

Surface modified Al₂O₃ in fluorinated polyimide/Al₂O₃ nanocomposites: Synthesis and characterization

ZIVAR GHEZELBASH, DAVOUD ASHOURI*, SAMAN MOUSAVIAN, AMIR HOSSEIN GHANDI and YAGHOUB RAHNAMA

Department of Chemistry, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran

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Abstract. Organic–inorganic hybrid materials consisting of inorganic materials and organic polymers are a new class of materials, which have received much attention in recent years. In the present investigation, at first, the surface of nano-alumina (Al₂O₃) was treated with a silane coupling agent of γ -aminopropyltriethoxysilane (KH550), which introduces organic functional groups on the surface of Al₂O₃ nanoparticles. Then fluorinated polyimide (PI) was synthesized from 4,4'-(hexafluoroisopropylidene) diphthalic anhydride and 4,4'-diaminodiphenylsulfone. Finally, PI/modified Al₂O₃ nanocomposite films having 3, 5, 7 and 10% of Al₂O₃ were successfully prepared by an *in situ* polymerization reaction through thermal imidization. The obtained nanocomposites were characterized by fourier transform infrared spectroscopy, thermogravimetry analysis, X-ray powder diffraction, UV-Vis spectroscopy, field emission scanning electron microscopy and transmission electron microscopy. The results show that the Al₂O₃ nanoparticles were dispersed homogeneously in PI matrix. According to thermogravimetry analysis results, the addition of these nanoparticles improved thermal stability of the obtained hybrid materials.

Keywords. Al₂O₃ nanoparticles; γ -aminopropyltriethoxysilane; polyimide nanocomposite; *in situ* polymerization.

1. Introduction

Aromatic polyimides (PI) with specific criteria, such as outstanding thermal resistance, mechanical strength, low specific density, high conductivity, high thermal, electrical, or superior flame resistances are considered to be high-performance materials (HPM). This family of polymer has been extensively applied in the fields of microelectronics and aerospace industries (Barikani *et al* 2001; Yeganeh *et al* 2002; Watanabe *et al* 2005; Zhang *et al* 2007; Ghaemy *et al* 2009). Due to their unique properties, extensive research has been carried out for development of PI-based nanocomposites. In fact, a unique set of properties through a combination of PI and different inorganic nanoparticles by rational selection of the raw materials and the preparative approaches, could be achieved (Yu *et al* 2011; Li and Hsu 2011; Pan *et al* 2011).

There are several methods for preparation of PI hybrid films. Intercalation approach involves the introduction of a guest group into a host structure without a major structural modification of the host. This method takes into account *in situ* intercalation polymerization, exfoliation adsorption and melts intercalation. Preparing the PI hybrid materials at lower temperatures, offer an advantage for sol-gel processing compared to intercalation approach. In this

method, precursors are mixed in appropriate amounts at the very beginning of the process. The sol-gel process includes hydrolysis of alkoxides, followed by polycondensation of the hydrolyzed intermediates. Its unique low-temperature processing characteristics provide unique opportunities to prepare PI hybrid materials (Dzunuzovic *et al* 2009; Wang and Chen 2010; Alias *et al* 2011; Bu *et al* 2011; Liao *et al* 2011; Romero *et al* 2011).

Nano-sized materials with different properties, compared to their bulk counterpart, show unique properties (thermal, electronic, magnetic, structural, and so on) depending on nano-structure size (Li *et al* 2009). Among numerous nano-sized metal oxides, aluminum alkoxides (Al₂O₃) with good potential applications in many fields, such as in varnishes, textile impregnation, cosmetics, and as an intermediate in pharmaceutical production, can be a good candidate for preparation of PI hybrid materials (Cai *et al* 2003; Ma *et al* 2010). Al₂O₃ nanoparticle was found to have a substantial stabilization effect on polymer degradation (Chrissafisa and Bikiaris 2011). While the addition of nano-Al₂O₃ had demonstrated to be very effective in improving properties of PI, but direct mixing of the nanoparticles with polymer often lead to their aggregations within polymer matrix and can reduce the expected efficiency of naocomposite by the decrease of interfacial areas between nanoparticle and polymer chains (Hamming *et al* 2009). This aggregation of particles can greatly destroy the integrity of microstructure in PI matrix and decrease the properties of PI hybrid films. Therefore, to decrease the aggregation and

