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Synthesis & study of Polyethylene/Polyaniline/Montmorillonite ductile nano composites properties

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ABSTRACT

Conducting polymers, because of their special properties, are used to introduce conductive polymeric composites. Also, clays have recently been used for preparation of polymer composites with enhanced mechanical and thermal properties. The aim of this work is to study the synergetic effect of the co-presence of conducting polyaniline and montmorillonite in the polyethylene matrix. Polyethylene /montmorillonite /polyaniline nanocomposite was prepared by in-situ polymerization of polyaniline in the presence of PE and MMT. All nanocomposites contain 5wt% of OMMT and different amounts of conducting PANI vary 5, 10, 15 and 20wt%. Electrical conductivity was measured and characterized by FTIR, DSC, SEM, XRD and DMA.The thermal behavior of PANI chains in the nanocomposites was investigated by DSC and it was observed that OMMT causes a remarkable increase in thermal stability and it improved mechanical properties. SEM and XRD patterns clearly showed dispersal of PANI and exfoliation/intercalated in the polymer matrix.

Keywords: *Composite; Nanocomposite; Polyaniline; Montmorillonite; Nano clay; Polyethylene; Conduct polymer.*

INTRODUCTION

Since the discovery of conducting polymers, a large volume of research associated with the physics and chemistry of conducting polymers has been performed [1-3]. These polymers are used in applications such as batteries, through-hole electroplating for printed circuits and electrical dissipation, electro chromic displays, light-emitting devices, ion-exchange materials, membranes, sensors, corrosion protection, shielding of electromagnetic interference, microwave absorbers, antistatic materials, etc. Special interest was focused on polyaniline (PANI) due to its low production cost, relatively high level of electrical conductivity, and good environmental stability.

Polyaniline has a rather unique structure, containing an alternating arrangement of benzene rings and nitrogen atoms. The nitrogen atoms can exist either as an imine (in a sp2 hybridized state) or an amine (sp3 hybridized). Depending on the relative composition of these two states of nitrogen and further on whether they are in their quaternized state or not, various forms of polyaniline could be obtained. The structures of these forms can be best represented by choosing a minimum of four repeating units.

The green protonated emeraldine, among the four, is the only conducting form which has both the oxidized iminium and reduced amine nitrogen equally (i.e., it is half oxidized). Thus, the blue insulating emeraldine form can be transformed into the conducting form by lowering the pH of the medium and vice-versa. Another interesting feature of polyaniline is that, by use of an organic counter ion (x⁻), for instance, by using camphor sulfonic acid as the doping acid, polyaniline can be retained in solution even in the doped conducting form, further enhancing its versatility. The transport of charge in these systems can be understood in a simple fashion, by causing the imine and amine nitrogen to exchange places along the polymer backbone (in protonated emeraldine).

One of the key problems related to the potential application of the electro active polymers is their poor process ability and mechanical properties. The most promising approach to remove these problems is to prepare nanocomposite materials with Montmorillonite. Montmorillonite shows hydrophilic nature, it must be made organophilic (hydrophobic) to become compatible with most guest polymers that are hydrophobic polymers. To incorporate montmorillonite into the polymer phase, it is organically modified by a cation exchange reaction. Owing to its cation exchange properties, the clay gallery ions can be replaced by organic cationic species such as alkyl ammonium ions. As the gallery cation changes from inorganic to organic, the surface property changes from hydrophilic to organophilic. This improves the compatibility of montmorillonite with the polymer.

Montmorillonite is used in the formation and production of nanocomposites because the polymer material is easily inserted between its layers, although it requires minimizing of the surface energy difference between the matrix and the clay. To reduce this difference in surface energy, the clays are organically modified to render them organophilic [4, 5]. This treatment also increases the interplanar distance between the lamellae, facilitating the insertion of the monomer and resulting in defect-free polymers with specific properties. In conductive polymers, this chain-wise organization is even more crucial because it raises intra-chain conductivity [6, 7].

Generally composite materials can be defined as materials consisting of two or more components with different properties and distinct boundaries between the components. The idea of combining several components to produce a new material with 6 new properties that are not attainable with individual components has been used intensively in the past. Correspondingly, the majority of natural materials that have emerged as a result of prolonged evolution process can be treated as composite materials [8, 9]. Nanocomposites are generally defined as composites in which the components have at least one dimension (i.e., length, width or thickness) in the size range of 1-100 nm. Nanocomposites differ from traditional composites in a sense that interesting properties can result from the complex interaction of the nanostructured heterogeneous phases. In addition, nanoscopic particles of a material differ greatly in the analogous properties from a macroscopic sample of the same material [10-11].

