

Thermally Stable Poly(amide-imide)/Nanocomposites Reinforced Silicate Nanoparticles Containing Bicyclo Segment and Dibenzalacetone Moiety: Synthesis and Characterization

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ABSTRACT

Two new samples of poly(amide-imide)/nanocomposites containing bicyclo segment and dibenzalacetone moiety in the main chain were synthesized by a solution intercalation technique. Poly(amide-imide) (PAI) 8 as a source of polymer matrix was synthesized by the direct polycondensation reaction of N,N'-bis(4-carboxyphenyl)bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide 3 with 2,6-bis(4-aminobenzylidene)cyclohexanone 7 in the presence of triphenyl phosphite (TPP), CaCl₂, pyridine and N-methyl-2-pyrrolidone (NMP). Morphology and structure of the resulting PAI-nanocomposite films 9a and 9b with 5 and 10% silicate particles were characterized by FTIR spectroscopy and X-ray diffraction (XRD). The effect of clay dispersion and the interaction between clay and polymeric chains on the thermal properties of nanocomposites films were investigated by using thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC).

Keyword: Nanocomposite; poly(amide-imide); polycondensation; dibenzalacetone; bicyclo.

1. INTRODUCTION

Polymer-clay nanocomposites typically exhibit 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 homogeneous-

ly 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

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easily separated and dispersed in many polymers. To achieve this purpose, silicate layers are usually modified with an inter-calating agent to obtain organically modified clay prior to use in nanocomposite formation [10-11].

Aromatic polyimides are well recognized as a class of high performance materials due to their remarkable thermal and oxidative stabilities and excellent electrical and mechanical properties for long term periods of operation [12]. Unfortunately, strong interaction between polyimide chains and their rigid structure make them intractable. Poor thermoplastic fluidity and solubility are the major problems for wide application of polyimides. Thus, to overcome these processing problems various approaches have been carried out by incorporating flexible units such as -NHCO-, -O-, and -SO₂-, and some of which are commercialized [13-15]. Among them, polyamide-imide (PAI) is the most successful material, which combines the advantages of high-temperature stability and processability [16-22].

In this article two PAI-nanocomposite films with 5 and 10% silicate particles containing bicyclo segment and dibenzalacetone moiety in the main chain of polymer were prepared by using a convenient solution intercalation technique.

2. EXPERIMENTAL

2.1. Materials

Bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (from Aldrich), 4-aminobenzoic acid, 4-nitrobenzaldehyde, cyclohexanone, acetic acid, triphenyl phosphite (TPP), CaCl₂, pyridine and N-methyl-2-pyrrolidone (NMP) were purchased from Merck Chemical Company and used without previous purification. Organically-modified Cloisite® 20A supplied by Southern Clay Products (TX), were used as polymer nanoreinforcement.

2.2. 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).

Thermal Gravimetric Analysis (TGA and DTG) data were taken on a Mettler TA4000 System under N₂ atmosphere at a rate of 10°C/min and differential scanning calorimeter (DSC) was conducted with a DSC Mettler 110 (Switzerland) at a heating and heating rate of 10°Cmin⁻¹ in a nitrogen atmosphere. X-ray diffraction (XRD) were performed on Philips X-Pert (Cu-Kα radiation, λ = 0.15405 nm).

2.3. Monomer synthesis

2.3.1. Synthesis of diacid 3

N,N'-bis(4-carboxyphenyl)bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide 3 was prepared according to a typical procedure [16].