*Author for correspondence (davoud_ashouri@iaug.ac.ir, dawood_ashouri@yahoo.com)

also to control the size distribution of the nanosized particles, surface modification of nanoparticles is required. Coupling agent which usually has a long alkyl tail shows a good compatibility with polymer matrix and therefore, allows high homogeneous dispersion of nanoparticles in organic matrix (Joni *et al* 2009). Small amounts of Al_2O_3 nanoparticles dispersed in an epoxy matrix simultaneously improve its stiffness and impact strength whereas failure strain is increased (Wetzel *et al* 2003). $\alpha\text{-Al}_2\text{O}_3$ is the hardest form of alumina, which is usually used as a filler to improve the mechanical and thermal properties of polymers (Li *et al* 2010).

Herein, we wish to report the synthesis and characterization of fluorinated PI- Al_2O_3 nanocomposite films via *in situ* polymerization using different contents of surface modified Al_2O_3 nanoparticles as filler and fluorinated PI as the matrix. PI which was used as matrix for preparation of nanocomposites was prepared by polycondensation reaction of 4,4'-(hexafluoroisopropylidene) pyromellitic dianhydride and 4,4'-diaminodiphenylsulfone. In addition, Al_2O_3 nanoparticles were treated with coupling agent of γ -aminopropyltriethoxysilane (KH550) to introduce organic functional groups on the surface of Al_2O_3 . The synthesized hybrid materials were subsequently characterized by Fourier transform infrared spectroscopy (FT-IR), thermogravimetry analysis (TGA), X-ray diffraction (XRD), UV/vis spectroscopy, field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) techniques.

2. Experimental

2.1 Materials

Solvents and chemicals were obtained from Merck Chemical Co., Germany and Aldrich Chemical Co., Milwaukee, WI, USA. 4,4'-(hexafluoroisopropylidene) pyromellitic dianhydride (benzene-1,2,4,5-tetracarboxylic dianhydride) diphthalic anhydride (6FDA) and 4,4'-diaminodiphenylsulfone were purified by vacuum sublimation and stored under vacuum. *N,N'*-dimethylacetamide (DMAc) was dried over BaO, then distilled in vacuum. The silane coupling agent, KH550, was obtained from Merck Chemical Co. Nanosized Al_2O_3 powder was purchased from Neutrino Co. with an average particle size of 30–40 nm.

2.2 Equipments

A Jasco-680 FT-IR spectroscope (Japan) was employed to examine the chemical bonds on the polymer and nanocomposites. Spectra of solids were obtained with KBr pellets. Vibration bands were reported as wavenumber (cm^{-1}). The band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). TGA was performed

with a STA503 win TA at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ from 25 to $800\text{ }^\circ\text{C}$ under nitrogen. XRD pattern was acquired by using a Philips Expert MPD X-ray diffractometer. The diffractograms were measured for 2θ , in the range of $10\text{--}100^\circ$, using $\text{Cu K}\alpha$ incident beam ($\lambda = 1.51418\text{ \AA}$). The dispersion morphology of the nanoparticles on PI matrix was observed using FE-SEM (HITACHI, S-4160) and TEM (Philips CM 120) UV/vis absorption of pure PI and PI/ Al_2O_3 nanocomposites were measured in solid state samples by a UV/vis spectrometer in the spectral range between 200 and 800 nm.

