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Synthesis and Characterization of thermal behaviours of a New Series of Polyimide-Nanocomposite Reinforced by Modified Layered Silicate Based on 3,3′,4,4′-Biphenyl tetracarboxylic Dianhydride

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ABSTRACT

In this research, three new reinforced nanocomposites polyimides films (**9a-c**) by modified organoclay (MMT) (**8**) containing 1, 3 & 5 wt% were successfully prepared by in situ polymerization technique through the thermal imidization up to 200°C into a solution of N, N′-dimethyl acetamide (DMAc). Synthetic polyimide (**4**) that used as a matrix was prepared through the polycondensation reaction of 4,4′-diamino diphenyl sulfone (**1**) and 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA) (**2**) into N, N′-dimethyl acetamide as solvent. Montmorillonite Na^+-organoclay (MMT) (**5**) was modified via a cationic exchange method by the reaction between the sodium cations of Na^+-MMT clay and quaternary alkyl ammonium ions of 4-amino benzoic acid (**6**) (*p*-ABA) as intercalation agent. Resulting polyimide chains (**4**) diffused into the interlayer of modified organoclay layers (**8**) by intercalation polymerization technique. The resulting nanocomposite films (**9a-c**) containing 1, 3 & 5 wt% of modified organoclay prepared by casting method were characterized by Fourier-Transform infrared (FT-IR) spectroscopy, wide-angle powder X-ray diffraction (XRD), scanning electron microscopy (SEM). Results by thermo gravimetric analysis (TGA) indicated shown a sharp increase into thermal stability of their nanocomposites as compared to pristine polyimide.

KEYWORDS: *Nanocomposite, Organoclay, Polyimide, In situ intercalation, Thermal stability*

1. Introduction

Polyimides (PIs) are a main class of polymers with important properties such as high thermal stability, radiation resistance, low density, toughness, flexibility, high mechanical stability and good chemical properties [1, 8, 23]. They are widely used in aerospace, solar cell, microelectronics, sensors, biomedical engineering and insulation layers [2, 21, 23]. The unique problems of polyimides include high softening temperature and low solubility in common organic solvents [3]. Improving the properties of polyimides has been widely investigated for application in various industries. In order to find good compatibility, fillers have been used to prepare polyimide nanocomposites [1]. The fillers commonly used in polyimide nanocomposites include clay, carbon nanotubes and graphene [8, 22]. Among the nano additives, montmorillonite nano clays are preferred due to their naturalness, charge density, cation exchange capacity (CEC), swell ability and low cost [4-7]. Polymer/clay nanocomposites are produced via in situ polymerization. In this method, nanocomposites are formed by embedding montmorillonite clay into a polymer matrix [9-13]. Montmorillonite clay, with a surface area of 700-800 m^2/g, greatly improves the properties of nanocomposites behaviors when used in small amounts [5, 8]. Montmorillonite consists of silicate sheets with a thickness of about 1.0 nm and a length of about 100 nm containing exchangeable alkali or alkaline earth cations such as Na^+, K^+, Ca^{2+} [14]. The layered structure of MMT consists of two tetrahedral sheets of silica or one octahedral sheet with common edges of aluminum or magnesium hydroxide. Due to the hydrophilic nature of MMT, its organic modification is an important step in the preparation of Na^+/MMT polymer nanocomposites. The Ca^{2+} present in the interlayer regions can be replaced by organic cations such as alkyl ammonium ions through a cation exchange reaction to minimize the hydrophilic layer of the organophilic silicate, leading to hydrophobic behavior [9, 15, 16]. Organic montmorillonite (OMMT) can be decomposed into nanoscale blocks and uniformly dispersed in a polymer matrix to form sheet-like nanocomposites during the polymerization process [9].

In our study, three new polyimide layer silicate (PLS) nanocomposite films (**9a-c**) were prepared and then structure and properties of them were fully characterized by means of Fourier-transform infrared (FT-IR) spectroscopy, Wide-angle powder X-ray diffraction (XRD), Scanning electron microscopy (SEM), Thermo gravimetric analysis (TGA) and Oxygen limitation index (LOI).

2. Experimental

2.1. Starting Materials

N, N- dimethyl acetamide (DMAc), 4-amino benzoic acid (p-ABA), 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA), 4,4′-diamino diphenyl sulfone and Sodium montmorillonite (Na-MMT) were purchased from Merck Chemical Co. (Germany). Sodium montmorillonite (Na-MMT), with a cation exchange capacity (CEC) of 95 Meq /100g was supplied and have been modified with *p*-amino benzoic acid (*p*-ABA) to preparation of nanocomposite films were synthesized in our lab.