2.3.2. Synthesis of diamine 7

2.3.2.1. 2,6-bis(4-nitrobenzylidene)cyclohexanone 6
0.548 g (5.6 mmol) of cyclohexanone 5c, 1.691 g (11.2 mmol) of 4-nitrobenzaldehyde 4, 15 mL of ethanol, and a stirring bar were placed into a 50-mL round-bottom flask. Then this mixture was heated in 50°C for 1 h and 5 mL of NaHCO₃ (1%) was added slowly at this temperature and refluxed for 3 hrs. Then the reaction mixture was cooled to ambient temperature and 50 mL cooled water was added. A yellow crude product formed and was collected by filtration, washed thoroughly with water, and dried to afford 1.67 g (82%). Mp: 251-253°C. FTIR (KBr): 3103 (w), 2922 (w) 1670 (m), 1589 (s, sh), 1512 (s), 1433 (w), 1342 (s), 1298 (s) 1265 (s), 1141 (s), 1107 (m), 1012 (m), 850 (m), 719 (m) cm⁻¹. ¹H-NMR (300 MHz, DMSO-d₆, TMS): δ; 7.46 (s, 2H), 7.27 (d, 4H), 6.59 (d, 4H), 2.8 (s, 4H), 1.8 (s, 2H) ppm. Elemental analysis: calculated for C₂₀H₁₆N₂O₅: C, 65.93; H, 4.43; N, 7.69; found: C, 65.23; H, 4.41; N, 7.61.

2.3.2.2. 2,6-bis(4-aminobenzylidene)cyclohexanone 7

To a solution 0.8 g (10.2 mmol) of Na₂S and 0.35 g (4.16 mmol) of NaHCO₃ in 5 mL water, 10 mL methanol was added. The mixture stirred for 30 min in room temperature. The precipitate was filtered, and added to a mixture 0.28 g (0.770 mmol) of 2,6-bis(4-nitrobenzylidene)cyclohexanone 6c, and

15 mL methanol, and stirred for 3 hrs under reflux conditions. The mixture was concentrated using rotary evaporator, and the residue poured into water and formed a dark red crude was collected by filtration, washed thoroughly with water, and dried to afford 0.21 g (91%). MP: 285-287°C. FTIR (KBr): 3348 (m), 3223 (w), 2930 (w), 1628 (s, sh), 1579 (s), 1512 (s), 1435 (m), 1344 (w), 1286 (s), 1161 (s), 968 (m), 829 (m), 495 (m) cm^{-1} . $^1\text{H-NMR}$ (300 MHz, DMSO-d_6 , TMS): δ : 7.47 (s, 2H), 7.27 (s, 4H), 6.61 (s, 4H), 5.95 (s, br, 4H), 2.82 (s, 4H), 1.70 (s, 2H) ppm. $^{13}\text{C-NMR}$ (300 MHz, DMSO-d_6): δ : 188.39, 149.91, 136.85, 132.93, 131.61, 123.77, 114.24, 28.67, 23.16 ppm. Elemental analysis: calculated for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}$: C, 78.92; H, 6.62; N, 9.20; found: C, 78.56; H, 6.61; N, 9.16.

2.4. Polymer synthesis

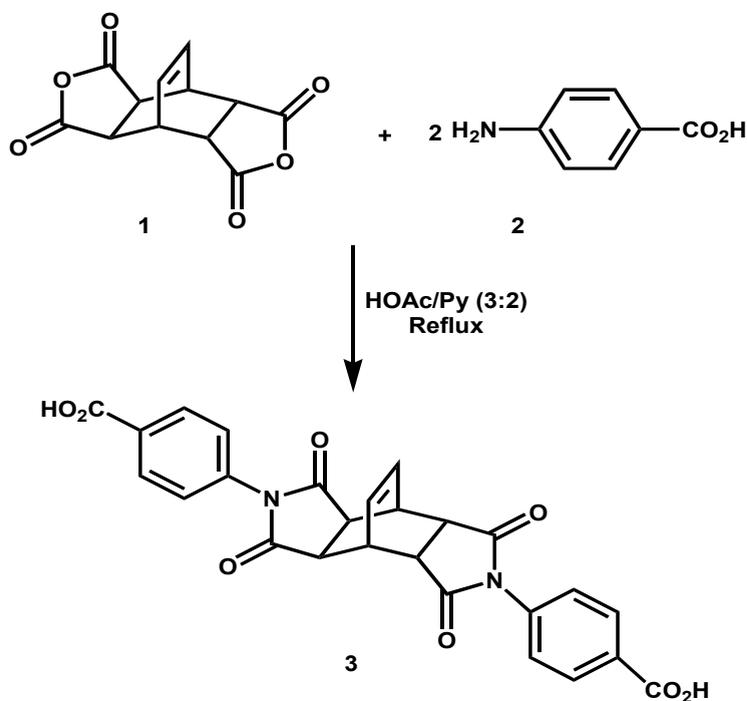
Into a 100 mL round bottomed flask were placed a mixture of diacid 3 (0.002 mol), 2,6-bis(4-aminobenzylidene)cyclohexanone 7 (0.002 mol), 0.60 g of calcium chloride, 1.0 mL of triphenyl phosphite, 1.0 mL of pyridine and 4.0 mL NMP. The mixture was heated for 1 h at 60°C, 2 h at 90°C