2.3 Modification of nano- Al_2O_3 particles using silane coupling agent

The coupling agent (KH550) was firstly pre-hydrolysis treated before use by using hydrochloric acid to adjust the pH value to 4–5. Nano- Al_2O_3 was dried at $120\text{ }^\circ\text{C}$ in an oven for 24 h to remove adsorbed water. Then these particles (5 g, 0.04902 mol) were dispersed in ethanol absolute and heated in water bath at $70\text{--}75\text{ }^\circ\text{C}$. After that, an appropriate amount of pre-hydrolysis treated coupling agent (15% w/w) was added to the alumina solution under the agitation of ultrasonic wave. The mixture was stirred mechanically for another 4 h, followed by heating to $100\text{ }^\circ\text{C}$ for 16 h, and then recovered for further use.

2.4 Synthesis of reference PAAs and PI

Into a 100 ml three-neck round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and drying tube containing calcium chloride were placed in 4,4'-diaminodiphenylsulfone (2.00 g) and DMAc (10 ml). The solution was stirred until diamine completely dissolved. Then 6FDA with the same molar ratio of diamine was added into the solution six times within 1 h. The viscosity increased quickly over 2 h. The mixture was stirred under nitrogen at room temperature for another 12 h. The resulting yellow poly(amic acid) (PAA) solution was clear and viscous. The solution was subsequently used to prepare thin films for characterization.

FT-IR (KBr, cm^{-1}): 2700–3500 (m, br), 1668 (m), 1603 (w), 1550 (s), 1490 (w), 1395 (m), 1270 (w), 1238 (m), 1107 (w), 1074 (br), 1031 (s), 1013 (w), 874 (w), 807 (m), 758 (m), 654 (w), 621 (m), 5740 (w) and 431 (m).

Neat PI film was fabricated by casting PAA solution onto a glass plate. After the film was dried at room temperature for 3 h, it was heated at 80, 100, 120, 200 and $250\text{ }^\circ\text{C}$ for 1 h each, and at $300\text{ }^\circ\text{C}$ for 2 h, to obtain yellow coloured transparent films.

FT-IR (KBr, cm^{-1}): 3346 (m), 1776 (m), 1723 (s), 1600 (m), 1534 (w), 1457 (m), 1440 (m), 1376 (s), 1320 (s), 1276 (w), 1238 (m), 1124 (w), 1097 (s), 1071 (w), 1010 (m), 936 (w), 830 (s), 754 (m), 722 (s), 677 (m), 618 (m) and 565 (w).

2.5 Preparation of PI/ Al_2O_3 nanocomposites by *in situ* polymerization

First, PAA was synthesized by appropriate 6FDA and diamine in DMAc. The solid content of PAA solution was controlled at 10 wt%. A calculated amount of modified nano- Al_2O_3 (2 wt%) particles was added to PAA solution and the mixture was stirred mechanically for 10 h to form a homogeneous Al_2O_3 /PAA solution. The Al_2O_3 /PAA solution was cast on clean glass substrate and heating with the following curing procedure: 80, 100 and 140 °C for 1 h, 220 °C for 2 h and 300 °C for 3 h in an air circulating oven. The PI nanocomposite films with modified Al_2O_3 with KH550 were obtained after being peeled off from the glass substrate.

Other series of PI/ Al_2O_3 nanocomposite films with different contents of modified Al_2O_3 (5, 7 and 10%) were prepared by a similar procedure.

3. Results and discussion

3.1 Surface modification of Al_2O_3 nanoparticles and preparation of PI/ Al_2O_3 NCs

Nanoparticles possess high surface energy which may cause agglomeration. One approach to decrease the aggregation of inorganic Al_2O_3 is surface modification of these nanoparticles with coupling agent which usually has a long alkyl tail and shows a good compatibility with polymer matrix. In this study, KH550 was used to modify Al_2O_3 nanoparticles. In this way, hydroxyl groups on the surface of silica react with KH550 to form Al–O–Si bonds by elimination of ethanol. In modified Al_2O_3 , the organic chains of KH550 can fulfil steric hindrance between inorganic nanoparticles and prevent their aggregation (figure 1).

