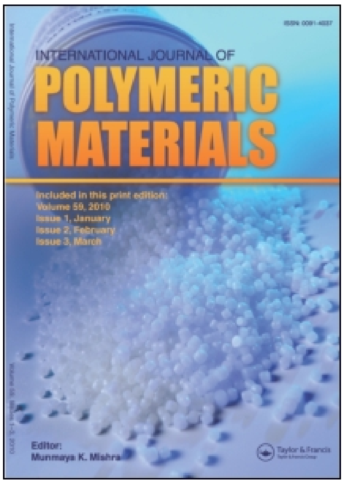

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Aniline (ANI) was polymerized under inert atmosphere in the presence and absence of natural clay initiated by peroxydisulphate (PDS) in an aqueous acidic medium. While increasing the amount of clay the rate of polymerization (R_p) was decreased and showed first order dependence with respect to amount of clay. The % yield was also decreased while increasing the amount of clay due to the confinement of monomer radical cation by the clay. The FTIR spectrum confirmed the presence of benzenoid and quinoid units in the polyaniline (PANI) structure. DSC inferred the absence of T_m due to cross-linking reaction of PANI because of de-doping process. AFM showed the distorted spherical morphology of uniformly dispersed clay platelets in the PANI. The % weight residue remain above 700°C is increased with the increase of amount of clay, which was confirmed by TGA method. Due to confinement effect the intrinsic viscosity value of PANI—nanocomposites were decreased with the increase of amount of clay in the system. PANI-nanocomposites showed improved d.c. conductivity value than the pristine PANI. Suitable mechanism was proposed to explain the experimental results obtained.

Keywords: AFM, conductivity, DSC, FTIR spectroscopy, intrinsic viscosity, mechanism, polyaniline, TGA

INTRODUCTION

Synthesis and characterizations of electrically conducting polymers have become one of the most important areas of research in polymer

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engineering and science due to their excellent electroactive behavior [1–3]. Among the conducting polymers, polyaniline (PANI) has stood in the electroactive polymer queue as a first member because of its ease of preparation and environmental stability with very high electrical conductivity [4,5]. For the first time Anbarasan and co-workers reported the peroxomonosulphate initiated polymerization of aniline [6]. Currently synthesis and characterization of conducting polymer nanocomposites is a fascinating field of research. Polymerization of aniline between the interlayers of nano materials improves the mechanical properties, thermal stability, crystallization behavior, and conductivity of PANI. In this connection we tried to improve the thermal stability of PANI. Zarbin and Belez [7] synthesized organic-inorganic hybrids of conducting polymers and crystalline Antimonic acid. Biswas and Ballav [8] reported the high yield polymerization of aniline and pyrrole in the presence of montmorillonite clay. In the aforementioned article they reported about SEM, TEM, XRD, and conductivity measurements. In situ chemical oxidative graft copolymerization of ANI from silica nanoparticles was reported by Liu and research team [9] in which they characterized the PANI-nanocomposites by FTIR, XPS, TGA, TEM, SEM, and UV-Visible techniques. The literature also includes the nanocomposites of PANI and sulfonated PANI with V_2O_5 [10]. Exfoliated PANI – Clay nanocomposites were prepared by in-situ polymerization of ANI onto pre-exfoliated water soluble poly(styrene sulfonic acid-co-aminostyrene) clay nanocomposites [11]. Poly(o-methoxyaniline) and poly (o-methylaniline) intercalated layered Vanadyl phosphate was reported by Brazilian scientists [12]. Frisch et al. [13] prepared a PANI intercalated hybrids by an intercalative polymerization method. In 2002, Zeng et al. [14] reported the intercalative in-situ polymerization of ANI with montmorillonite. The present communication reports here about the kinetics of polymerization of ANI in the presence of Natural Clay and their characteristics.

