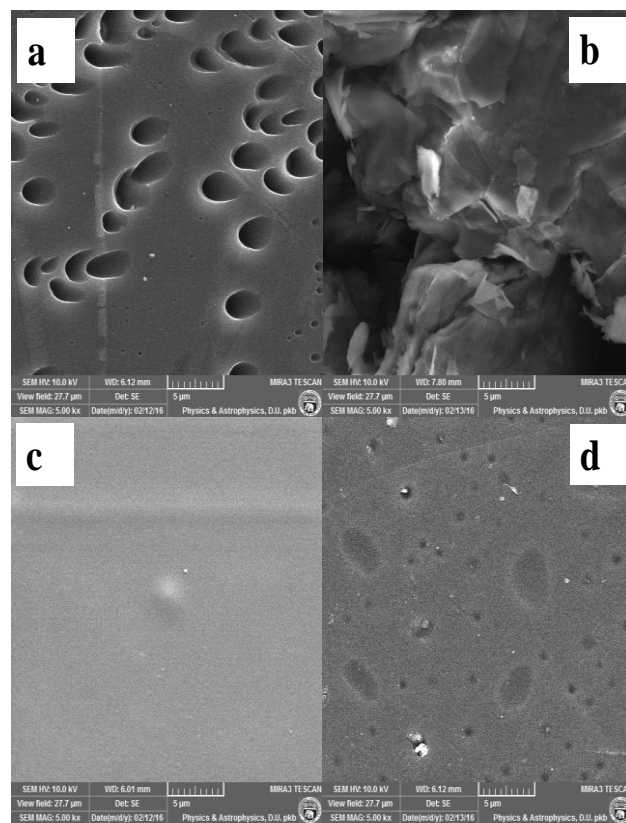


Fig. 3. FESEM image of polystyrene and VMT polystyrene composites (a) pristine PS (b) OVMT (c) 4% wt. VMT (d) 10% VMT.

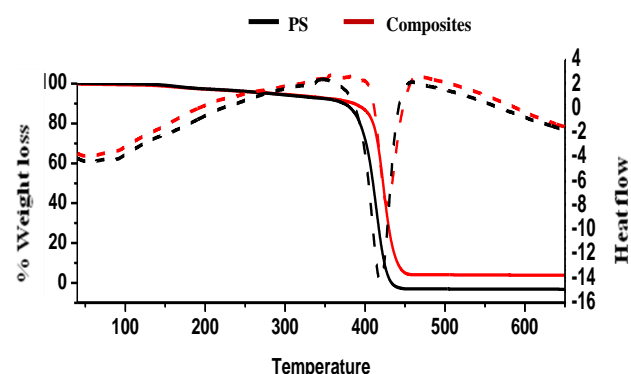


Fig. 4. Thermo grams of polystyrene and its composite.

Physical properties of film

The physical properties of OVTPS composite film is given in **Table 1**. The data reveals the significant impact of clay on polystyrene, which improves the mechanical properties of PS. The decrease in porosity, solvent retaining behaviour and swelling behaviour supports the flexibility in composite film than pure PS. It supports the interaction between clay and polymer matrix as well better processability.

Table 1. Porosity and swelling properties of PS and PS OVMT composite.

Sample	Porosity	Solvent content per unit volume (cm ³) in mg	Swelling behaviour (%)
OVMT/PS Composite	1.336	1.336	0.0317
OVMT/PS Composite	0.83	0.863	0.021

Burning behaviour

The result of flame retardant behaviour of composite is studied by vertical ignition (UL-94) and data is shown in **Table 2**. The result clearly reveals the decrease in flammability of polystyrene by twenty-three percentage after making its composite with OVT. It is a significant improvement in flame retardant behaviour of PS due to addition of OVT and extends the application of PS as flame retardant materials.

Table 2. Flammable behaviour of PS and PS OVMT composite.

Sample	Time to ignite (second)	Dripping behaviour(s econd)	Ignition of cotton
Pure PS	42	2	Yes
OVMT/PS composite	52	4	Yes

Conclusion

In this study, the PS/OVT composite is prepared by simple solution blending method and further casted in the form of a film by solvent casting technique. The dispersion of OVT demonstrates the improvement in thermal stability, mechanical and flame retardant nature of PS along with decrease in crystalline behaviour and porosity of PS. The technique promises to be a method to prepare better thermally stable and non-flammable composite. The finding also offers several other advantages like excellent yields, use of inexpensive equipment and relatively shorter time and better scalability prospects

Acknowledgements

We are thankful to CSIR for providing financial support and University of Delhi for providing infrastructural facilities.

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