

**SYNTHESIS, CHARACTERIZATION AND PHOTO BEHAVIOR OF NEW
POLY(AMIDE-IMIDE)/MONTMORILLONITE NANOCOMPOSITE
CONTAINING N,N'-PYRROMELLITOYL-BIS-L-ALANINE**

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ABSTRACT. Two new samples of poly(amide-imide)-nanocomposites were synthesized by insertion nano silicate particles in poly(amide-imide) (PAI) chains using a convenient solution intercalation technique. PAI as a source of polymer matrix was synthesized by the direct polycondensation reaction of N,N'-pyromellitoyl-bis-L-alanine with 4,4'-diamino diphenyl ether in the presence of triphenyl phosphite (TPP), CaCl₂, pyridine and N-methyl-2-pyrrolidone (NMP). Morphology and structure of the resulting PAI-nanocomposite films with 5 and 10% silicate particles were characterized by FTIR spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The effect of clay dispersion and the interaction between clay and polymeric chains on the properties of nanocomposites films were investigated by using UV-Vis spectroscopy, thermogravimetric analysis (TGA) and water uptake measurements.

KEY WORDS: Nanocomposite, Poly(amide-imide), Silicate particle, Polycondensation, Thermal behavior

INTRODUCTION

Polymer-clay nanocomposites typically exhibited good mechanical, thermal and gas barrier properties, which are superior to those of the corresponding pure polymers [1-9]. Unique properties of the nanocomposites are usually observed when the ultra fine silicate layers are homogeneously dispersed throughout the polymer matrix at nanoscale. The uniform dispersion of silicate layers is usually desirable for maximum reinforcement of the materials. Due to the incompatibility of hydrophilic layered silicates and hydrophobic polymer matrix, the individual nanolayers are not easily separated and dispersed in many polymers. For this purpose, silicate layers are usually modified with an intercalating agent to obtain organically modified clay prior to use in nanocomposite formation [10-11]. Also thermally stable polyamides (PA)s have received much attention over the past decade, owing to increasing demands for high-performance polymers materials for several applications such as high strength, high-modulus fibers, high-temperature coating and high-efficiency semi-permeable membranes. But, due to their low solubility, their applications have been restricted [12-16]. Much effort has been made to create structurally modified aromatic polyamides having better characterization in terms of both solubility and processability with retention of their high thermal stability. Thus, to overcome these processing problems various approaches have been carried out by incorporating flexible units such as -NHCO-, -O-, N=N and -SO₂-, and some of which are commercialized. On the other hand introduction of flexible chains into the PAs backbone, the use of meta-oriented monomers and synthesis of PAs with non-coplanar unit in the polymer chains, resulted in a number of modified PAs. Another strategy is based on the introduction of bulky side groups into the polymer chains [17-24].

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In this article two PAI-nanocomposite films with 5 and 10% silicate particles containing N,N'-pyrromelitoyl-bis-L-alanine moiety in the main chain were prepared by using a convenient solution intercalation technique.

EXPERIMENTAL

Materials

Pyromellitic anhydride, L-alanine, 4,4'-diamino diphenyl ether, acetic acid, triphenyl phosphite (TPP), CaCl₂, pyridine and N-methyl-2-pyrrolidone (NMP) were purchased from Merck Chemical Company and used without further purification. Purified organically modified Cloisite 20A supplied by Southern Clay Products (TX, USA) was used as polymer nanoreinforcement.

Techniques

¹H-NMR spectrum was recorded on a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on Galaxy Series FTIR 5000 spectrophotometer (England). UV-visible spectra were recorded at 25 °C in the 250-700 nm spectral regions with a Perkin Elmer Lambda 15 spectrophotometer in NMP solution using cell lengths of 1.0 cm. Thermal gravimetric analysis (TGA and DTG) data were taken on a Mettler TA4000 System under N₂ atmosphere at a rate of 10 °C/min. The morphology and structure of nanocomposite film were investigated on Cambridge S260 scanning electron microscope (SEM). X-ray diffraction (XRD) were performed on Philips X-Pert (Cu-Kα radiation, λ = 0.15405 nm). The water absorption of PAI-nanocomposite films were carried out using a procedure under ASTM D570-81 [25].