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) 8 was dried under vacuum. The inherent viscosity of this soluble PAI 8 was 0.73 dL/g.

FTIR (KBr): 3373 (w), 1778 (w), 1726 (s), 1676 (w), 1375 (s), 1107 (m), 746 (m) cm^{-1} . Elemental analysis: calculated for $\text{C}_{46}\text{H}_{34}\text{N}_4\text{O}_7$ (754.78): C, 73.20; H, 5.54; N, 7.42; found: C, 71.43; H, 5.49; N, 7.41.

2.5. PAI-Nanocomposite synthesis 9a and 9b

PAI-nanocomposites 9a and 9b were produced by solution intercalation method. Two different amounts of organoclay particles (5 and 10-wt.%) were mixed with the appropriate amounts of PAI solution in N-methyl-2-pyrrolidone (NMP) to yield particular nanocomposite concentrations. To control the dispersibility of organoclay in polymer matrix, constant stirring was applied at 25°C for 24 h. Nanocomposite films were cast by pouring the



Scheme 1: Synthesis route of diacid 3.

solutions for each concentration into Petri dishes placed on a leveled 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.

3. RESULTS AND DISCUSSION

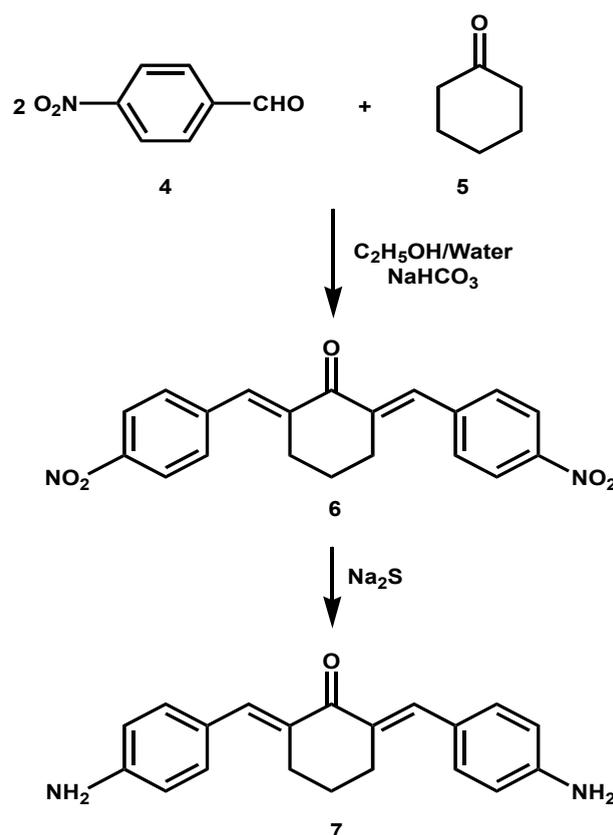
3.1. Study of monomers synthesis routes

3.1.1. Synthesis route of diacid 3

Diacid 3 was synthesized from one equimolar Bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride 1 and two equimolar of 4-aminobenzoic acid 2 in a solution of acetic acid and pyridine (scheme 1) [16].