2.2. Techniques

Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solid were performed by using KBr pellets. Vibration transition frequencies were reported in wave number (cm^{-1}). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Wide angle XRD study of the samples was performed with a X” pert pw 3064 X-ray diffractometer with a copper target at a scanning rate of 4°/min. The morphologies of the fractured surfaces of the extrusion samples were investigated using a LEO 1455 VP scanning electron microscope (SEM). Thermal Gravimetric Analysis (TGA) data for polyimide and nanocomposites were taken on a Perkin-Elmer TGA/DTA System under N_2 atmosphere at rate of 10°C/min.

2.3. Preparation of organomodified clay (8)

The modified organoclay (**8**) was prepared by a cationic exchange method by the reaction between the sodium cations of Na^+-MMT clay (**5**) and quaternary alkyl ammonium ions of *p*-amino benzoic acid (**6**) (*p*-ABA) as intercalation agent [17]. In this method, 5.0 g of pure montmorillonite (**5**) has been dispersed into 500 ml of distilled water (beaker A) by using a mechanical stirrer at room temperature overnight. In another beaker, 1.0 g of the organ filer (*p*-ABA) (**6**) was dissolved into 100 mL of distilled water and adjusted pH around 3-4 by hydrochloric acid solution. After 3 h while string continued a solution of amino acid (**7**) into distilled water was added to the Na^+-MMT suspension at room temperature. Then the mixture was stirred for 24 h and after completion of reaction, organomodified MMT (**8**) recovered using centrifugation and filtered. The filter cake was washed several times with distilled water to remove residual ammonium ions (Scheme 1).

2.4. Preparations of pristine poly(amic-acid) (PAAs) (3)

Pristine poly(amic-acid) (**3**) was prepared by using a molar ratio of 1:1 via polycondensation reaction of 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (**2**) (BPDA) and 4,4′-diamino diphenyl sulfone (**1**) as following [18]:

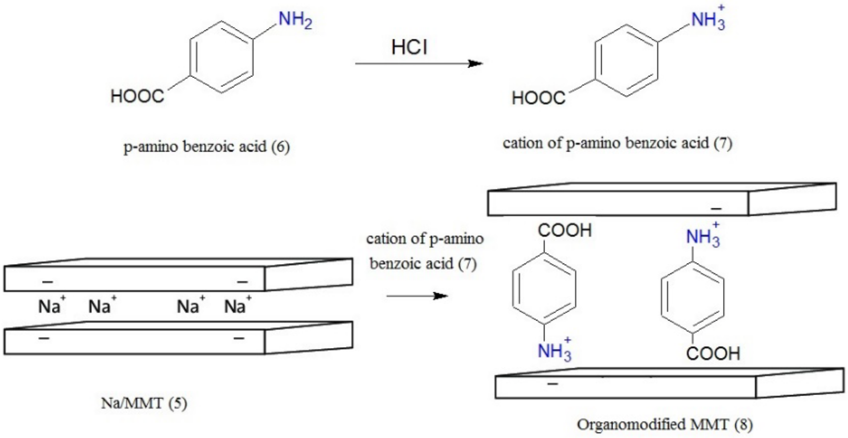
A mixture of 0.248 g (1.0 mmol) 4,4′-diamino diphenyl sulfone (**1**) into 3.0 ml of DMAc was stirred by using magnetic stirrer around 1 h under nitrogen atmosphere at room temperature (Cup A). Another mixture of 0.294 g (1.0 mmol) 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (**2**) (BPDA) into 2 mL of DMAc (Cup B) were prepared separately by stirring by the same condition. Cup A was poured into cup B followed by followed agitation stirring for 24 h under N_2 atmosphere at room temperature, to produce yellow viscous solution of poly(amic-acid) (**3**) (Scheme 2).