For preparation of nanocomposites, fluorinated PI was chosen as a matrix and it was synthesized by polymerization reaction of 6FDA and 4,4'-diaminodiphenylsulfone in

dry DMAc as shown in scheme 1. There are some suggestions for interaction of modified nanoparticles with PI such as the formation of H-bond between a carbonyl group and the amine group or surface hydroxyl group of Al_2O_3 . And also interaction is the formation of hydrogen bonding between fluor groups of PI with amine or surface hydroxyl group of Al_2O_3 .

3.2 Characterization of NCs

Figure 2 exhibits FT-IR spectra of Al_2O_3 and KH550 treated Al_2O_3 . The broad absorption peak from 400 to 1000 cm^{-1} is attributed to the characteristic absorption band of Al_2O_3 . The bands at 1628, 1385 and 1124 cm^{-1} are the characteristic absorption band of Al_2O_3 . The bands at 1130 and 1635 cm^{-1} appear in the spectra of KH550 treated Al_2O_3 resulting from the stretching of Si–O bond and N–H bond, respectively. FT-IR spectrum of functionalized Al_2O_3 with KH550 compared to KH550 coupling agent gave a broad absorption band located at 3419 cm^{-1} , which is attributed to –OH and –NH₂ groups. The peaks at 2928 and 1016 cm^{-1} can be assigned to the symmetric methylene stretch (–CH₂), and the Si–O stretch, respectively. As the KH550 treated Al_2O_3 was washed by 95% ethanol for 6 times, so there should be no KH550 left. It reveals that KH550 has been chemically connected to the surface of Al_2O_3 by the Si–O bond. FT-IR indicated that coupling agents have been successfully grafted onto the surface of Al_2O_3 nanoparticles.

FT-IR spectra were used to study the chemical structure of the matrix polymer; for example, FT-IR spectra of the neat PAA, PI and PI/ Al_2O_3 NCs with 5 and 10 wt% of Al_2O_3 is shown in figure 3. Thus, FT-IR spectrum of PI showed distinct features that clearly indicate imide ring formation during the thermal cyclization step. The characteristic absorption bands of amic acid and carboxyl groups in the 2600–3500 cm^{-1} and 1650 cm^{-1} regions disappear and those of the imide ring appear near 1770 cm^{-1} (asym. C=O stretching),