In this study, PE-PANI-OMMT nano composite was prepared by polymerization of aniline in the presence of OMMT and PE in an aqueous medium using an emulsion exfoliation-intercalation method.

DBSA works as a doping agent. It also helps to exfoliation of silicate layers in OMMT [12-14]. Aniline polymerization was carried out by ammonium persulphate (APS) as an oxidizing agent [15].

Exfoliation/intercalation configuration was confirmed by X-Ray diffraction. In the PE-PANI-OMMT nano composites, the OMMT content was kept constant (5wt %). The amount of PANI varied 5, 10, 15 and 20 wt%. To get information about the influence of presence of OMMT on the electrical and mechanical properties in this compound, another compound without OMMT (PE-PANI) was prepared.

EXPERIMENTAL

Materials

The HDPE powder properties used for the preparation of composite (PE+PANI) and nanocomposites (PE+PANI+OMMT) were: density = 952±2 g/l, MFR = 4-6 gr/10min with the average particle size of 500μm. Aniline monomer (Fluke AG) was dried and distilled 2 times and stored in a refrigerator at 4°C prior to use. Hydrochloric acid (HCl) was purchased from Merck and dodecyl benzene sulfunic acid (DBSA) solution in 2-propanol (70%wt) was purchased from Aldrich as a doping and ammonium persulfate $((NH_4)_2S_2O_8)$(APS) as an oxidant. Oxygen montmorillonite (OMMT) $M_x(Al_{4-x}Mg_x)$ $Si_8O_{20}(OH)_4$ was employed as an inorganic material as a nano-filler for the nanocomposite preparation, is Cloisite 15A by Southern Clay. Methanol was purchased from Merck and anti oxidant: Irganox and Irgafos (Ciba specialty chemicals, Switzerland).

Synthesis of PE-PANI composites and PE-PANI-OMMT nanocomposites

A suspension of HDPE powder was prepared using water/methanol mixture (volume ratio=1/1). In this project, DBSA was selected as a doping with molar ratio of [aniline]/[DBSA] = 5/1 because this composite was prepared with HCl doping but it didn't get any conductivity. 5% wt OMMT was used in all of the nanocomposites.

A suspension of 100 gr of HDPE powder and OMMT particles was dispersed in 500ml of water/methanol mixture; aniline was added to mixture in 5, 10, 15 and 20 wt%. After 2 hours of intensive stirring, the suspension was treated with ultrasound for 10min to obtain exfoliated/intercalated nanocomposites. Then the oxidant, ammonium persulphate ([APS]/ [aniline] =1.25) dissolved in 250ml water, was added drop-wise with vigorous continuous stirring. The oxidation- polymerization of aniline proceeded for 4 hours with stirring. After 24 hr, the product was filtered off, washed with distilled water followed by methanol to remove by products, and dried under 60°C for 48 hr. all composites and nanocomposites were stabilized with anti oxidant additives (2000ppm). Both prepared composites were processed by compression molding at 160°C for 10min with a pressure of 50 MPa.

RESULTS AND DISCUSSION

Conductivity measurement

For conductivity measurement, all test samples were prepared in disc form (diameter: 30 mm, thickness: 0.45 mm) at pressure of 50MPa using a SPECAC, England model Press. The four-probe method was used to measure the conductivity of the composites and nanocomposites. The insulating silicate layers weaked the electronic interactions between the PANI chains and depressed the interchain conductivity. Therefore in these composites the conductivity is still reasonably more than nanocomposites. This trend is in agreement with the results reported by B.H. Kim et al. and A. Shakoor[6,16].(Figure 1, Table 1)
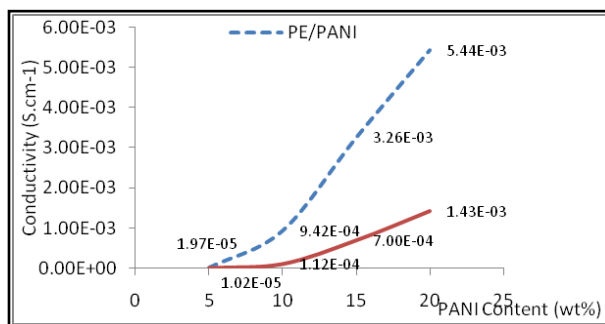