2.5. Preparations of polyimide (4) through thermal imidization:

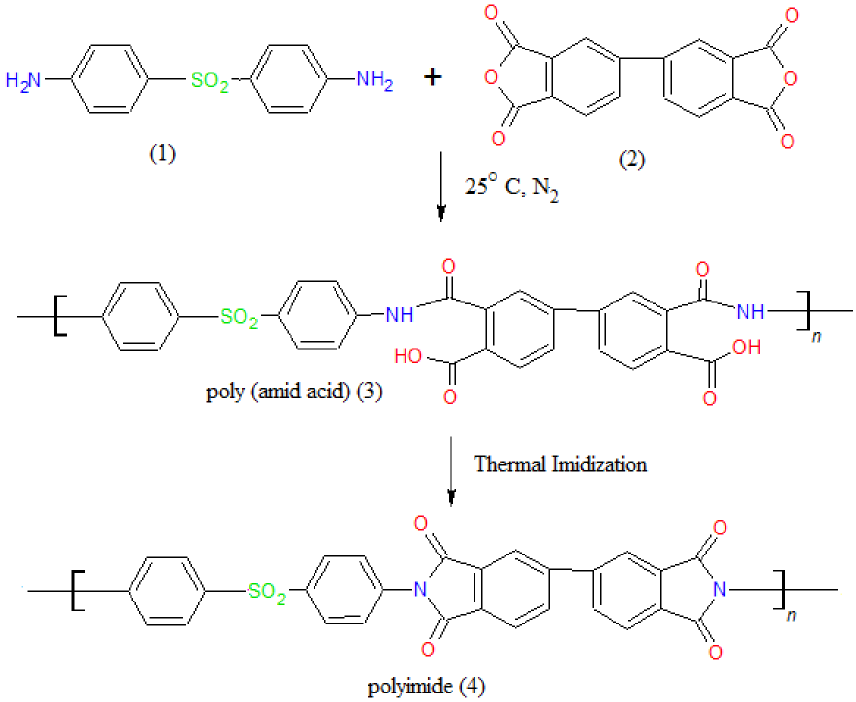
The new polyimide (PIs) film (4) was prepared by thermal imidization of intermediate poly(amic-acid) (**3**) by casting method of PAAs solution onto a glass plate under a programmed heat treatment into the vacuum oven as following: 2h at 80°C, 2h at 110 °C, 2h at 170°C, 4h at 200°C. The resulting film was changed from yellow to golden.

2.6. Synthesis of nanocomposite by in situ polymerization:

New nanocomposites (**9a-c**) were prepared by an in-situ polymerization approach [19]. An appropriate amount of organo modified MMT (1, 3 & 5 wt %) was added into 3.0 ml of DMAc by using magnetic stirring around 24 h under N_2 atmosphere at room temperature (Cup A), and 0.294 g (1 mmol) of dianhydride (**2**) (BPDA) was added into 1.5 ml



Scheme 1. Schematic representation for organo modified clay (**8**)



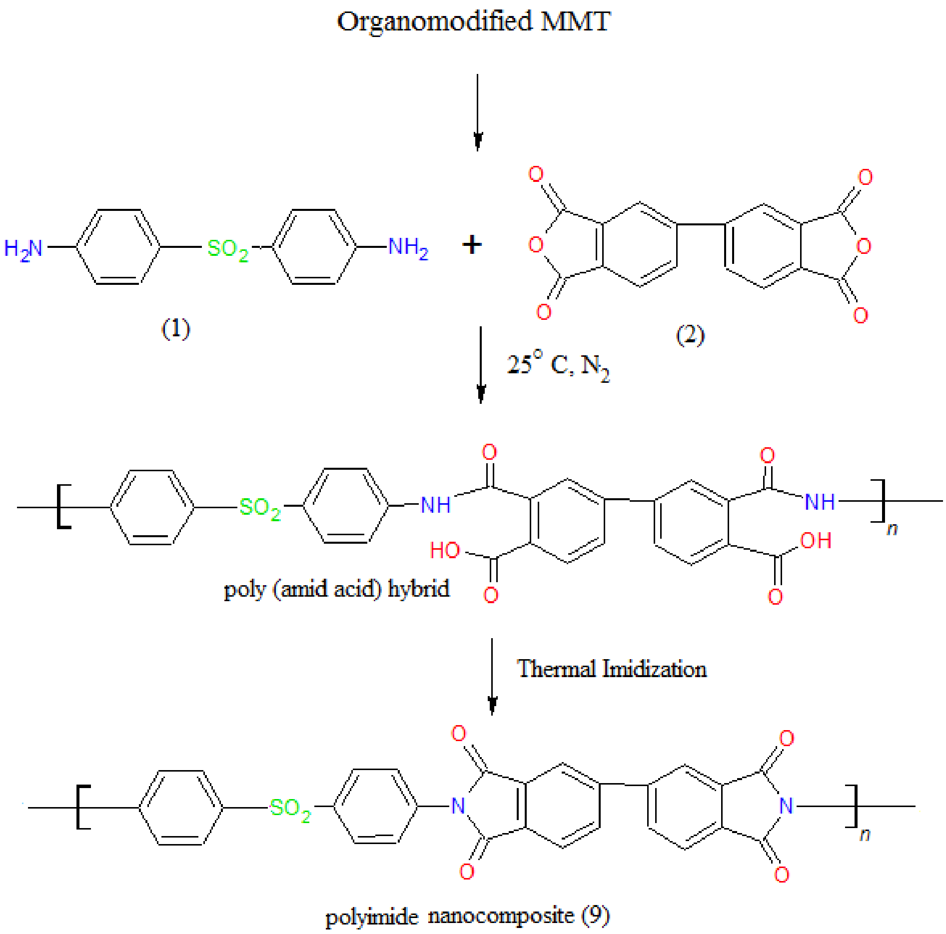
Scheme 2. Schematic presentation for polyimide (PIs) (**4**)