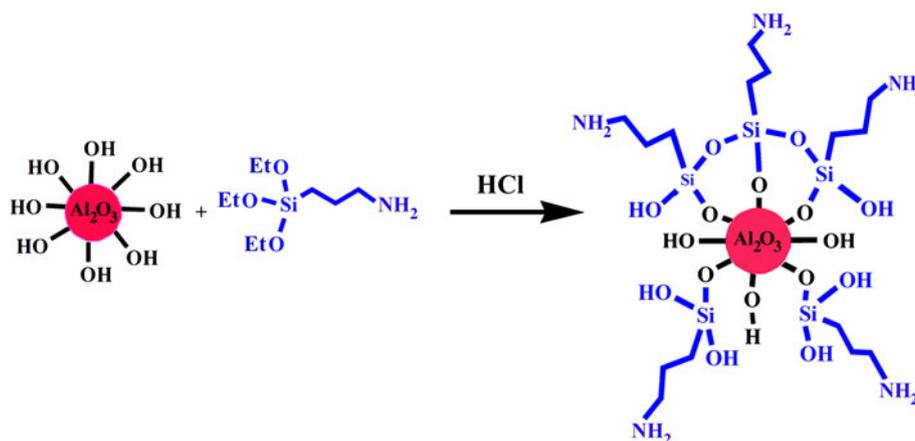
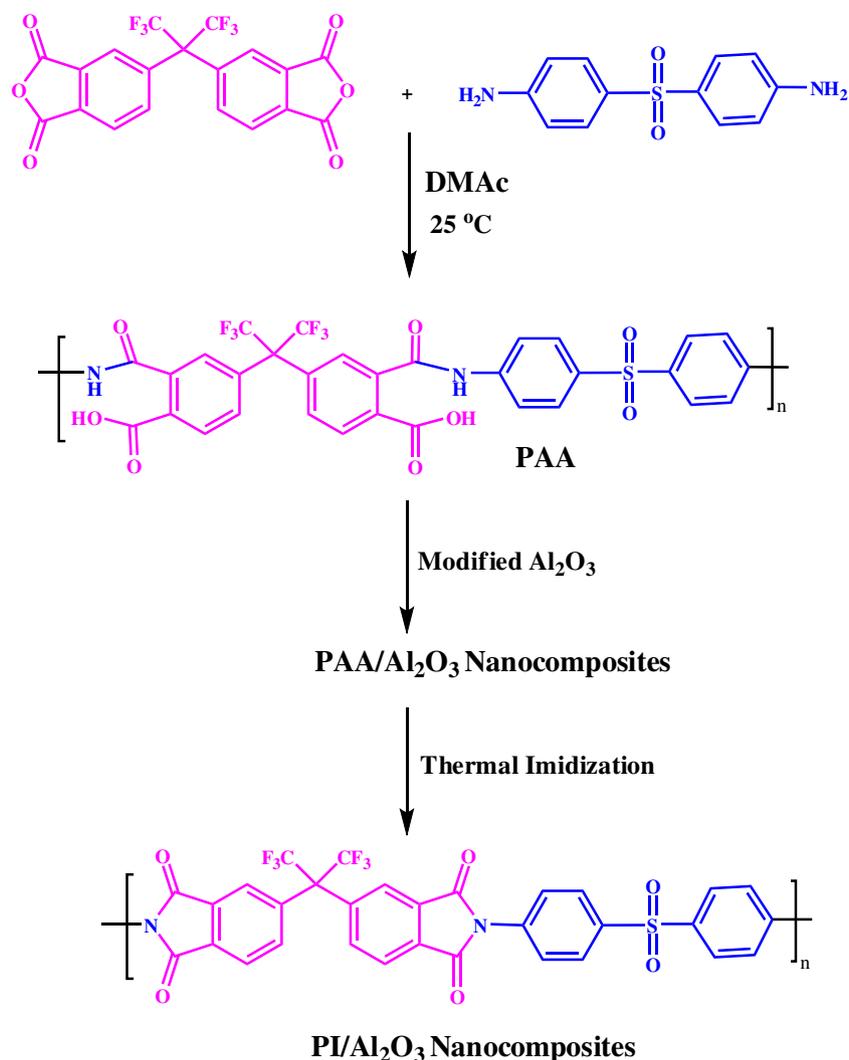


Figure 1. Modification of Al_2O_3 nanoparticles with KH550.



Scheme 1. Preparation of PI/Al₂O₃ nanocomposites.

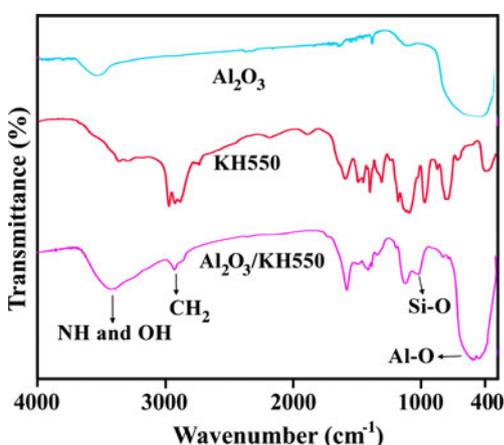


Figure 2. FT-IR spectra of Al₂O₃ nanoparticles and surface modified Al₂O₃ nanoparticles.