EXPERIMENTAL

Materials Used

The monomer Aniline (ANI) AR Grade, was purchased from S.D. Fine Chemicals, India and distilled prior to use. Potassium salt of peroxy disulphate (PDS), A.R. grade, was purchased from S.D. Fine Chemicals, India and used as such. LR grade HCl was obtained from S.D. Fine Chemicals, India and used as received. Natural Clay (Hectorite type) was collected from the KCET campus and pre-treated with acid and alkali to remove impurities. The pre-treated clay was dried, ground, and stored in a zipper bag.

Synthesis of Poly(aniline)

The required amount of ANI monomer was taken in a 500 ml Round Bottom Flask (RBF) containing 200 ml of 1 M HCl solution and vigorously stirred for 30 min at 45°C. Inert atmosphere was created inside the RBF by Nitrogen gas purging. After 30 min the calculated weight of PDS was added with vigorous stirring, and the polymerization was continued for the next 3 h. While adding PDS the reaction medium becomes dark green color after certain induction period. In the absence of PDS there was no polymerization at all. After 3 h of polymerization reaction the contents were filtered in a sintered crucible and the precipitate of polyaniline (PANI) was washed with 1 M HCl three times. Finally, the precipitate was washed with acetone to remove the adhered impurities or lower molecular weight compounds. The precipitate was dried for 4 h at 60°C and then weighed and stored in a zipper bag.

Synthesis of PANI Nanocomposites

The aforementioned procedure for the polymerization of ANI was followed here in the presence of the required amount of pre-treated natural clay.

Characterizations

Thus prepared PANI was characterized by various analytical techniques. FTIR spectra of the powdered samples were recorded by using Jasco FTIR 410 instrument through KBr pelletization method. DSC of the samples were measured by using DSC 7 TA instrument under nitrogen atmosphere at a heating rate of 10°C/min. The surface morphology of the samples were studied by Olympus OMC(L-TR) 800 psa type instrument (2D) with a resonance frequency of 24 KHz. Thermal stability of polymer and its nanocomposites were analyzed by thermogravimetric analysis method by using STA 1500 Instrument under air atmosphere at a heating rate of 10°C/min. The intrinsic viscosity (I.V.) of the polymer and polymer-nanocomposites were determined by dissolving the samples in N-methyl pyrrolidone (NMP). Before dissolution in NMP all the polymer samples were dedoped with 0.50 N aqu. NaOH solution. Conductivity of the powder samples were determined by using Four probe conductivity meter (Model DFP-02).

Rate of polymerization (R_p) was calculated by using the following formula:

$$R_p = \frac{\text{Weight of polymer formed}}{V \times t \times M} \times 1000$$

where V = Volume of the monomer solution, t = reaction time in second, M = molecular weight of monomer.

Conductivity of the polymer samples were calculated by using the following formula:

$$\sigma = \frac{\mathrm{Ln}(2) \times I}{\pi \times h \times \Delta V}$$

where σ = conductivity in S/cm, I = current in mA, h = thickness of sample, ΔV = potential drop in mV.

RESULTS AND DISCUSSION

Rate of Polymerization (R_p)

R_p represents the rate of polymerization and explains the chain-growing nature of PANI. R_p of ANI in the presence of clay was determined and compared with the results obtained in the absence of clay. R_p of ANI was calculated for different weight of clay. It was found that the R_p decreased linearly with increase in weight of clay. The order of reaction with respect to weight of clay was determined and is represented in Figure 1. The plot of $\log R_p$ Vs log (weight of clay) (Figure 1a) showed the slope value of 0.92 and has confirmed the first order dependence of R_p with respect to weight of clay. The first order dependence of R_p on weight of clay was further confirmed by plotting R_p Vs Weight of clay (Figure 1b). The decrease in R_p may be due to the restrictions of mobility of monomer radical cations by the added Natural nano-sized clay. The R_p for homo PANI was found to be 1.60×10^{-6} mol/l/sec.

