

Synthesis, Characterization, and Properties of Intercalated Poly(2-Ethyl Hexylacrylate)/Silicate Nanocomposites: XRD, TEM, IR, TGA, Superabsorbency, Pressure-Sensitive Adhesion, and Biodegradation

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ABSTRACT: Poly(2-ethyl hexylacrylate) (PEHA)/silicate composites were synthesized by the emulsion polymerization of ethyl hexylacrylate (EHA) in the presence of sorbitol and the composites were analyzed to be of nano order. The nanocomposites so prepared were shown to be intercalated by X-ray diffraction, transmission electron microscopy, and infrared spectroscopy. The thermal stability of the nanocomposites was found to be appreciably increased. These nano-

composites are potentially suitable for novel uses such as pressure-sensitive adhesives and superabsorbents. The biodegradability and superabsorbency of these nanocomposites were evaluated for their commercial potential. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1007–1011, 2004

Key words: nanocomposites; TEM; pressure sensitive adhesive; superabsorbency; biodegradability

INTRODUCTION

Polymer-layered silicate represents a new class of materials with high performance and is of great academic and industrial interest. The improved properties of these nanocomposites include mechanical,^{1–3} thermal,^{4,5} and flammability⁶ properties and are related to the dispersion and nanostructure of the layered silicate in the polymer. There are four methods to make nanocomposites: exfoliation-adsorption, *in situ* intercalative polymerization, melt intercalation, and template synthesis.⁷ With favorable interactions between the polymer and silicate, two types of structures, intercalated and exfoliated, are generally possible. The intercalation of polymer chains results in the finite expansion of the silicate layers being disturbed. Therefore, intercalated structures consist of well-ordered multilayers of polymer and silicate layers a few nanometers thick. Exfoliated structures, however, are formed because of extensive penetration of polymer into the silicate layers, resolution in the determination of the silicate layers, and therefore, a loss of the ordered structure.⁸ Despite the considerable number of studies

concerned with the preparation, characterization, and material properties of various types of polymer/silicate nanocomposites,^{9–12} no report has been published regarding biodegradability and pressure sensitive adhesiveness (PSA) of polymer/silicate nanocomposites. Thus, synthesis of novel intercalated nanocomposites of poly(2-ethyl hexylacrylate) (PEHA)/silicate is of great interest for possible use as superabsorbents and pressure-sensitive adhesives, and study of their biodegradability.

EXPERIMENTAL

Materials

Monomer, 2-ethyl hexylacrylate (EHA), was purchased from SRL India Ltd. (Mumbai, India) and sorbitol (AR grade) was purchased from S. D. Fine Chemicals Ltd. (Mumbai, India). Sodium silicate (SS) was a gift solid granular sample (CAS 1344-09-8, Batch no. 2D23BB H₂O-1) from PQ Corp. (Maastricht, The Netherlands) and its solution was prepared in distilled water.

Preparation of nanocomposites

Distilled ethyl hexylacrylate (EHA) was dispersed in deionized water via stirring with the sorbitol. Silicate solution was prepared on a weight percentage basis. The mixture was slowly heated to 80°C and potassium

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persulfate dissolved in water was added. Emulsion polymerization was carried out with a constant stirring speed at 80°C. After 3 h of reaction, polymerization was terminated by the addition of a 0.1M solution of ferrous ammonium sulfate solution. The coagulated products were purified by washing with distilled water, and dried at 65°C.

CHARACTERIZATION

The insertion of PEHA into the silicate layer was confirmed by using an XRD monitoring diffraction angle 2θ from 1.5° to 10° on a Philips PW-1847 X-ray crystallographic unit equipped with a Guinier focusing camera with $\text{CuK}\alpha$ radiation ($\lambda = 0.15059$ nm) with a 0.02 2θ step size and a 2-s count time.

Nanoscale structure of PEHA/silicate was investigated by means of a TEM (H-7100, Hitachi Co.), operated at an accelerating voltage of 100 kV. The ultrathin section (the edge of the sample sheet perpendicular to the compression mold) with a thickness of 100 nm was microtomed at -80°C .

Thermal properties were measured by using a Shimadzu DTA-500 system. It was carried out in air from room temperature to 800°C at a heating rate of 10°C/min.

The IR spectra of silicate, PEHA, and PEHA/silicate, in the form of KBr pellets, were recorded with a Perkin-Elmer model Paragon-500 FTIR spectrophotometer.