Monomer synthesis

N,N'-pyrromelitoyl-bis-L-alanine **1** was prepared according to a typical procedure [23].

Polymer synthesis

Into a 100 mL round bottomed flask were placed a mixture of N,N'-pyrromelitoyl-bis-L-alanine **1** (0.002 mol), 4,4'-diamino diphenyl ether **2** (0.002 mol), 0.60 g of calcium chloride, 1.0 mL of triphenyl phosphite, 1.0 mL of pyridine and 4.0 mL NMP. The mixture was heated for 1 h at 60 °C, 2 h at 90 °C and then refluxed at 140 °C for 8 h until a viscous solution was formed. Then it was cooled to room temperature and 30 mL of methanol was added to reaction mixture. The precipitate was formed, filtered off and washed with methanol. The resulting poly(amide-imide) **3** was dried under vacuum. The inherent viscosity of this soluble PAI **3** was 0.55 dL/g. Elemental analysis (CHN) for C₂₈H₂₀N₄O₇: calculated: C, 64.12; H, 3.84; N, 10.68. Found: C, 63.04; H, 3.77; N, 10.61.

PAI-Nanocomposite synthesis 4a and 4b

PAI-nanocomposites **4a** and **4b** were produced by solution intercalation method. Two different amounts of organoclay particles (5 and 10-wt.%) were mixed with appropriate amounts of PAI solution in N-methyl-2-pyrrolidone (NMP) to yield particular nanocomposite concentrations. To control the dispersibility of organoclay in polyamide matrix, constant stirring was applied at 25 °C for 24 h. Nanocomposite films were cast by pouring the solutions for each concentration into petri dishes placed on a levelled surface followed by the evaporation of solvent at 70 °C for 12 h. Films were dried at 80 °C under vacuum to a constant weight.

The water absorption analysis

The water absorption of PAI-nanocomposite films was carried out using a procedure under ASTM D570-81 [25]. The films were dried in a vacuum oven at 80 °C to a constant weight and then weighed to get the initial weight (W_0). The dried films were immersed in deionized water at 25 °C. After 24 h, the films were removed from water and then they were quickly placed between sheets of filter paper to remove the excess water and films were weighed immediately. The films were again soaked in water. After another 24 h soaking period, the films were taken out, dried and weighed for any weight gain. This process was repeated again and again till the films almost attained the constant weight. The total soaking time was 168 h and the samples were weighed at regular 24 h time intervals to get the final weight (W_f). The percent increase in weight of the samples was calculated by using the formula $(W_f - W_0)/W_0$.

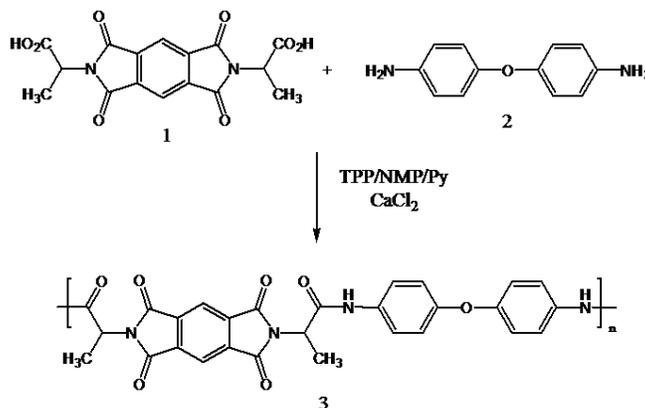
RESULTS AND DISCUSSION

Monomer synthesis

N',N'-pyrromellitoyl-bis-L-alanine **1** was synthesized from one equimolar pyrromellitic anhydride and two equimolar of L-alanine in acetic acid [23].