Figure 2 shows the % yield of PANI while changing the weight of clay. The % yield was found to decrease with increased weight of clay. This may be due to (1) the confinement of anilinium radical cations by the natural clay, (2) increase in viscosity of the reaction medium by the added clay, or (3) solubility of dimer or tetramer in the reaction medium and hence its mobility is restricted by the added clay. The % yield of pristine PANI was calculated as 95% whereas by increasing the amount of clay the % yield slowly decreased.

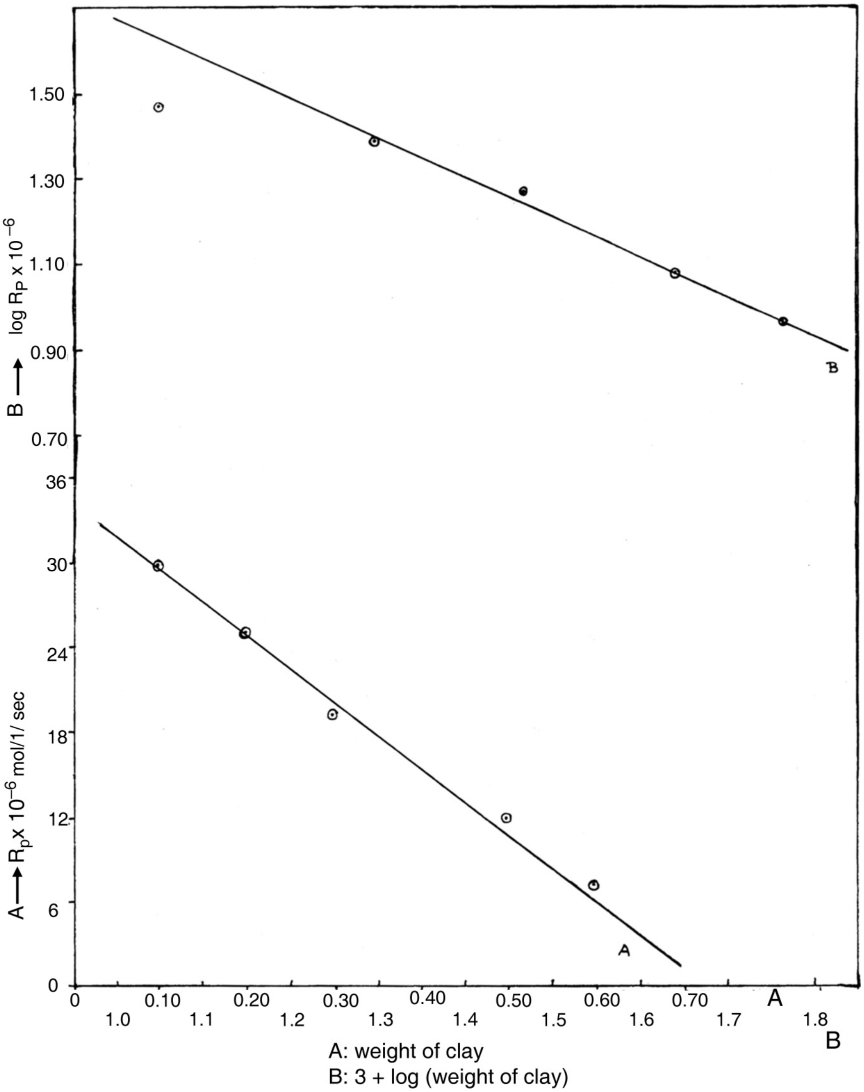

FIGURE 1 Effect of weight of Natural Clay on R_p. [ANI] = 0.10 M, [PDS] = 0.10 M, time = 3 h, temperature = 45°C.