1720 cm⁻¹ (sym. C=O stretching), 1373 cm⁻¹ (C-N stretching), 1053 cm⁻¹ and 723 cm⁻¹ imide (ring deformation) confirm the formation of PI. The inorganic segment of

the Al-O-Al band is observed at 400–800 cm⁻¹ and its absorbance intensity increased with increasing Al₂O₃ content. The bands near 1623 and 1105 cm⁻¹ are also assigned to the Al-O and Al-O-C stretching modes. After hybridization, the band in 600–1000 cm⁻¹ become broadening, intensity at 917 cm⁻¹ becomes stronger while peaks at 800 and 938 cm⁻¹ become very weak. It is due to the incorporation of Al₂O₃ nanoparticles in PI matrix. The incorporation Al₂O₃ nanoparticles in PI caused the slight changes in the intensities of absorption bands as well as the formation of new absorption bands in the range of 600–400 cm⁻¹ is attributed to the Al-O stretching. This result confirmed the existence of Al₂O₃ nanoparticles in the PI matrix.

3.3 Morphology investigation

3.3a FE-SEM: The morphological images of the pure PI, NC3% and NC10% were studied by FE-SEM with different magnifications (figure 4). Pure PI shows massive, aggregated morphology and in some instances, there are some

bulky flakes. For NCs 3 and 10%, the FE-SEM images show that Al_2O_3 nanoparticles are homogeneously dispersed in the polymer matrix and their sizes are estimated to be

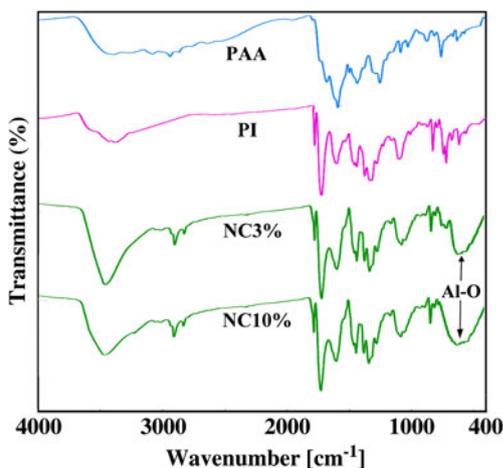


Figure 3. FT-IR spectra of PI/ Al_2O_3 -KH550 nanocomposites: (a) PAA, (b) pure PI, (c) PI/ Al_2O_3 (3 wt%) and (d) PI/ Al_2O_3 (10 wt%).

between 40 and 80 nm. They also indicate that there is a good adhesion between organic and inorganic phases and the distance between Al_2O_3 nanoparticles is much larger than the diameter of the nanoparticles. In addition, the results demonstrate that the structure of the prepared hybrid thin film NC3% is more compact and uniform than that of NC10%.

3.3b TEM: TEM is supplementarily employed as an effective means of developing insights into the internal structure and spatial distribution of the various components, through direct visualization. Figure 5 shows representative TEM micrographs of PI/ Al_2O_3 -KH550 (7 wt%) with different magnifications. The micrographs confirmed that the Al_2O_3 -KH550 particles were well dispersed in the polymer matrix. The nanoparticles size ranged from 20 to 40 nm and showed to be rather spherical. The obtained results indicate that the effect of coupling agent plays an important role in dispersion of the nanoparticles. The relatively strong interactions between PI matrix and alumina nanoparticles are responsible for observing nanoparticles with almost spherical shapes. For coupling agent KH550, functional group that