Polymer synthesis

Poly(amide-imide) **3** was synthesized by the direct polycondensation reaction of an equimolar mixture of diacid **1**, an equimolar mixture of diamine **2** by using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 1).



Scheme 1. Synthetic route of PAI **3**.

PAI **3** was obtained in good yield (99%) and inherent viscosity 0.55 dLg⁻¹. The structure of resulting polymer **3** was confirmed as PAI by using FTIR spectroscopy and elemental analyses. The resulting polymer have absorption band at 1680 cm⁻¹ due to amide carbonyl groups. Absorption bands at 3300 cm⁻¹ demonstrated the presence of the amide N-H stretching absorption in this polymer (Figure 1). The elemental analysis value of the resulting polymer was in good agreement with the calculated values for the proposed structure.

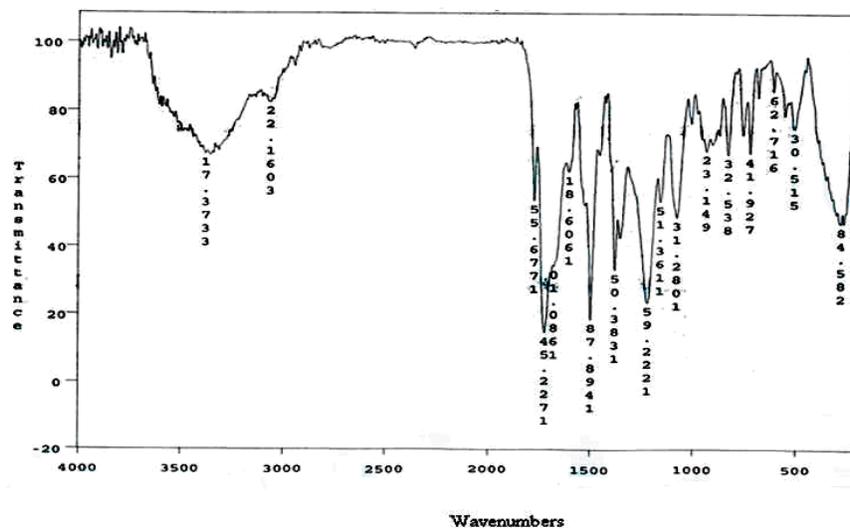
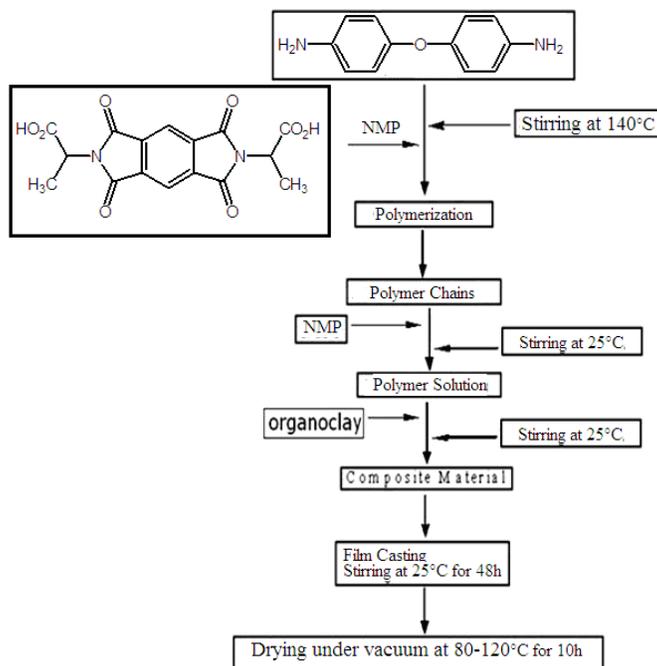


Figure 1. FTIR spectrum of PAI 3.

PAI-nanocomposite films

Scheme 2 shows the flow sheet diagram and synthetic scheme for PAI-nanocomposites film **4a** and **4b**.