Fig. 1. Conductivity of PE/PANI and PE/PANI/OMMT

Table 1. Conductivity of PE/PANI and PE/PANI/OMMT

Sample	Conductivity (S/cm)
PE	Below detection limit
OMMT	Below detection limit
PE+(x%)PANI (HCl doping)	Below detection limit
PE+(x%)PANI+OMMT (HCl doping)	Below detection limit
PE+5%PANI (DBSA doping)	1.97E-05
PE+10%PANI (DBSA doping)	9.42E-04
PE+15%PANI (DBSA doping)	3.26E-03
PE+20%PANI (DBSA doping)	5.44E-03
PE+5%PANI+OMMT (DBSA doping)	1.02E-05
PE+10%PANI+OMMT (DBSA doping)	1.12E-04
PE+15%PANI+OMMT (DBSA doping)	0.0007
PE+20%PANI+OMMT (DBSA doping)	1.43E-03

Fourier transforms infrared analysis

The structural and optical properties of the samples were checked using Fourier transform infrared (FTIR) spectroscopy. Presence of conductive form of PANI in the OMMT was confirmed by FT-IR studies. 30 scans were performed using Bruker, tensor 27 spectrophotometer with 4 cm^{-1} resolution, and measuring rang 400-4000 cm^{-1}. During the analysis the chamber of apparatus was purged with N_2.

There are 2 FTIR spectra of the PE, PE+PANI and PE+PANI+OMMT in Figure 2a, b. The bands at 1600 and 1560 cm^{-1} consist of benzenoid and quinonoid form of polyaniline backbone and also these bands imply that the charge neutralization with the counter ion is present in the polyaniline chain. The peaks at 1305 cm^{-1} which are associated with the C-N stretching mode[17,18], showed bands at 1048 and 1151 cm^{-1} (C-H stretching belongs to para substituted aromatic ring of the page), 1304 cm^{-1} (N-H bending), 1374 and 1292 cm^{-1} (C-N stretching). In the higher frequency side a peak at 3250 cm^{-1} is assigned for the N-H stretching vibrations. The peak at 1041 cm^{-1} (Si-O stretching) and the peaks at 912 cm^{-1}(Al-OH stretching), 523 cm^{-1}(Si-O-Al stretching) and 840 cm^{-1} are the characteristic vibrations of OMMT.
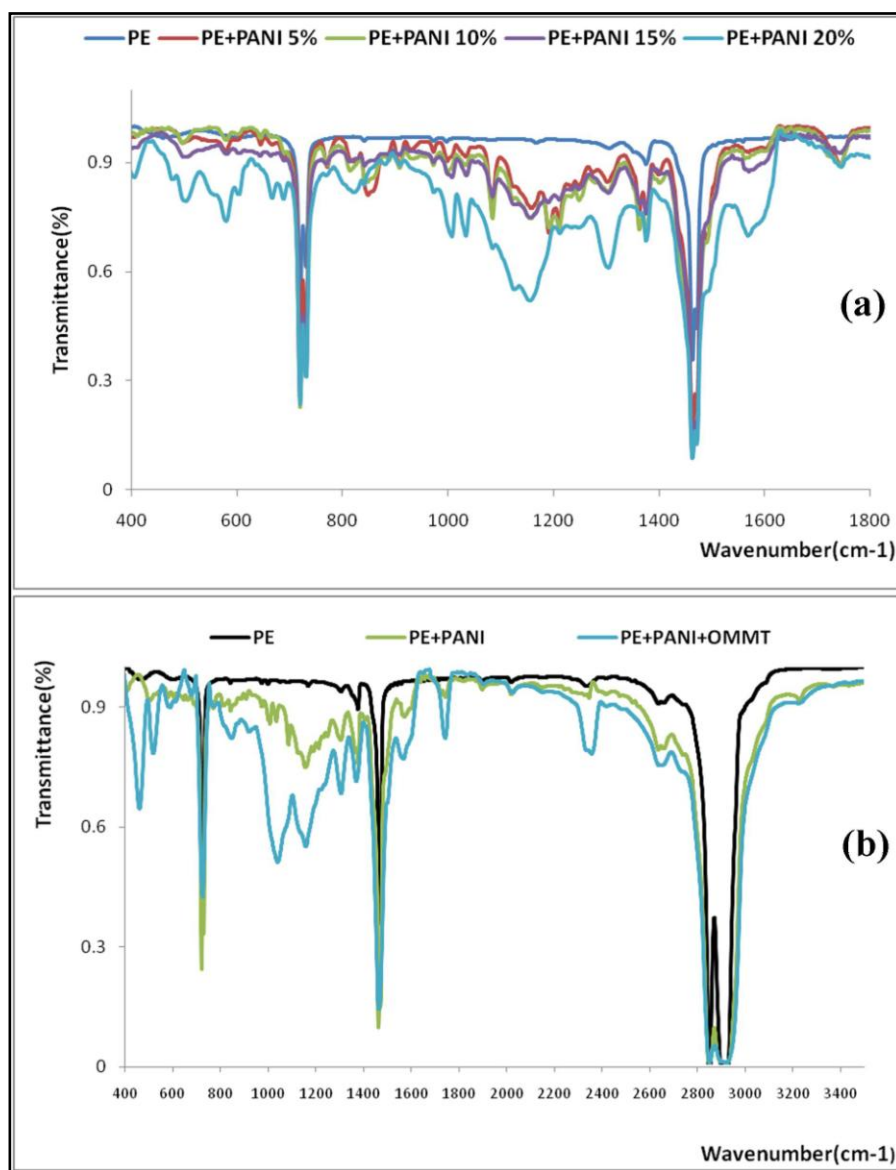