FTIR Spectroscopy

Figure 3 shows the FTIR spectra of PANI and its nanocomposites. Figure 3 confirms the structure of PANI. A peak at 1484 cm^{-1} indicates the C–C aromatic stretching vibration (due to benzenoid structure of

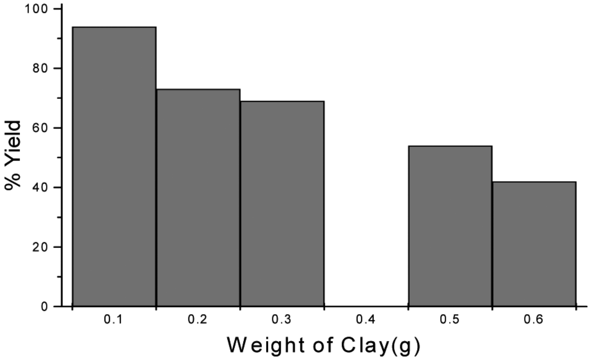

FIGURE 2 Bar diagram of weight of Natural Clay with % yield. [ANI] = 0.10 M, [PDS] = 0.10 M, time = 3 h, temperature = 45°C.

PANI). Peaks at 1215 and 1589 cm^{-1} correspond to C–N and C=N, respectively. Appearance of the latter peak confirms the presence of quinoid ring structure in the PANI backbone. A peak at 805 cm^{-1} is

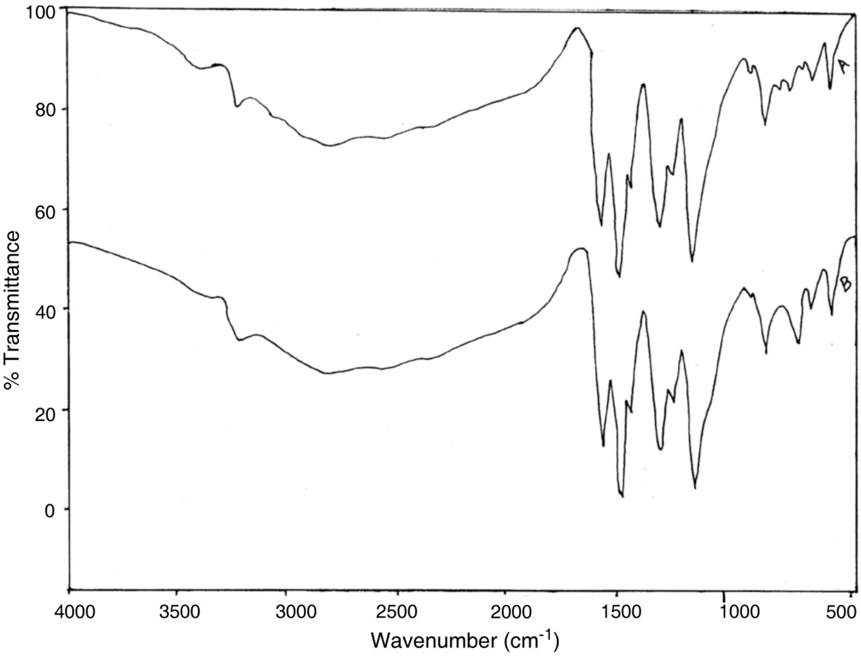

FIGURE 3 FTIR spectrum of (a) PANI, (b) PANI–Natural clay—0.10 g. [ANI] = 0.10 M, [PDS] = 0.10 M, time = 3 h, temperature = 45°C.

due to the C−H out of plane bending vibration of the p-substituted benzene ring. The presence of the Cl^-(dopant) can be identified from the peak at 1307 cm^{-1}. The vibration band of quinine nitrogen can be seen at 1169 cm^{-1}. Figure 3b showed the FTIR spectrum of PANI-nanocomposites. Here also can be seen peaks similar to that of HCl doped PANI. Peaks due to silicate structure appear in the region of 450 to 700 cm^{-1}. Thus the FTIR spectrum confirms the presence of natural clay in the PANI nanocomposites.

DSC Study

The DSC scans of PANI and its nanocomposites failed to show a melting peak of PANI or its nanocomposites due to crosslinking reaction. When heated, the HCl (dopant) is removed from PANI backbone and immediately crosslinking occurs. Because of this, it is not possible to get a melting peak. Wang et al. [15] reported the DSC of PANI and its derivatives. But Ikkala and co-workers [16] reported the DSC of PANI when it was blended with DBSA. The present case could not get the melting peak for PANI-HCl system nor for PANI-nanocomposite system. Again, it is due to crosslinking reaction of PANI. Added clay does not show any melting peak.