Scheme 2. Flow sheet diagram for the synthesis of PAI-nanocomposites film **4a** and **4b**.

FT-IR spectroscopy analyses

FT-IR spectrum of PAI-nanocomposite films **4a** and **4b** showed the characteristic absorption bands of the Si-O and Mg-O moieties at 1076, 513 and 466 cm^{-1} , respectively. The incorporation of organic groups in PAI-nanocomposite films was confirmed by the presence of peaks at 3292 and 1664 (amide N-H stretching and carbonyl group) (Figure 2).

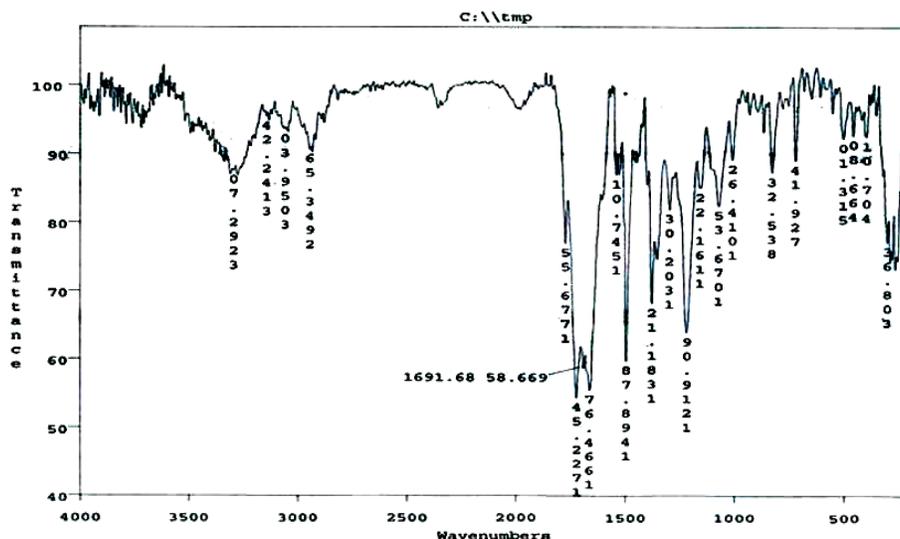


Figure 2. FTIR spectrum of PAI-nanocomposite films **4a**.

X-ray diffraction analysis

Figure 3 shows the XRD patterns of PAI-nanocomposite films **4a** and **4b** containing 5 and 10-wt.% of silicate particles. These results indicated significant expansion of the silicate layer after insertion PAI chains. The shift in the diffraction peaks PAI-nanocomposite films confirms that intercalation has been taken place. This is direct evidence that PAI-nanocomposites have been formed as the nature of intercalating agent also affects the organoclay dispersion in the polymer matrix. Usually there are two types of nanocomposites depending upon the dispersion of clay particles. The first type is an intercalated polymer clay nanocomposite, which consists of well ordered multi layers of polymer chain and silicate layers a few nanometers thick. The second type is an exfoliated polymer-clay nanocomposite, in which is there is a loss of ordered structures due to the extensive penetration of polymer chain into the layer silicate. Such part would not produce distinct peaks in the XRD pattern [27]. In our PAI-nanocomposite films there are coherent XRD signal at 5.32° and 4.46° related to 5 and 10 wt.% nanocomposite films, respectively.

Scanning electron microscopy

The surface morphology of the PAI-nanocomposite films prepared by solution intercalation technique is compared by SEM analyses. Figure 4 shows the morphological images of 5 and 10 wt.% nanocomposite films, respectively. The SEM images show that PAI matrix has a smooth

morphology. Also SEM micrographs of PAI-nanocomposite containing 5 and 10 wt.% clay platelets were uniformly distributed without agglomeration.