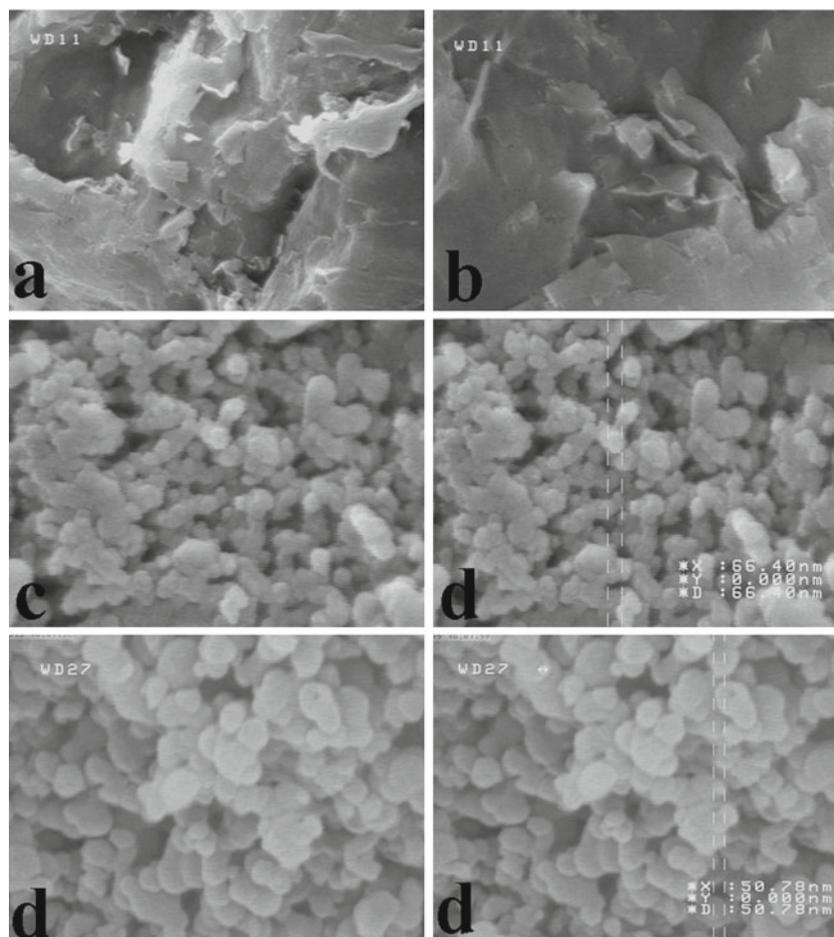


Figure 4. FE-SEM images of pure PI and PI/ Al_2O_3 (3 and 7 wt%).

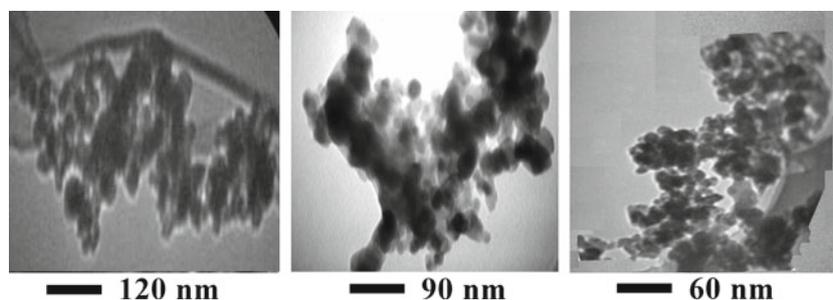


Figure 5. TEM micrograph of PI/Al₂O₃ (7 wt%) with different magnifications.

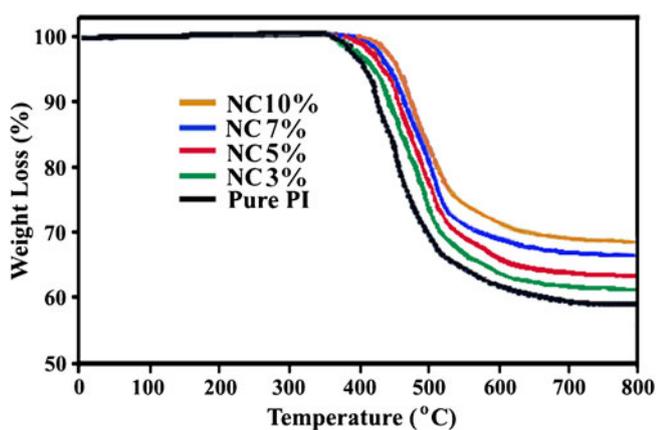


Figure 6. TGA thermograms of pure PI and PI/Al₂O₃ NCs with different nanofiller contents.

provides the interaction with PI matrix is the amino group that can interact with the amide group (C=O), CF₃ and –NH of PI via hydrogen bonding.