3.1.2. Synthesis route of diamine 7

Diamine 7 was synthesized by using a two-step reaction. At first dinitro compound 6 was prepared from the reaction of two equimolar 4-nitrobenzaldehyde 4 with one equimolar of cyclohexanone 5 in a solution of ethanol/water (2:1) and NaHCO₃. Then dinitro compound 6 was reduced by using Na₂S (Scheme 2).



Scheme 2: Synthesis route of diamine 7.

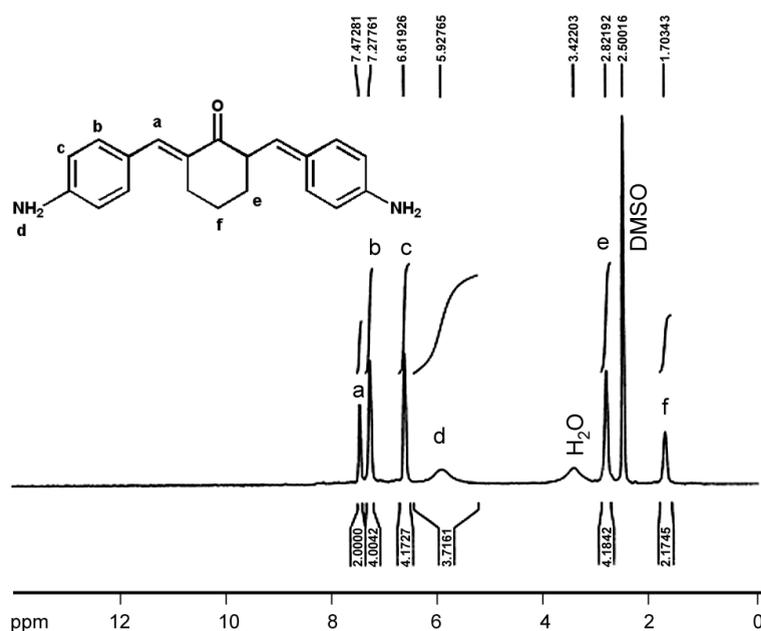


Figure 1: ¹H-NMR spectrum of diamine 7.

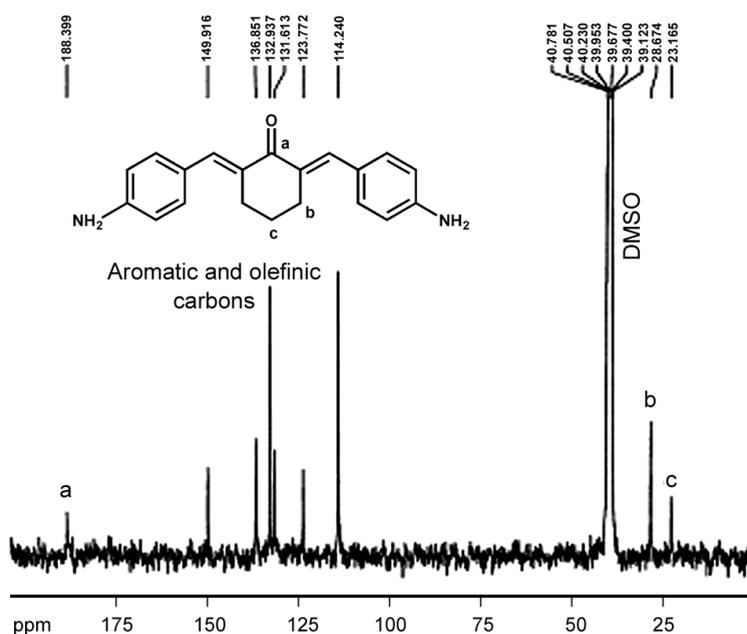


Figure 2: ^{13}C -NMR spectrum of diamine 7.