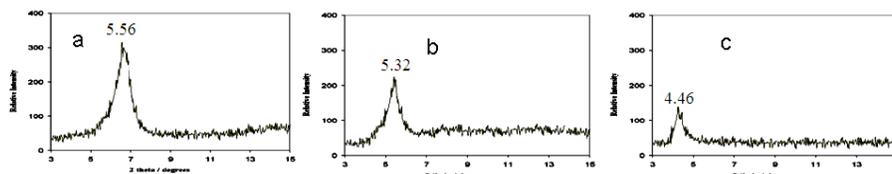


Figure 3. X-ray diffraction patterns of organoclay (a), PAI-nanocomposite films **4a** (b) and **4b** (c).

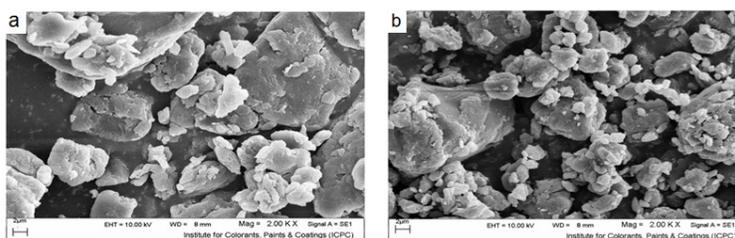


Figure 4. Scanning electron micrographs of PAI-nanocomposite films **4a** (a) and **4b** (b).

Optical clarity of PAI-nanocomposite films

Optical clarity of PAI-nanocomposite films containing 5 and 10 wt.% clay platelets and neat PAI was compared by UV-Vis spectroscopy in the region of 200-800 nm. Figure 5 shows the UV-Vis transmission spectra of pure PAI and PAI-nanocomposite films containing 5 and 10 wt.% clay platelets. This spectrum shows the UV-Visible region (220-500 nm) is affected by the presence of the clay particles and exhibiting low transparency reflected to the primarily intercalated composites. Results shows that the optical clarity of PAI-nanocomposite films system is significantly lower the neat PAI system.

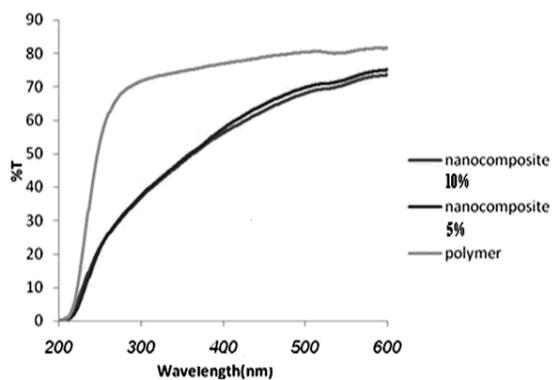


Figure 5. UV-Vis spectra of PAI **3**, PAI-nanocomposite films **4a** and **4b**.

Thermogravimetric analysis

The thermal properties of PAI-nanocomposite films containing 5 and 10 wt.% clay platelets and neat PAI were investigated by using TGA in nitrogen atmosphere at a rate of heating of 10 °C/min, and thermal data are summarized in Table 1 (Figure 6). These samples exhibited good resistance to thermal decomposition, up to 112 °C in nitrogen, and began to decompose gradually above this temperature. T_5 for these polymers ranged from 112-114 °C and T_{10} for them ranged from 136-138 °C, and residual weights at 600 °C and 800 °C ranged from 43.85 and 38.73% in nitrogen, respectively. Incorporation of organoclay into the PAI matrix also enhanced the thermal stability of the nanocomposites. Figure 6 shows the TGA thermograms of PAI-nanocomposites under nitrogen atmosphere. Thus, we can speculate that interacting PAIs chains between the clay layers serve to improve the thermal stability of nanocomposites. The addition of organoclay in polymeric matrix can significantly improve the thermal stability of PAI.

Table 1. Thermal behaviors and water uptake of neat PAI **4** and PAI-nanocomposite films **4a** and **4b**.