Fig. 2. a) FTIR PE and PE-(x%)PANI Composite b) FTIR PE, PE-PANI, PE-PANI-OMMT

The Si-O-Si stretching frequency (1041 cm^{-1}) of the OMMT merged with the peak at 1151cm^{-1} corresponds to quinoid ring as a broad one. This indicates the strong interaction between OMMT as well as PANI. This band was referred to as electronic-like band and considered as delocalization of electrons. The broadening and intensity of that shows increasing of conductivity.

Scanning electron microscopic

To confirm the relationship between the electrical properties and the proposed structures of nanocomposites, SEM measurements were carried out for the same samples by SEM with Philips XL30 (The Netherland). The distribution of PANI+OMMT in PE matrix particles in nanocomposite sample was analyzed by an acceleration voltage 20 Kv on gold-sputtered surfaces. Fig shows SEM micrographs of two series samples (PE+PANI (10%) +OMMT), before press molding (Figure 3a-f) and after press molding (Figure 3a'-f'). As a result, this SEM data strongly support the fact that the PANI chains shown play an important role in the electrical conductivity of the nanocomposites. The pressed specimens were then fractured in liquid nitrogen, and the fracture surface was sputtered with gold prior to observation.
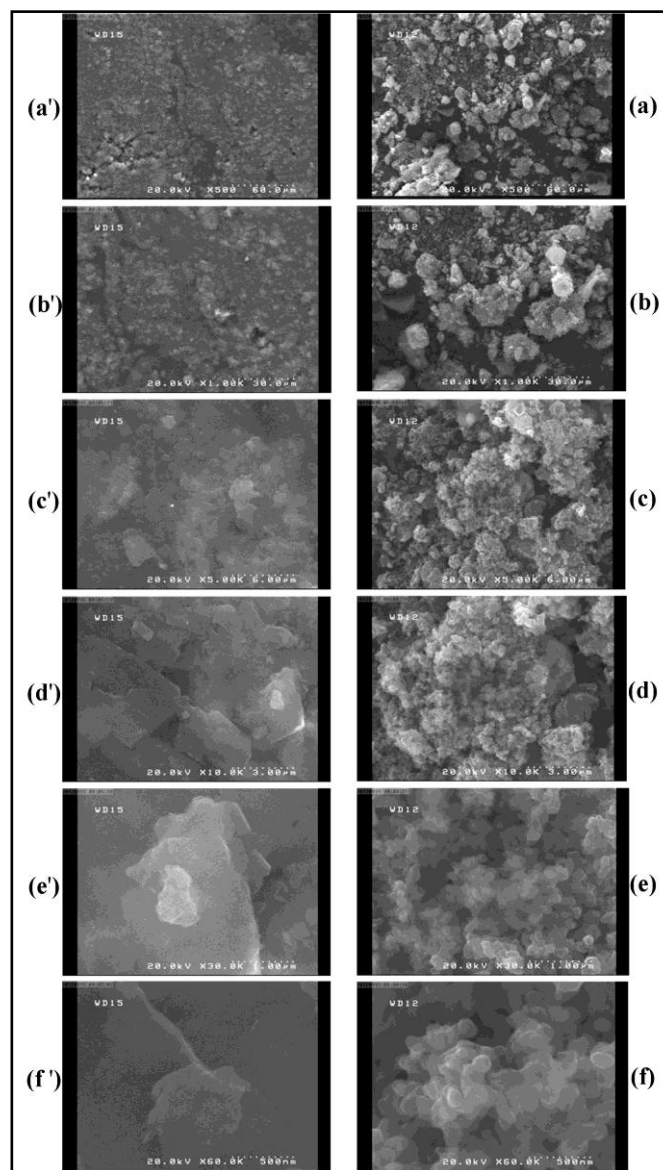

Fig. 3. SEM photograph, (a-f) before compression moulding and (a'-f') after compression moulding

The nanocomposite surface fracture is characterized by smooth (a'-f') and rough (a-f) regions, the latter is related to PANI formed in corners. The addition of OMMT to the system resulted in a surface with more rough regions. Such behavior is due to reduced plasticity properties in the presence of OMMT. It can be seen that the silicate layers are dispersed non-uniformly in the PANI matrix and the interlayer spacing of OMMT is expanded for the intercalated morphology. These SEM results were in good agreement with the results of the XRD patterns. After compression molding, PE, PANI and OMMT components were mixed well and the compatibility was more than before compression molding.