3.1.3. Characterization of monomers

The chemical structure and purity of dinitro compound 6 was proved with elemental analysis, ^1H -NMR and FTIR spectroscopy and diamine compound 7 was proved with elemental analysis, FTIR, ^1H -NMR, and ^{13}C -NMR spectroscopy. The measured results in elemental analyses of these compounds were closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained.

The FTIR spectrum of diamine 7 showed two peaks at 3348 and 3223 cm^{-1} , which were assigned to the NH_2 groups. Also ^1H -NMR spectrum of diamine 7 showed two peaks at 7.27 ppm and 6.61 related to aromatic protons and a peak as a singlet at 7.47 ppm, which was assigned to the H(a) related to olefin protons. Also a singlet and broad peak at 5.92 ppm which was assigned to the H(d) protons of the NH_2 groups. Peaks at 2.82 and 1.70 ppm (as a singlet) which were assigned to the H(e) and H(f) protons of the methylene groups (Figure 1). Also ^{13}C -NMR spectrum of diamine 7 showed nine different carbon atoms (Figure 2).

3.2. Study and characterization of PAI 8

Poly(amide-imide) 8 was synthesized by the direct polycondensation reaction of an equimolar mixture of diacid 3, an equimolar mixture of diamine 7 by using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 3).

PAI 8 was obtained in a good yield (95%) and inherent viscosity which measured in a solution of DMF was 0.73 dLg^{-1} . The structure of resulting

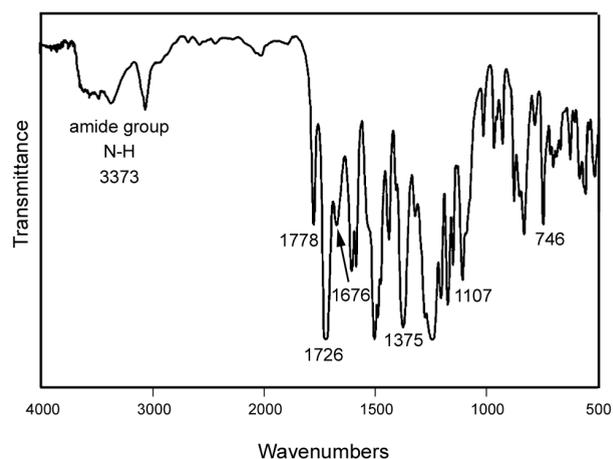
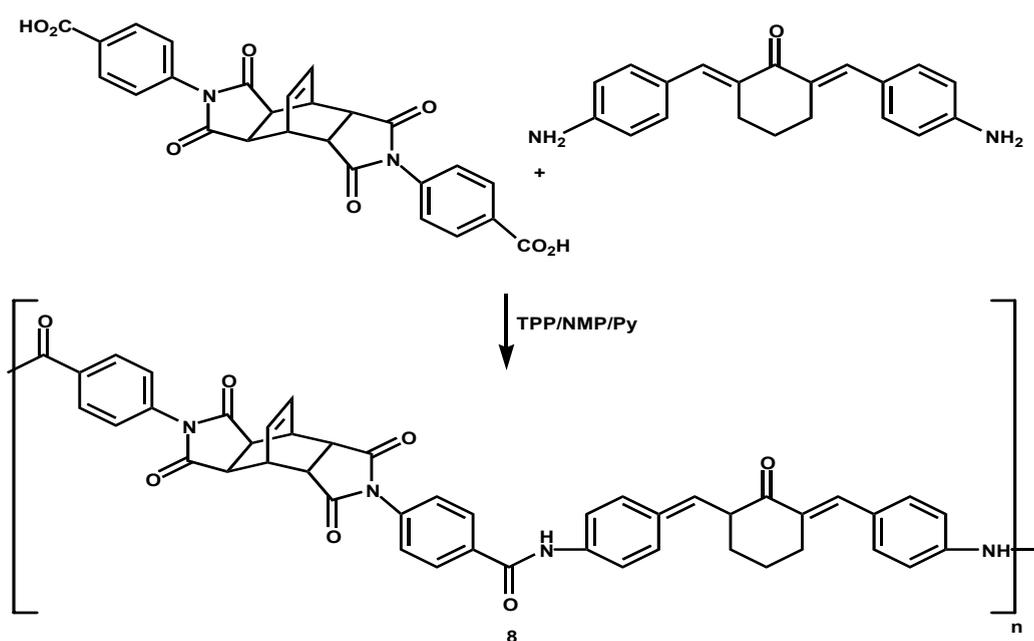