of DMAc with the aid of magnetic stirring for 30 min at room temperature (Cup B). Then cup B was poured into cup A and stirred around 24 h under N_2 atmosphere at room temperature. In the separated beaker 0.248 g (1 mmole) of diamine monomer (**1**) was dissolved into 1.5 ml of DMAc by stirring for 30 min at room temperature (Cup C). Cup C was added into mixture of cup A+B and stirred around 24 h under N_2 atmosphere at room temperature to form the poly(amic-acid). The final steps to preparing polyimide nanocomposite films is same as the pure PI film. The resulting mixture were transparent and changed color from yellow to golden.

3. Results and Discussion

The new polyimide (**4**) was prepared by a two steps process. First by reaction of 4,4´-diamino diphenyl sulfone (**1**) and 3,3',4,4'-biphenyl tetracarboxylic dianhydride (**2**) (BPDA) in room temperature a solution of pristine poly(amic-acid) (**3**) was prepared. In continue the heating of poly(amic-acid) solution (**3**) into refluxing DMAc as solvent caused the imide rings were closed and polyimide (**4**) was formed. Also the modified organoclay (**8**) was prepared by a cationic exchange method by the reaction between the sodium cations of Na^+-MMT clay (**5**) and quaternary alkyl ammonium ions of *p*-amino benzoic acid (**6**) (*p*-ABA) as intercalation agent.

The FTIR spectrum of polyimide (**4**), modified organoclay (**8**), PI/clay nanocomposites (**9a-c**) are shown in Figure 2. The spectrum of modified organclay (**8**) shows the characteristic bands of organoclay skeleton at 1047 cm^{-1} (Si-O), 524 cm^{-1} (Al-O) and 466 cm^{-1} (Mg-O). Into the spectrum of polyimide (**4**) NH_2 stretching vibrations at 3300-3400 cm^{-1} corresponding to primary diamine were disappeared and related absorption



Scheme 3. Synthesis of PI/clay nanocomposites (PCNs)