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char Yield ^{c(600)}	Char Yield ^{c(800)}	Water uptake (%)
4	112	136	43.85	38.73	6.1
4a	134	165	49.31	44.15	1.9
4b	215	306	57.35	49.43	0

^{a,b}Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10 °C/min in N₂ respectively ^cPercentage weight of material left undecomposed after TGA analysis 600 °C and 800 °C .

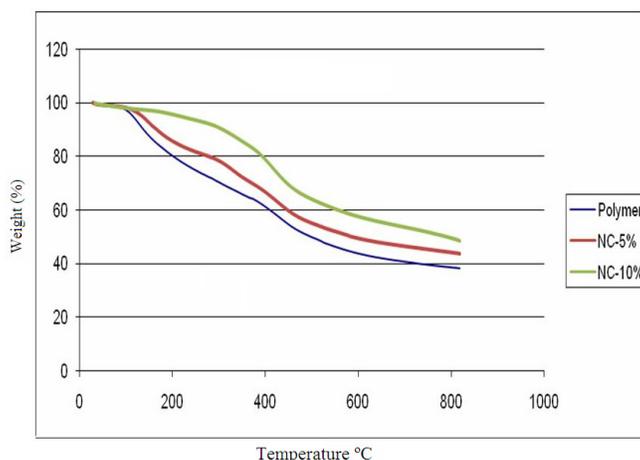


Figure 6. TGA thermograms of neat PAI **3** and PAI-nanocomposite films **4a** and **4b**.

Water absorption measurements

The PAI under investigation contains polar amide groups in the backbone that have the tendency to uptake water through hydrogen bonding. Thus water absorption measurements become necessary for neat PAI **3** and PAI-nanocomposite films **4a** and **4b** and data are shown in Table 1 (Figure 7). In the water permeability studies, we found that the incorporation of clay platelets into PA matrix results in a decrease of water uptake relative to pure PAI by forming the tortuous path of water permeant. Water permeability depends on length, orientation and degree

of delamination of layered silicate [25]. It should be noted that a further increase in clay concentration resulted in an enhanced barrier property of nanocomposites which may be attributed to the plate-like clays that effectively increase the length of the diffusion pathways, as well as decrease the water permeability.

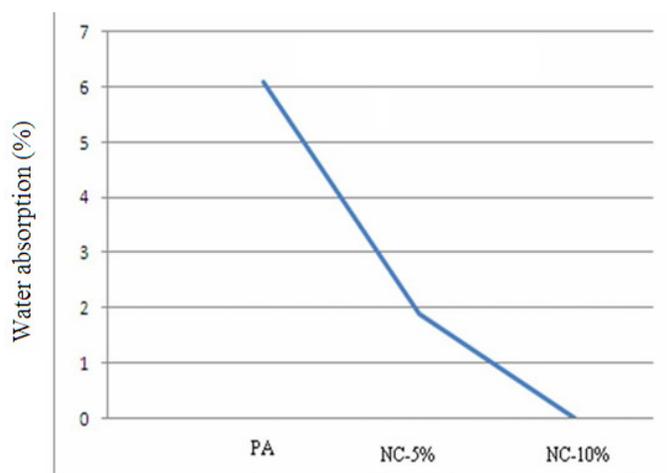


Figure 7. Water absorption measurements become necessary for neat PAI **3** and PAI-nanocomposite films **4a** and **4b**.

CONCLUSIONS

The PAI-nanocomposites were successfully prepared using solution intercalation method. The structure and the uniform dispersion of organoclay throughout the PAI matrix were confirmed by FTIR, XRD and SEM analyses. The optical clarity and water absorption property of PAI-nanocomposites were decreased significantly with increasing the organoclay contents in PAI matrix. On the contrary the thermal stability of PAI-nanocomposites was increased significantly with increasing the organoclay contents in PAI matrix. The enhancements in the thermal stability of the nanocomposites films **4a** and **4b** caused by introducing organoclay may be due to the strong interactions between polymeric matrix and organoclay generating well intercalation and dispersion of clay platelets in the PAI matrix.

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