Figure 3: FTIR spectrum of PAI 8.



Scheme 3: Synthetic route of PAI 8.

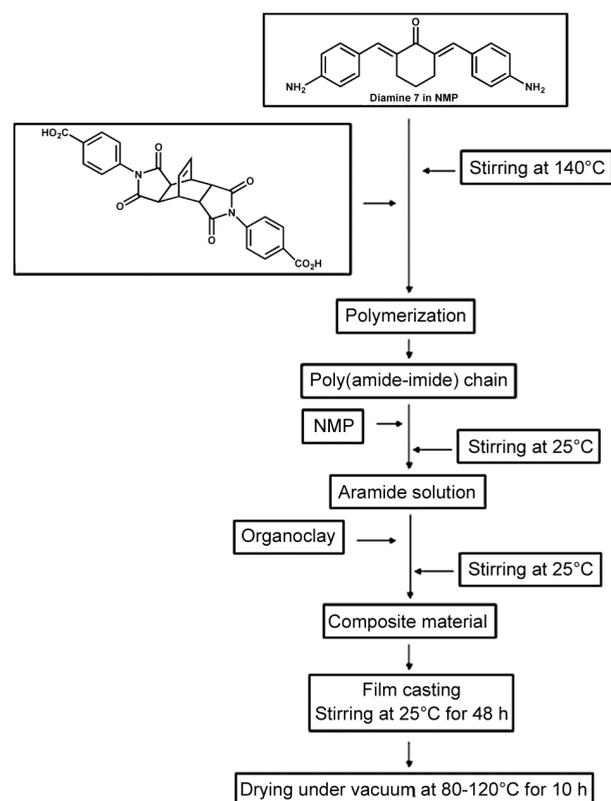
polymer 8 was confirmed as PAI by using FTIR spectroscopy and elemental analyses. The resulting polymer have absorption band at 1676 cm^{-1} due to amide carbonyl groups. Absorption bands at 3373 cm^{-1} demonstrated the presence of the amide N-H stretching absorption in this polymer (Figure 3). The elemental analysis value of the resulting polymer was in good agreement with the calculated values for the proposed structure.

3.3. Study and characterization of PAI-nanocomposite

Scheme 4 shows the flow sheet diagram and synthetic scheme for PAI-nanocomposites film 9a and 9b.

3.3.1. FT-IR spectroscopy analysis

Figure 4 shows FT-IR spectrum of PAI-nano-composite film 9b. This spectrum shows the characteristic absorption bands of the Si-O moiety at 1082 cm^{-1} , Al-O moiety at 541 cm^{-1} and Mg-O moiety at 512 cm^{-1} . The incorporation of organic groups in PAI-nanocomposite films was confirmed by the presence of peaks at 3337



Scheme 4: Flow sheet diagram for the synthesis of PAI-nanocomposite films 9a and 9b.