X-ray Diffraction measurement

XRD is a technique that can be used to accurately determine the spacing between clay layers and is used to determine any change that occurs when the clays are incorporated into a polymer matrix. The d-spacing of the clay when combined with either polymer matrix produces a very strong XRD signal [19-21].

XRD patterns of the samples were obtained using Phillips, D500 diffract meter Cu k_{α} radiation was used at 40kv and 30mA (step 0.02, 2-10° range). Figure 4 shows X-Ray diffraction patterns of nanocomposites with 5, 10, 15 %wt PANI. The diffract grams show the silicate layers exfoliated-intercalated in ternary nanocomposites. The diffraction curves of OMMT show two peaks corresponding to 3° and 7.2° for 2θ. The gallery distance of OMMT is increases by being covered with conductive PANI layers corresponding with model of morphology presented by R.Moucka[8].
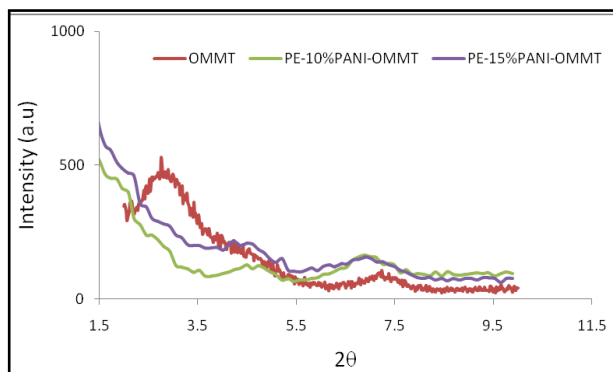

Fig. 4. X-Ray diffraction patterns of OMMT and PE-(x%)PANI-OMMT

Polyaniline formed by oxidative polymerization contains positive charge on chains. OMMT layers are negatively charged on silicate layers and during aniline polymerization, which can be compensated by sulfate ions. On the other hand, when the positive charges on the PANI chains were increased by the doping agent, a larger amount of them were inserted between OMMT layers and then wider interlayer distances can be expected in the final nanocomposite.

It was predicted, in the nanocomposites, PE particles and the silicate layers in OMMT were coated with PANI. However, the silicate layers array in these composites is in exfoliated-intercalated configuration. It should be noted that, the intercalation array in final nanocomposites structure increase the conductivity, corresponding with model of morphology presented by R. Moucka[8].

Differential Scanning Calorimetry

DSC is an analytical tool which helps to understand the thermal behavior of polymer nanocomposites. It helps in finding polymer composites. Exciting developments can be expected in the area of polymer nanocomposites and structures in the near future. Investigations on polymer nanocomposite can thus pay rich dividends. Mettler Toledo DSC 823e/400FRS5 was used to analyze the thermal transitions in the composites and nanocomposites.

- #### Thermal behavior

A small amount (5-10 mg) of the sample was encapsulated in an aluminum pan placed in an insulated chamber and heated to 160°C to eliminate the thermal history and then were cooled to 50°C at a rate of 10°C/min under nitrogen gas purging. After isothermal crystallization, second heating runs were performed at a rate of 10°C/min for measuring the melting point(T_m), onset and of melting point, crystallization temperature(T_c), crystallinity percent(X_c), heat of fusion(ΔH) obtained by integration of the area under the thermal peaks in Table 2 were shown.

It is of great interest to study the crystallization and melting behavior of neat PE, PE+PANI and PE+PANI+OMMT because crystal structures and crystallinity play significant roles in the mechanical and other properties of crystalline polymers.