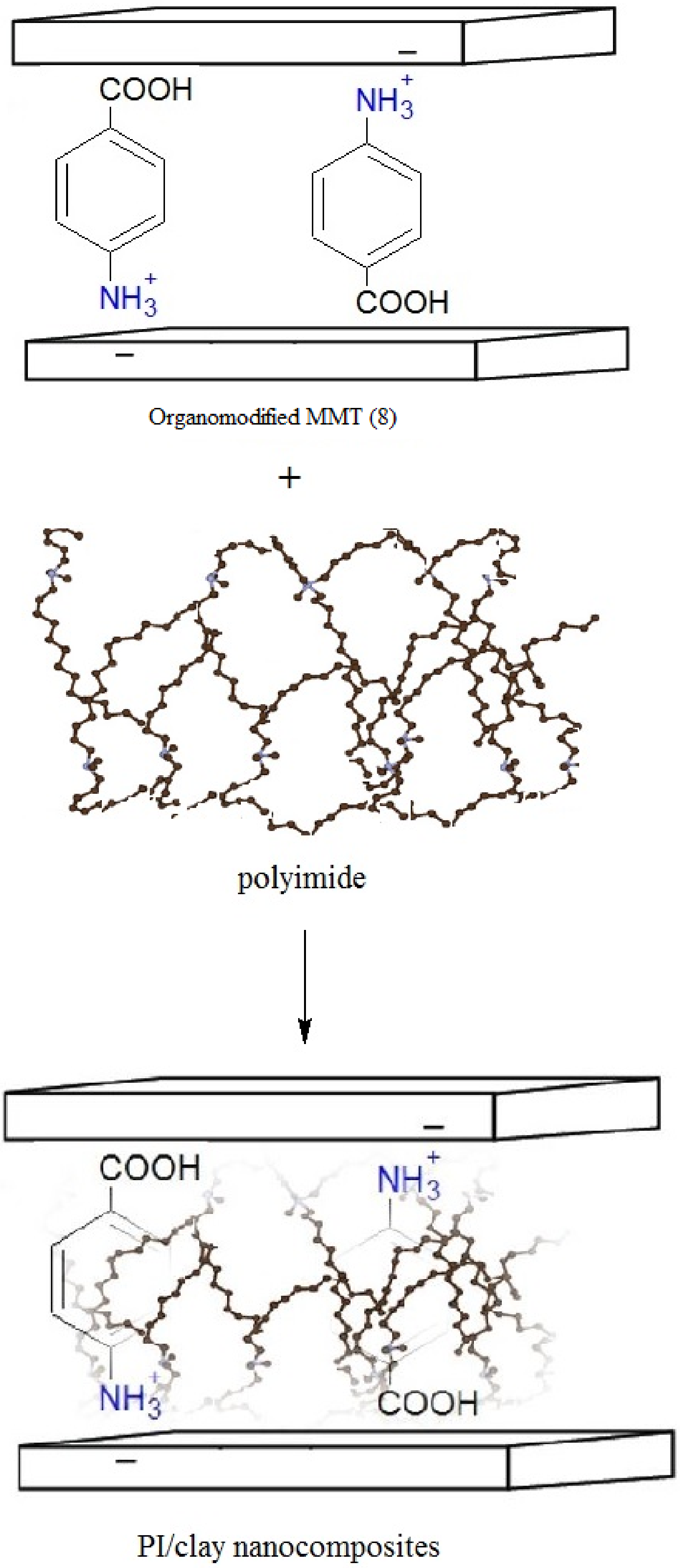


Fig. 1. Schematic diagram of preparation of PI/clay nanocomposites (**9a-c**)

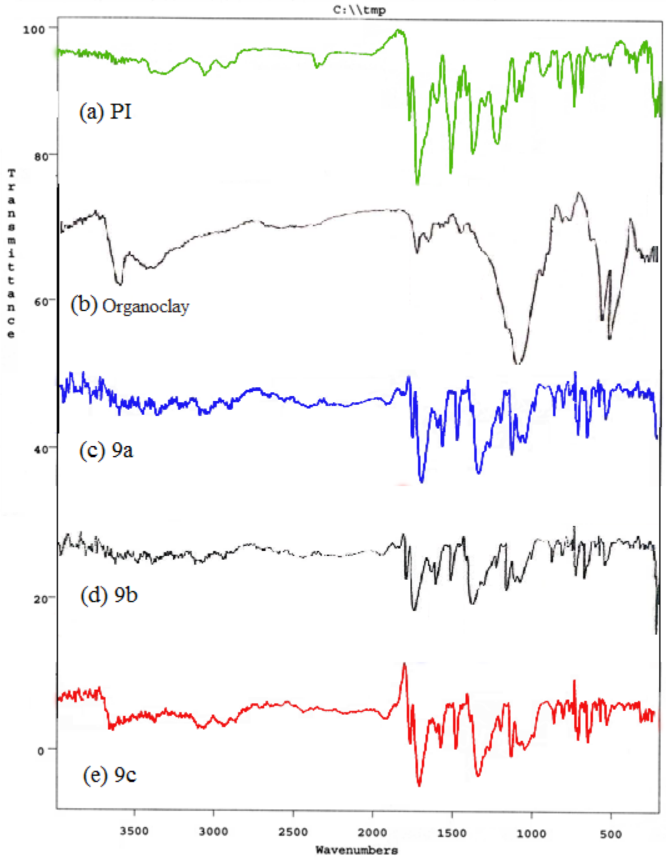


Fig. 2. FTIR spectra of (a) pure PI (4), (b) modified organoclay (**8**), (c) PI/clay nanocomposites (**9a**), (d) PI/clay nanocomposites (**9b**) and (e) PI/clay nanocomposites (**9c**)