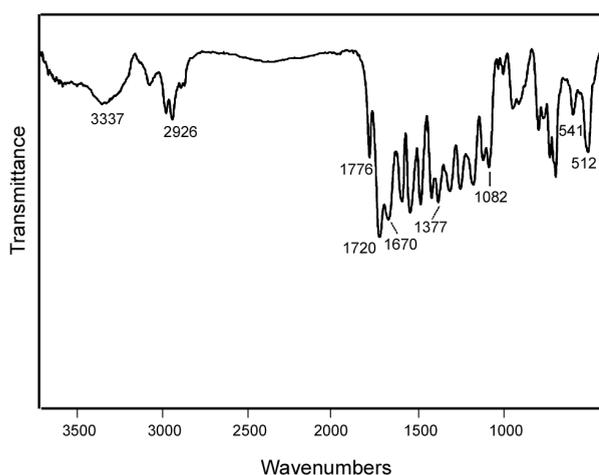


Figure 4: FTIR spectrum of PAI-nanocomposite films 9b.

and 1670 (amide N-H stretching and carbonyl group) and the peaks appeared at 1776 and 1720 cm^{-1} related to carbonyl group in imide ring.

3.3.2. X-ray diffraction analysis

Figure 5 shows the XRD patterns of PAI-nanocomposite films 9a and 9b 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 a 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 of a few nanometers thick. The second type is an exfoliated polymer-clay nanocomposite, in which there is a loss of