Table 2. Thermal properties

	Crystalinity (%)	$T_m(^\circ C)$	$T_C(^\circ C)$	Onset ($^\circ$C)	Endset ($^\circ$C)	ΔH (J/g)	Integral (mJ)
PE	66.02	133.98	119.78	121.59	137.62	194.50	1637.67
PE+PANI 5%	59.84	134.81	118.40	124.44	140.09	179.98	1565.87
PE+PANI 10%	57.10	135.82	118.32	123.68	140.00	167.77	1452.85
PE+PANI 15%	53.03	135.41	117.64	122.46	140.13	156.86	1375.66
PE+PANI 20%	50.52	136.09	117.30	123.91	141.16	148.86	1308.49
PE+5%PANI+OMMT	56.38	135.02	118.01	121.72	140.70	163.91	926.07
PE+10%PANI+OMMT	55.27	135.56	117.91	124.08	140.56	161.94	1149.80
PE+15%PANI+OMMT	49.68	136.06	117.34	121.75	140.99	144.71	1098.34
PE+20%PANI+OMMT	44.64	134.33	118.23	122.01	138.35	131.40	1179.99

DSC analysis is a generally convenient method for analyzing first order transitions like melting and crystallization. The samples possess a melting endothermic peak(T_m) during heating and a crystallization exothermal peak (T_c) during cooling it can be observed that T_m increases very slightly compared with those in neat PE with increase of PANI concentration, which indicates that the OMMT presence does not prevent PE melting point, and crystallization temperature and acts as a nucleation reagent because T_c nanocomposites slightly decreases. Comparison of DSC and conductivity data showed that the electrical conductivity increased around the melting temperature. The authors explained this by the fact that the PANI chains contacted more frequently and facilitated electron transfer through the hydrogen bonding between PANI and PE. Thermal analysis indicates a decrease in heat of fusion (ΔH) of the PE crystals for binary composites with increasing PANI content. Furthermore, ΔH decreases with the increase of PANI-DBSA content, and at first glance this seems to be logical, since the amount of PE in the blends also decreases as well. The decrease in ΔH is consistent with low miscibility of the PANI with PE. The DSC thermographs of composites are presented in Figure 5a, b.
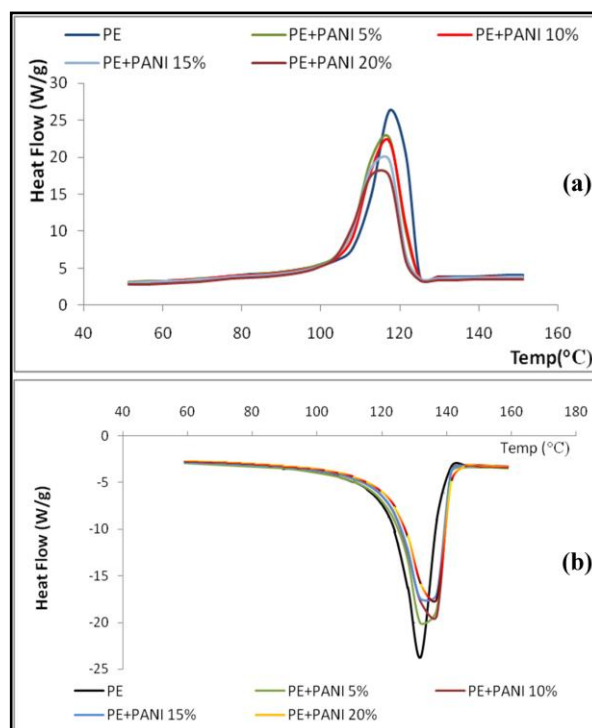

Fig. 5. a) DSC graph, cooling region of composites. b) DSC graph, heating region of composites

The presence of OMMT in ternary nanocomposites was caused an increasing in ΔH in comparison with binary composites. Results show

that modified clay increases the miscibility between PE and PANI as limited. The DSC thermographs of nanocomposites are presented in Figure 6a,b.

Disordered PANI chains and OMMT cause the decreasing of crystallinity in PE matrix. This trend result was accurate for samples up to 15%PANI but after that in 20%PANI this trend was not accurate. More than 20% PE and PANI cannot blend very well.
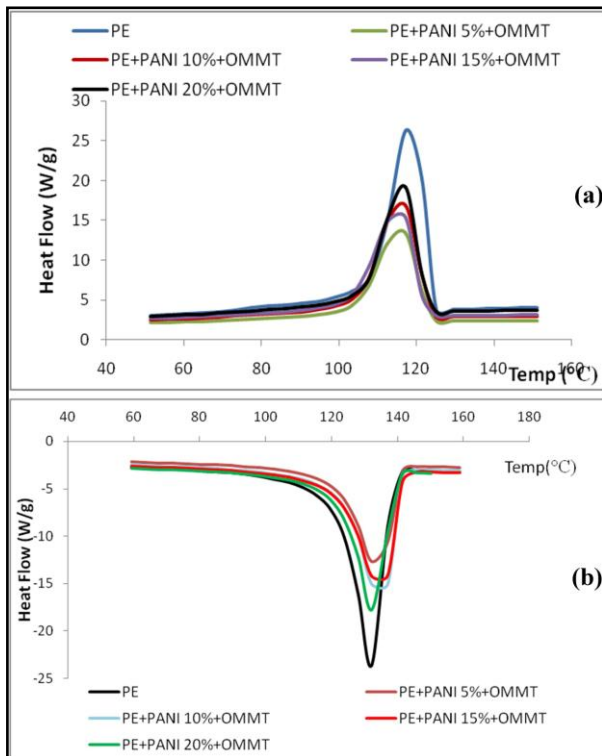