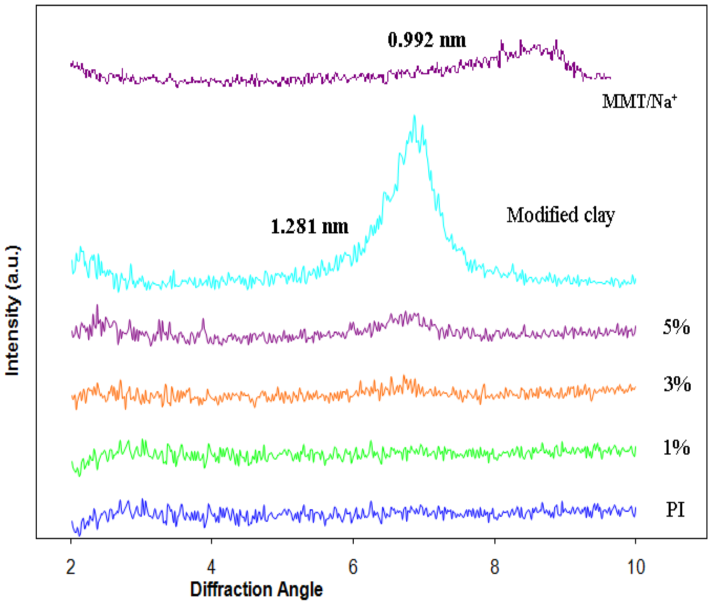


Fig. 3. Wide-angle powder X-ray diffraction patterns for pristine organoclay (**5**), modified organoclay (**8**), PI/clay nanocomposites (**9a-c**) and PI (**4**).

peaks at 1782 and 1718 cm^{-1} (asymmetric and symmetric stretching vibrations of C=O of cyclic imide groups), 1377cm^{-1} (C-N vibration), 1118 cm^{-1} (imide ring deformation) and 758 cm^{-1} (C=O bending vibration) showed the formation of polyimide. Also the characteristic peaks of aromatic ring skeletal vibrations occurred at 1608, 1510 and 1454 cm^{1}.

3.1. X-ray diffraction

Figure 3 shows results of the X-ray diffraction patterns (XRD) for pristine montmorillonite (Cloisite-20A) (**5**) modified organoclay (**8**), starting polyimide (**4**), PI/clay nanocomposites films (**9a-c**) reinforced by 1, 3 & 5 wt % MMT contents in the angle range of 2ϴ=2-10. A diffraction peaks of Na^{+}-MMT appeared at 2ϴ (Theta)= 9.3 (*d*-spacing:

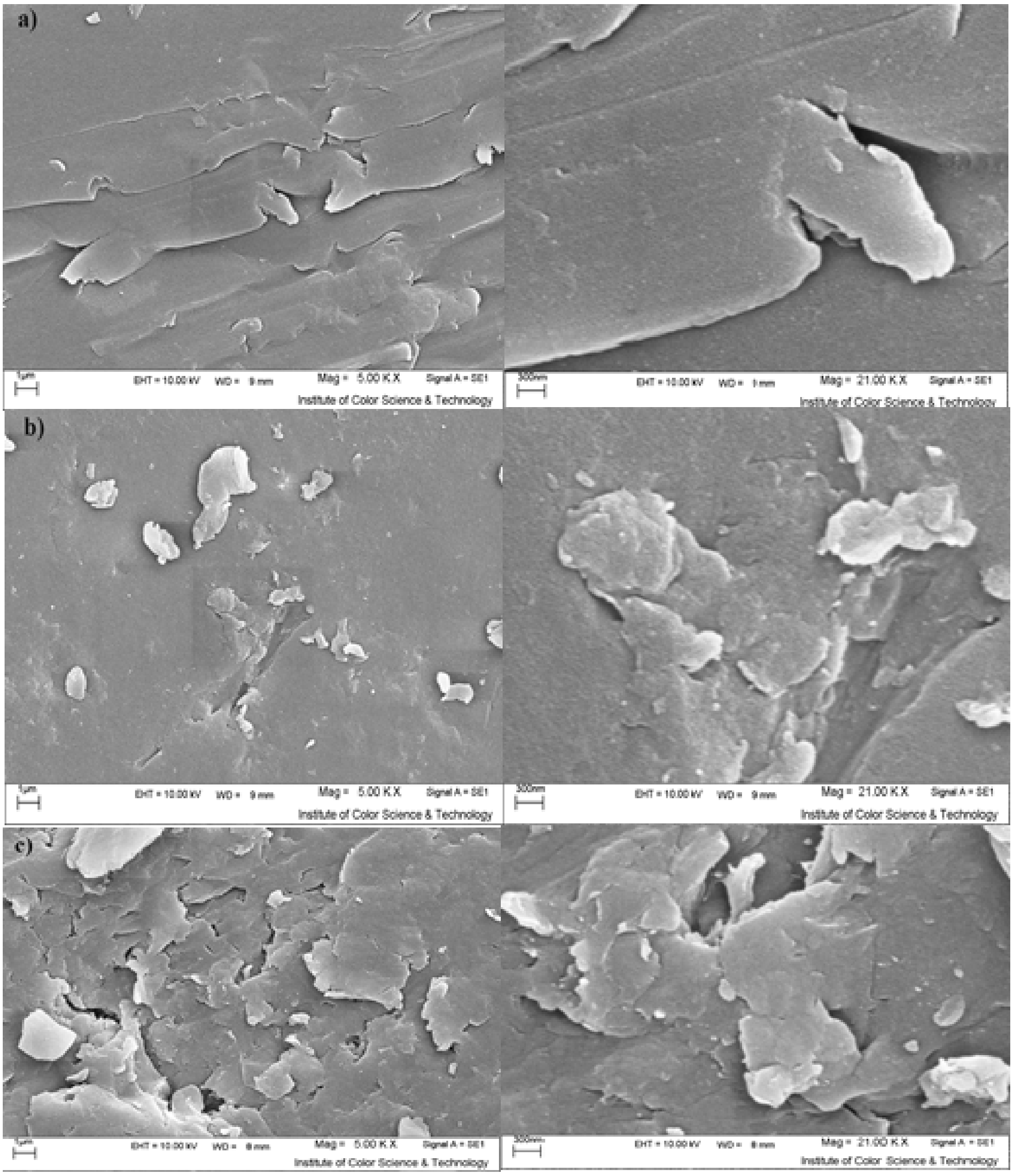


Fig. 4. Scanning electron micrograph image for (a) PI/clay nanocomposites (**9a**), (b) PI/clay nanocomposites (**9b**) and (c) PI/clay nanocomposites (**9c**)

0.992 nm) and organo-clay at 2θ=6.890 (*d*-spacing: 1.2818 nm) respectively. These results disclose 2θ absorptions at modified organoclay moved into the low angles in compare to pristine Cloisite Na^+ after ion exchange were take placed. No X-ray diffraction peak is discerning related the virgin PI. The absence of any peak in the range 2-10° 2θ into nanocomposite films with 1, 3 & 5wt% indicate formation of disarrange and individual silicate layers delaminated in the polyimide matrix that means an exfoliated dispersion of MMT into polymeric matrix. These result are in good compatibility according to observations noted in the SEM micrographs in Figures 3.

3.2. Scanning Electron Microscopy

The morphological pictures of resulting nanocomposites were studied by SEM technique and their images mentioned shown in Figures 4(a), 4(b) and 4(c). Into the SEM images the white strands corresponded to organoclay layers. The SEM picture of film related to 5 wt% of organoclay is well regularly dispersed in the Polyimide matrix.

3.3. Thermal stability of Polyimide clay nanocomposites (9a-c)

Thermal stability of the nanocomposites was study by thermogravimetric techniques (TGA & DTG) under N_2 atmosphere at a heating rate of 10 °C min^{-1} Figure 5. showed the TGA curves of polyimide nanocomposite films with 1, 3 & 5wt% of MMT contents. Usually the thermal stability of the nanocomposites was increased by increasing MMT content [20]. TGA results showed imidization of residual polyamide acid is about 339°C and also decomposition temperature of related polyimides at about 542 °C. The weight loss process can be observed at 500-680 °C into the TGA thermograms. The resulting data were mentioned in Table 1 showed the TGA results of