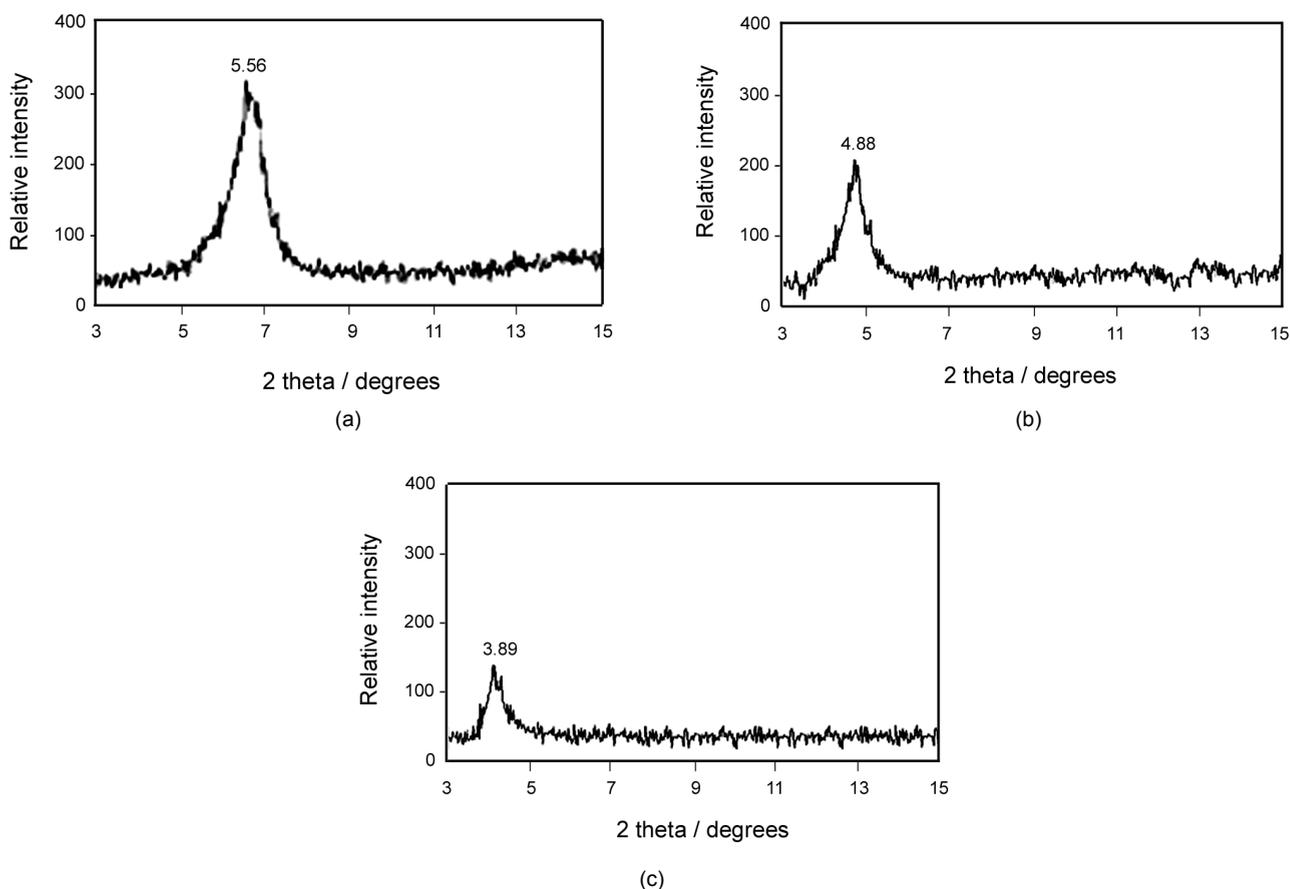


Figure 5: X-ray diffraction patterns of Organoclay (a), PAI-nanocomposite films 9a (b) and 9b (c).

Table 1: Thermal behaviors and Water uptake of neat PAI 8 and PAI-nanocomposite films 9a & 9b.

Sample	T _g ^a	T ₅ (°C) ^b	T ₁₀ (°C) ^b	Char yield ^c
PAI	190	250	360	19.91
9a	205	310	350	25.46
9b	218	320	370	35.12

(a) Glass transition temperature was recorded at a heating rate of 10°Cmin⁻¹ in a nitrogen atmosphere.

(b) Temperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10°C/min under N₂.

(c) Weight percentage of material left after TGA analysis at a maximum temperature of 600°C under N₂.

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. In our PAI-nano-composite films there are coherent XRD signal at 4.88° and 3.89° related to 5 and 10 wt.% nanocomposite films respectively.

3.3.3. Thermogravimetric analysis

The thermal properties of PAI-nanocomposite films containing 5 and 10 wt.% clay platelets and neat PAI were investigated by using TGA and DTG in nitrogen atmosphere at a rate of heating in 10°C/min, and thermal data are summarized in Table 1 (Figure 6). These samples exhibited good resistance to thermal decomposition, up to 250°C in nitrogen, and began to decompose gradually above this temperature. T₅ for polymer and nanocomposites ranged from 250-320°C and T₁₀ for

them ranged from 350-370°C, and residual weights at 600°C ranged from 19.91-35.12% 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.

4. CONCLUSIONS

In this work PAI 8 containing dibenzalacetone and bicyclo moieties was synthesized by the direct polycondensation reactions of diacid 3 with 2,6-bis(4-aminobenzylidene)cyclohexanone 7 by direct polycondensation. 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 and XRD analyses. 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 9a and 9b 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.

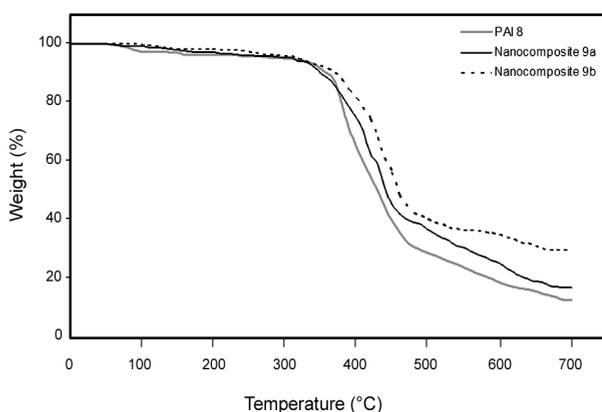


Figure 6: TGA curves of neat PAI 8 and PAI-nanocomposite films 9a & 9b.

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