Water absorbency

One gram of the sample was immersed in water at room temperature until equilibrium was reached. The water absorption was determined by weighing the swollen gel after it had been allowed to drain on a sieve for 10 min. The water absorbency¹³ Q (g H_2O /g sample) was calculated by using the following equation: Q (g H_2O /g sample) = $(m - m_0)/m_0$, where m and m_0 denote weight of the sample swollen by water and weight of the absorbent, respectively.

Peeling test

The peeling test was carried out with specimens having peel adhesion measurements of 20 mm width and 50 mm length. The specimens were applied to aluminum, tin, or paper substrates and pressed by using a 2-kg roller that passed slowly over the specimen at a rate of 300 mm/m two times each in a lengthwise direction. The PEHA/silicate, aluminum/tin/paper joints stored at room temperature for 48 h, and peel adhesion in the 180° direction was measured at a peel rate of 300 mm/m at room temperature by using an Instron type adhesion tester (Minebia Co., Japan, model TCM-1KNB).

Biodegradation by activated sludge

The activated sludge water was collected from a tank area receiving toilet and domestic wastewater. In most areas of our country, the waste materials after use are dumped usually near the sludge area and the sludge water contains many microorganisms (bacteria, fungi, yeast, etc.) responsible for the biodegradation of waste materials. The sludge was collected¹⁴ in a polypropylene container, which was filled completely and then fully closed. Then, the wastewater was brought to the lab immediately. After settling for about 1 h, the total solid concentration was increased to 5000 mg/L. The activated sludge water and a polymer sample (0.2 g) were incubated together in a sterilized vessel at room temperature ($28 \pm 2^\circ\text{C}$). Duplicate samples were removed at time intervals for biodegradation study via weight loss. Vessels containing polymer samples without sludge water were treated as controls.

RESULTS AND DISCUSSION

XRD

The periodic arrangement of the silicate layers of the intercalated states has been elucidated by X-ray diffraction in determining interlayer spacing.¹⁵ From XRD pattern, the d -spacings were calculated from Bragg formula, at peak positions. Due to the intercalation of PEHA into the galleries via emulsion polymerization, the d -spacing of PEHA/silicate nanocomposites increased from 1.83 to 2.16 nm in the dry state, even though the interlayer distances of the PEHA/silicate exhibited small deviation (Fig. 1). This is a strong indication that there is no trace for the occurrence of the delamination or exfoliation. The XRD patterns suggest that the strongly hydrophobic PEHA was inserted into the galleries of the hydrophilic silicate through emulsion polymerization¹⁶ (Scheme I). This result was further confirmed by comparison with XRD patterns of various polymeric systems such as polyaniline¹⁷ and poly(methyl methacrylate).¹⁸

TEM

The dispersion microstructure of the intercalated silicate layers was also examined by means of TEM. The high magnification TEM image of PEHA/silicate [Fig. 2(a)] demonstrates that the dark lines of the silicate layers are structured in good order, each of which is well dispersed homogeneously in the polymer matrix.¹⁹ The low-magnification TEM image [Fig. 2(b)] shows a general view of the dispersed silicates in the matrix. The smaller interlayer spacing in the figure indicates the intercalation is not exfoliated. The image confirms that the synthesized composite is a nanoscale material and no delamination of the silicate layers took place during intercalation.

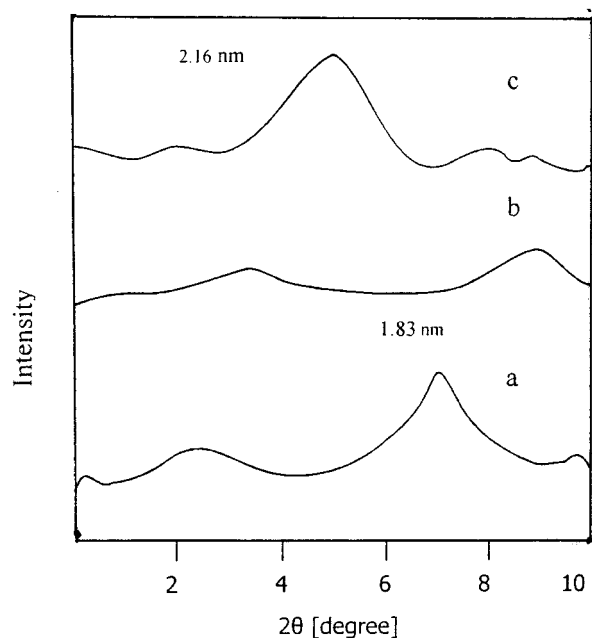


Figure 1 XRD curve of (a) sodium silicate, (b) PEHA, and (c) PEHA/SS.