Atomic Force Microscopy (AFM) Profiles

AFM images of PANI-nanocomposites are shown in Figures 4–6. Figure 4 shows the AFM of PANI-clay-0.10 g system. Here one can

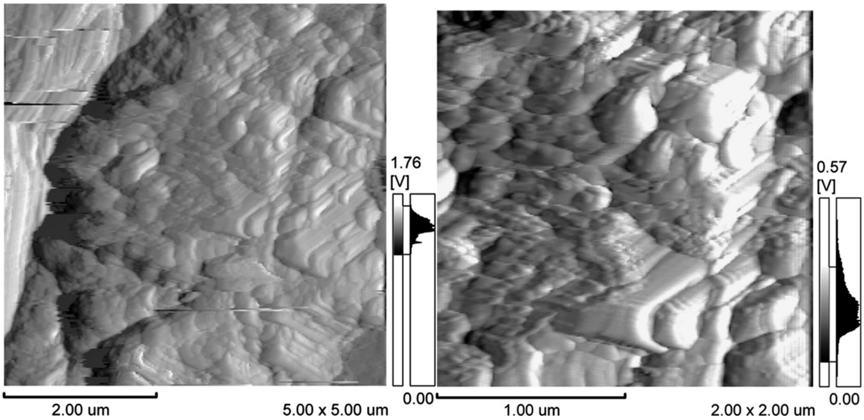

FIGURE 4 AFM of PANI—0.10 g Natural clay. [ANI] = 0.10 M, [PDS] = 0.10 M, time = 3 h, temperature = 45°C.

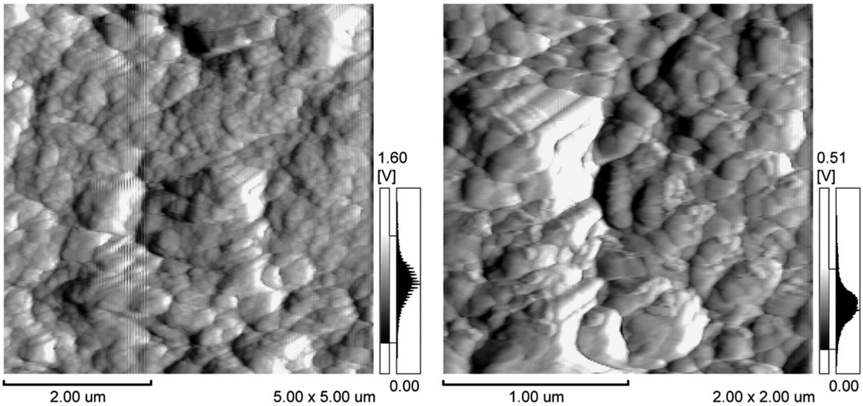

FIGURE 5 AFM of PANI—0.30 g Natural clay. [ANI] = 0.10 M, [PDS] = 0.10 M, time = 3 h, temperature = 45°C.

see the presence of nano-sized clay particles. The image shows the slightly distorted spherical morphology for the nanosized clay with the diameter of approximately 45 nm. The number of nano particle per square meter is less when compared with higher % of clay-PANI hybrid system.

Figure 5 shows the AFM of PANI-Clay-0.30 g system. More numbers of clay particles can be observed with a spherical morphology and a diameter of approximately 25 nm. Figure 6 shows the AFM of