Fig. 6. a) DSC graph, cooling region of nanocomposites. b) DSC graph, heating region of nanocomposites

- ***Thermal stability of nanocomposite PE+PANI+OMMT***

Polymer / Clay nanocomposites preparation involves high temperatures irrespective of the fabrication route. If the processing temperature is higher than the thermal stability of the organic component used for montmorillonite modification, decomposition will take place, leading to variations between the filler and polymer. Thus, determination of the onset temperature of degradation, resultant products of degradation and the stability of the polymer in the presence of layered silicates as well as understanding the relationship between the

molecular structure and the thermal stability (decomposition temperature, rate, and the degradation products) of the organic modification of the layered silicate is critical [22,23]. In particular, thermal stability was considered as an important factor playing a role in the nanocomposite structure and morphology formation [24]. The improvement in thermal stability is much more significant for the exfoliated nanocomposites than for the intercalated ones [11].

The increasing number of dispersed MMT layers per volume unit of polymer matrix causes the fact that clay particles arrange in more regular structures. When the OMMT loading was lower than 8 phr, the samples exhibited higher thermal stability than those with higher OMMT loading.

The changes of the activation energy might be due to the structure evolution as the OMMT loading increases. The researchers attributed the observed phenomena to the fact that when the OMMT loading was relatively low (below 8 phr), exfoliated layers are the dominant structures developed in nanocomposite. The increasing OMMT content was followed by a growing number of delaminated layers strengthening the retardant effects to heat and oxygen in the epoxy matrix. When the OMMT loading increased further, the nanocomposites developed an exfoliated-intercalated structure. In effect, the number of exfoliated silicate platelets, which are thought to be more effective in blocking heat and oxygen than tactoids, decreased with the OMMT loading. As a consequence, the activation energy tends to decrease when the OMMT loading was higher than 8 phr[25]. Thermal stability was obtained for a loading of 5 wt% in OMMT, and 15wt% PANI Figure 7, however, further increases in the filler content led to a decrease in thermal stability.

Dynamic mechanical thermal analysis

Dynamic mechanical analysis (DMA) measures the response of a given material to a cyclic deformation as a function of the temperature. DMA results are expressed by three main parameters: (a) the storage modulus (G'), corresponding to the elastic response to the deformation; (b) the loss modulus (G"), corresponding to the plastic response to the deformation and (c) tan δ, that is the (G'/G") ratio,

useful for determining the occurrence of molecular mobility transitions such as the glass transition temperature. DMA analysis has been studied to track the temperature dependence of storage modulus upon the formation of an exfoliated or intercalated PE nanocomposites [26]. Figure 8 shows the storage modulus (G') and tan δ spectrum versus temperature during the DMA scan for PE and composite and exfoliated-intercalated nanocomposite. DMA analysis was performed DMA/SDTA861 METTLER-TOLEDO using a shear mode at a frequency of 10Hz. All blends were heated from 20 to 250°C at a rate of 10°C/min. The storage shear modulus (G') is a function of temperature.
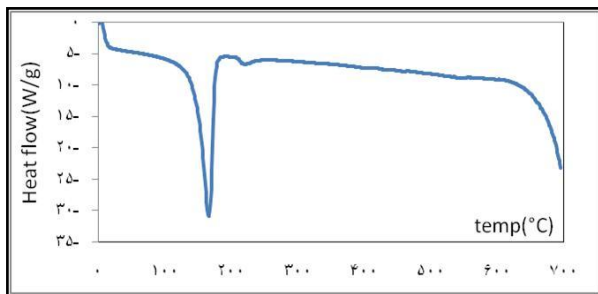

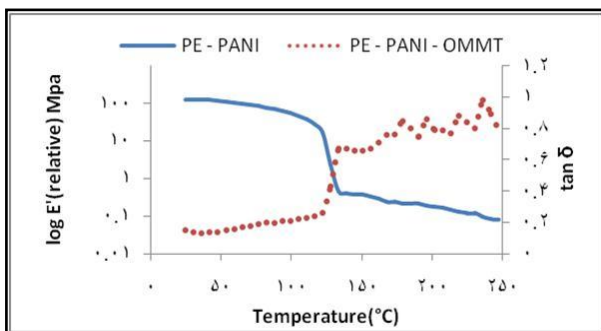**Fig. 7.** Thermal termograph of PE-PANI-OMMT