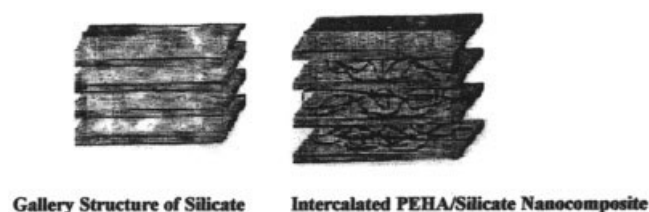
IR

FTIR spectral measurements of the PEHA/SS composite [Fig. 3(c)] revealed an interesting result when compared with the silicate [Fig. 3(a)] and PEHA [Fig. 3(b)]. Absorption bands at 1545, 1406, and 1015 cm^{-1} , assigned to the carbonyl group of the carboxylate of PEHA, and absorption bands 2148, 1468, and 990 cm^{-1} and fingerprint of 618 cm^{-1} , are due to the Si—O bond of silicate.

The observed absorption at 1468 cm^{-1} is characteristic of a partially ordered phase where the chains are mobile while maintaining some orientational order.²⁰ IR spectra of PEHA/SS contain all these peaks of silicate and PEHA, explaining the proof of intercalation.²¹

TGA

TGA of PEHA, SS, and PEHA/SS nanocomposites are shown in Figure 4. In contrast to PEHA [Fig. 4(b)], the onset of decomposition for PEHA/SS nanocomposite



Scheme 1

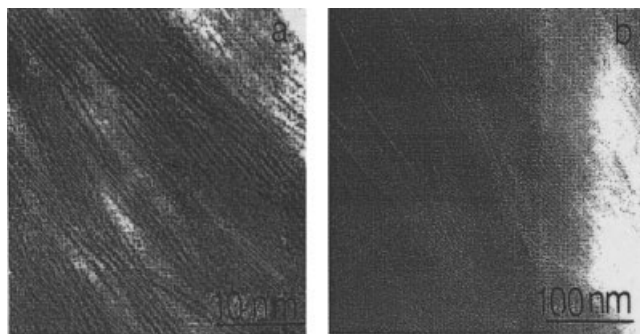


Figure 2 (a) High-magnification TEM of intercalated PEHA/SS and (b) low-magnification TEM of intercalated PEHA/SS.

is shifted toward a higher temperature with increased silicate content, indicating an enhancement of the thermal stability upon intercalation. The amounts of PEHA intercalated between the interlayer of silicate were proportional to the silicate content. The PEHA/SS nanocomposites exhibited higher thermal stability due to the higher decomposition onset temperature than that of PEHA, which can be attributed to the nanoscale silicate layers, preventing out-diffusion of the volatile decomposition products. It was in good agreement with the result of Chen et al.²²

Superabsorbency

An interesting finding was that the hydrophobic nature of PEHA polymer was converted into hydrophilic nanocomposite with the help of the silicate additive.

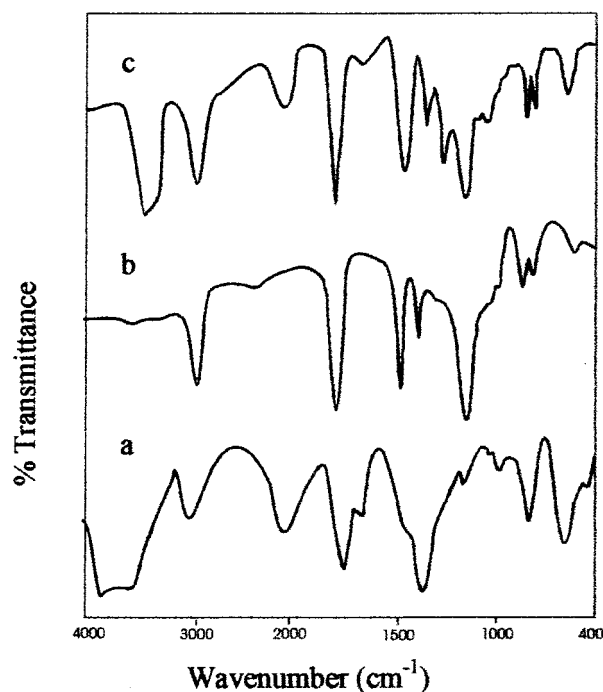


Figure 3 FTIR spectra of (a) sodium silicate, (b) PEHA, and (c) PEHA/SS.