3.4 Thermal properties

The thermal properties of PI and hybrid materials were studied by means of TGA at a heating rate of 10 °C/min under nitrogen atmosphere. Figure 6 displays the respective TGA profiles and the corresponding thermoanalysis data, including the temperatures at which 5% (T_5) and 10% (T_{10}) degradation occur and char yield at 800 °C (table 1). Pure PI film gives the decomposition temperatures of 412 °C at 5% weight loss under nitrogen atmosphere. However, by increasing Al₂O₃ composition, T_5 is enhanced to 421, 428, 430, 438 °C corresponding to Al₂O₃ content of 3, 5, 7 and 10%, respectively. The char yields at 800 °C of the nanocomposites with different Al₂O₃ content are higher than that of pure PI. As can be observed from table 1, PI shows 57% residue at 800 °C while the nanocomposite films show 61–71% residue at this temperature. It is worth pointing out that the thermal stability of PI was enhanced with increase in the modified Al₂O₃ nanoparticles. This enhancement in the char formation is ascribed to the high heat resistance exerted by Al₂O₃,

Table 1. Thermal properties of PI and PI/Al₂O₃–KH550 NCs.

Sample code	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c
PI	412	422	57
PI/Al ₂ O ₃ NC3%	421	443	61
PI/Al ₂ O ₃ NC5%	428	450	65
PI/Al ₂ O ₃ NC7%	430	460	67
PI/Al ₂ O ₃ NC10%	436	465	71

^aTemperature at which 5% weight loss was recorded by TGA at a heating rate of 10 °C/min under nitrogen atmosphere; ^btemperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C/min under nitrogen atmosphere and ^cweight percentage of material left undecomposed after TGA analysis at a temperature of 800 °C under nitrogen atmosphere.

because Al₂O₃ nanoparticles have high thermal stability, so the incorporation of Al₂O₃ nanoparticles can improve thermal stability of the nanocomposites. In addition, the Al₂O₃ is a nanoscale particle, which offers a larger surface area and improves the effect of thermal cover. It could be based on this fact that the Al₂O₃ modified with KH550 coupling agents reacted with the PAA principal chain and formed some coordinate bonds, such as hydrogen bonds. These coordinate bonds limited the thermal motion of PI molecular, prevented breakdown of the polymer molecular chain, enhanced the breaking energy during the heating process and improved the thermal stability of PI/Al₂O₃ films.

3.5 UV/vis absorption study

UV-Vis spectra of the prepared hybrid films with different inorganic contents show that with the increasing inorganic content, the absorption band moves toward longer wavelength. By appearance, all the hybrid films are transparent but become darker and darker with increasing Al₂O₃ contents. It can be concluded that the redshift of the absorption band in visible region can be easily controlled by adjusting the Al₂O₃ content in the hybrids while the transparency can still be maintained. The absorption bands in the UV region are due to the charge transfers of the chromophoric unit of the PI structure and that of Al–O–Al segment. All the prepared

hybrid thin films possess optical colourless transparency in the visible region.

4. Conclusions

PI/modified-Al₂O₃ hybrid films were synthesized through *in situ* polymerization, and the microstructure of the hybrid films was characterized by different techniques. In this way, at first Al₂O₃ nanoparticles were functionalized with KH550 as a bifunctional coupling agent. KH550 modified to introduce organic functional groups on the surface of Al₂O₃, which improved their compatibility and led to better dispersion of Al₂O₃ nanoparticles in polymer matrix. Fluorinated PI was synthesized from 6FDA and 4,4'-diaminodiphenylsulfone by thermal imidization and this polymer was used for preparation of PI/Al₂O₃ nanocomposites via *in situ* polymerization. Modified nanoparticles will combine with PI via the hydrogen bonding of NH₂ coupling agent with C=O, CF₃ and imide groups in PI. FE-SEM and TEM analysis indicated that the nano-Al₂O₃ particles were successfully dispersed in the PI matrix by means of the addition of coupling agent. TGA results indicated that the resulting nanocomposites have good thermal stability and the improvement of heat resistance is attributed to the introduction of Al₂O₃.

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