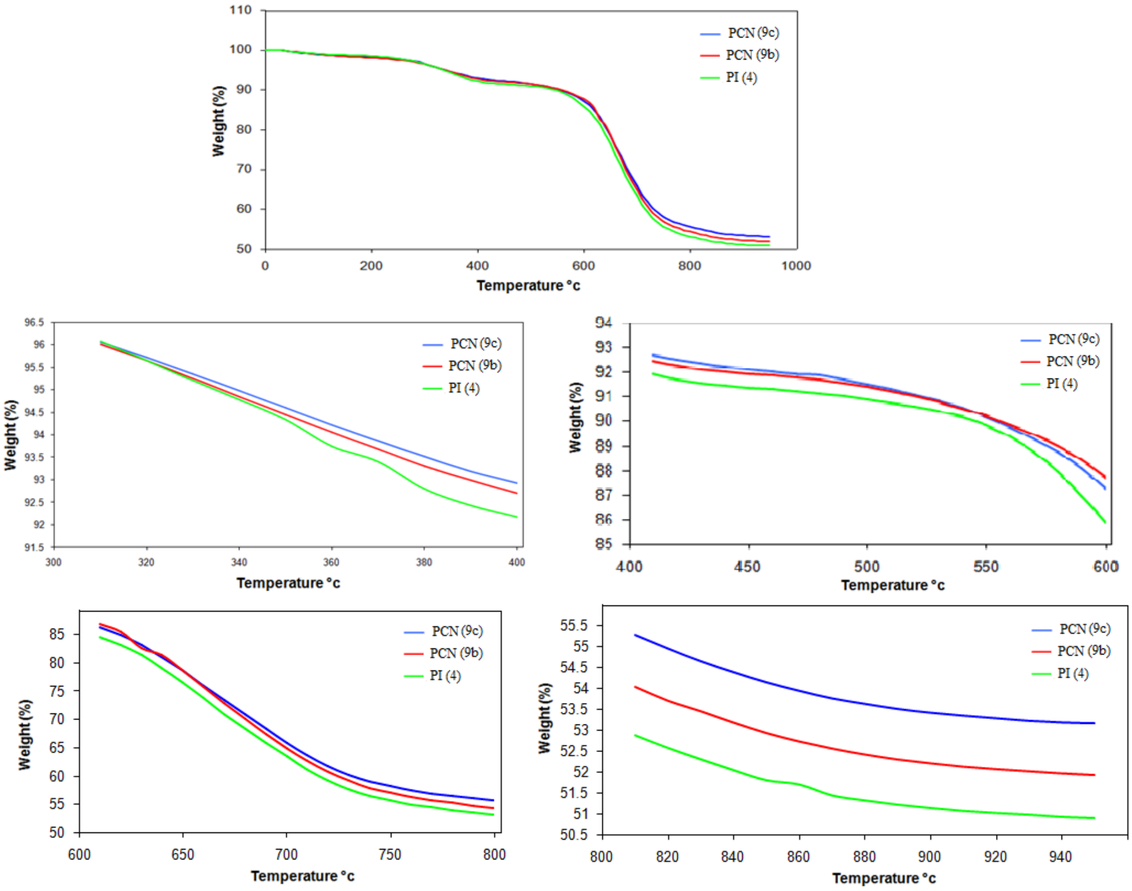


Fig. 5. TGA thermograms of PI (**4**), PI/clay nanocomposites (**9b**) and PI/clay nanocomposites (**9c**)

Table 1. Thermal behavior of PI (**4**), PI/clay nanocomposites (**9b**) and PI/clay nanocomposites (**9c**).

Feed Composition (Wt %)			**Thermal Properties (˚C)**			
Compound	PI	MMT	T_5(˚C)[a]	T_{10}(˚C)[b]	Char yield (%)[c]	LOI[d]
PI(4)	100	0	339	542	51.12	37.94
9b	97	3	341	552	52.19	38.37
9c	95	5	345	554	53.50	39.00

[a, b] Temperature at which 5% or 10% weight loss was recorded TGA at a heating rate of 10˚C/min in N_2

[c] Weight percentage of material left after TGA analysis at maximum temperature 800°C in N_2

[d] Limiting Oxygen Index

PI (**4**), PI/clay nanocomposites (**9b**) and PI/clay nanocomposites (**9c**). The thermal decomposition temperature at 3% and 5% weight loss were increased by more percent's of MMT content. Naturally MMT have high thermal stability and their layer structures exhibited great barrier effect as a barrier to evaporation of the small molecules that generated alongside of the thermal decomposition. So this process could be limited the continuous decomposition of the polyimide matrix. Also char yields and thermal stabilities of resulting nanocomposites were increased by using more MMT content.

Oxygen limitation index (LOI), is the minimum amount of oxygen in a mixture of oxygen and nitrogen that a polymer sample needs to start burning and catch fire. The index of oxygen limitation can be based on the equation of van Krieuilen-Haftezer (Relation 1) and estimated by using char yields of polymers and nanocomposites.

Relationship (1) $\quad \mathrm{LOI} = 5.17 + 0.4\ \mathrm{CR}$

CR: Char yield

In general, the polymer compounds whose LOI value is more than 26 are known as flame retardant compounds and shown fire resistance. This value (LOI) calculated for polyimide (**4**) and nanocomposites (**9b-c**) and shown in Table 1. According to the results LOI values were increase by increasing MMT content.

4. Conclusions

Polyimide-Layered Silicate nanocomposite films with various MMT contents were prepared by in situ polymerization process in this study. Pure montmorillonite (Na^+-MMT) was organically modified successfully with *p*-amino benzoic acid (*p*-ABA) as corroborated by X-ray diffraction. It had been shown that the MMT layers were basically exfoliated into the PLS nanocomposites when the 5% of MMT content used. Also dispersal of organoclay into the PI matrix caused a noticeable increasing in thermal stability and flame retardancy (LOI values).

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