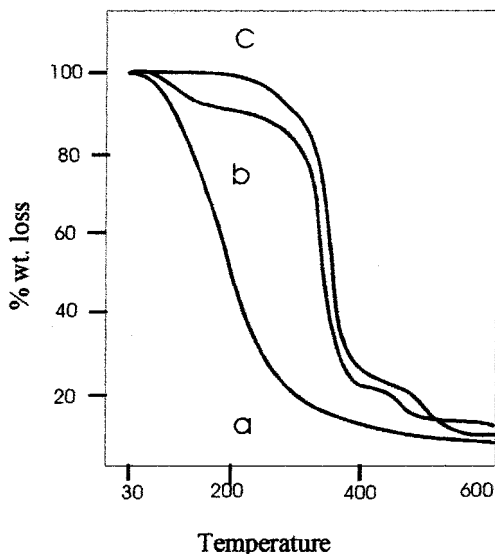


Figure 4 TGA thermogram of (a) sodium silicate, (b) PEHA, and (c) PEHA/SS.

The amount of water absorbed by the PEHA is much less than that of PEHA with additive (SS) samples (i.e., SS₁ to SS₅). The water absorption increases with additive concentrations increasing from 0.001 to 0.05 mol dm⁻³ and then decreases, as shown in Figure 5. This is explained on the basis of intercalation of hydrophilic PEHA into the silicate layers making more room for water molecules. The higher silicate concentration suppresses the degree of intercalation, thereby lowering the hydrophilicity of the composite.

Peel adhesion

The nanocomposites exhibit good performance as pressure-sensitive tapes on aluminum, tin, and paper (Table I). It shows better results for PSA on higher energetic surfaces such as aluminum and tin. The carbonyl group present in it plays an important role in adhesion with the surface. It is found that the peel strength increased with an increase in percentage of silicate content.

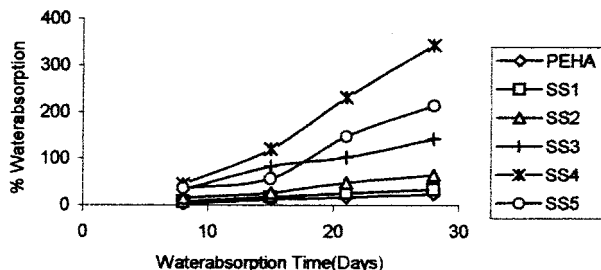


Figure 5 Water absorbcency of (◇) PEHA and PEHA/SS (SS₁₋₅).

TABLE 1
Peel Strength (kg/cm) of Aluminum, Tin, and Paper Pressure Sensitive Adhesive Tape Coated with PEHA/SS Composites

[SS] (mol dm ⁻³)	Peel strength (kg/cm)		
	Aluminium	Tin	Paper
0.001	0.251	0.148	0.073
0.005	0.432	0.173	0.094
0.01	0.507	0.198	0.112
0.05	0.571	0.246	0.136
0.1	0.612	0.293	0.153

Biodegradation

Degradation by activated sludge

Biodegradation by activated sludge is less in the case of PEHA than that of PEHA/SS₁₋₅ samples. The biodegradation is highest with additive [SS] = 0.05 mol dm⁻³, as shown in Figure 6, where water absorbcency is also highest. So, from this observation, it was confirmed that the growth of microorganisms was more because of the presence of more water in the sample. Further, because of the hydrophobic nature of PEHA, the water absorbcency is less, which results in its reduced biodegradation.

CONCLUSION

Novel PEHA/silicate nanocomposites were prepared by emulsion technique with layered silicate. XRD results showed a disordered layer structure due to intercalation of polymer into the silicate layer. These novel nanocomposites are further characterized by IR, TGA, and TEM and exhibited improved properties of higher thermal stability, pressure-sensitive adhesion, and superabsorbency for use as high-performance materials. For commercial potential, a study of their biodegradability was important and those samples having moderate silicate additive in sludge water showed better degradation by microorganisms than the PEHA without silicate. These biodegradable nanocomposites have the potential to be used as superabsorbents.

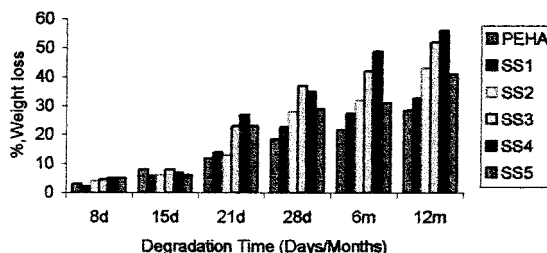


Figure 6 Biodegradation by activated sludge of (a) PEHA, (b) PEHA/SS (SS₁₋₅).

PSAs also exhibit significantly increased thermal stability.

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