Fig. 8. DMTA scan thermograph PE-PANI, PE-PANI-OMMT

In the solid region, the decrease storage modulus for PE+PANI in comparison with PE shows low miscibility between PANI with PE. PANI rigid chains cause the increasing G' against their content. Above melting point, G' is decreases intensively. In this region, the entanglement between PANI chains caused G' to increase (Figure 9). In the presence of OMMT in ternary nanocomposite, storage modulus (G') for

PE+PANI+OMMT is increases in solid regions, corresponding with (Figure 9b). This behavior is aroused by exfoliated silicate layer in the matrix. Above melting point, G' behavior is similar to binary composite. It is important to point out that the composites containing 20% of PANI did not show these different regions, presenting, instead, a single rough region characterizing a homogeneous microstructure.
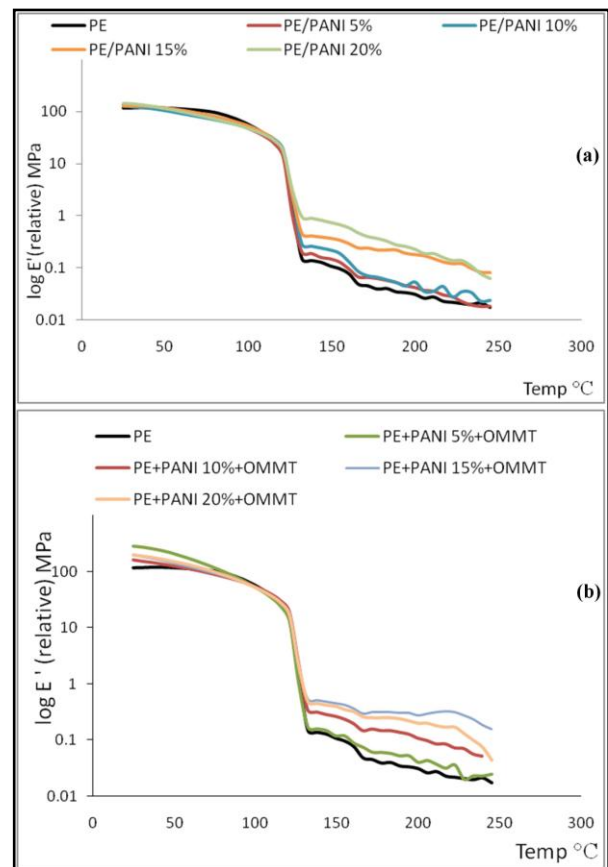

Fig. 9. a) DMA scan thermograph of composites. b) DMA scan thermograph of nanocomposites

CONCLUSIONS

New technologies require materials showing novel properties to improved performance compared to conventionally processed components. In this context, nanocomposites are suitable materials to meet the emerging demands arising from scientific and technological advances. This study confirmed the exfoliation/intercalation of PE/PANI into the galleries of OMMT in PE/PANI/OMMT nanocomposites. PE and PANI

enter between the galleries of the silicate during polymerization. The presence of the surfactant DBSA changes the gallery structure significantly and stabilizes it as well during subsequent processing operations, as confirmed by rheology and conductivity measurements. The processing conditions, the amount of conductive, and the presence of OMMT have an impact on the final conductivity of PE/PANI composites and PE/PANI/OMMT nanocomposites. Polyaniline and its composites with conventional polymers can be easily processed and produce desired thickness film. It was found that the percentage of PANI has a very important effect on mechanical and thermal stability of the composite and nanocomposites. The best amount for PANI was 15wt%. The electrical properties of PANI Films are highly dependent on the nature and the size of its dopant acid. Intercalated and exfoliated PE/PANI/OMMT was prepared by changing the molar ratio of PANI. PANI creates electrical properties and OMMT improves thermal stability of composites and nanocomposites. The thermal degradation behavior of PANI chains in the nanocomposites was investigated and it was observed that OMMT causes a remarkable increase in thermal stability and improved mechanical properties compared to conventional composites. XRD patterns clearly showed exfoliated of clay layers in the polymer matrix on the nanoscale. The XRD patterns suggest linearization of the PANI chain when synthesized in the presence of OMMT. The PE/PANI composite presented chain linearization, as well as exfoliation/intercalation of the montmorillonite lamellae. The addition of clay facilitated the synthesis of PANI and increased the reproducibility of the process. This is a relevant feature in the synthesis of conductive polymers, since one of the limiting factors for the wider use of this class of materials is precisely the reproducibility of the properties obtained.

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