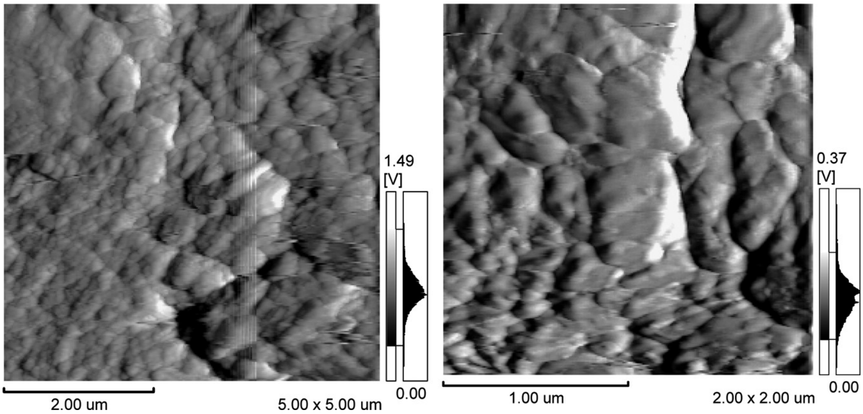

FIGURE 6 AFM of PANI—0.50 g Natural clay. [ANI] = 0.10 M, [PDS] = 0.10 M, time = 3 h, temperature = 45°C.

PANI-Clay-0.45 g. Figure 6 shows the agglomerated bigger size clay particles. It illustrates a pool of clay particles within average spherical diameter of approximately 35 nm.

Conductivity Measurements

HCl-doped PANI showed the conductivity value of 2.2×10^{-3} S/cm. In the case of PANI-nanocomposites the conductivity value increases with increase amount of clay. This may be due to the following reasons: (1) trapped water molecules in the clay resulting in increased number of mobile conducting species or (2) increase in number of Si–O structures of the natural clay. And also it confirms the existence of strong interaction between the clay and PANI. This result is consistent with the report of Biswas and Ballav [8]. Figure 7 shows the plot of amount of clay Vs conductivity value. The plot showed the increasing trend.

Thermogravimetric Analysis

Thermogram of pure PANI (HCl doped) (Figure not shown here) showed two step degradation process, that is, one minor and one major weight loss steps. The first, minor weight loss step appears around 100°C and accounts for the removal of moisture and physisorbed water molecules. The second major weight loss step appears at around 380°C. This is due to the degradation of PANI backbone. Degradation of PANI

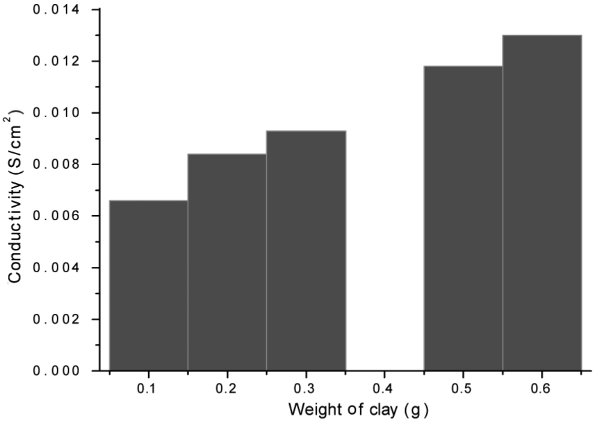

FIGURE 7 Bar diagram of weight of Natural clay with electrical conductivity. [ANI] = 0.10 M, [PDS] = 0.10 M, time = 3 h, temperature = 45°C.

backbone was completed at 507°C. Pure PANI exhibited 20% weight residue at 700°C. This infers that PANI has flame retarding property naturally. The thermogram can be further supported by a DTA scan. Here one interesting observation was noted as a small shoulder at 263°C due to crosslinking of PANI backbone (due to de-doping process).

Similar results, with minor changes, were observed in TGA scans of PANI with 0.20 g clay nanocomposites. (A) the PANI degradation takes place at somewhat lower temperature (455°C). This can be explained based on the confinement of anilinium radical cations by the added clay. (B) Degradation of PANI backbone has been completed at 537°C. This is definitely a higher degradation temperature when compared with the pure PANI (507°C). (C) Another important point noted was the % weight residue remaining at 700°C. Here it was calculated as 25.12%. Approximately 6% weight residue increase for 0.20 g addition of clay. This again points to the flame retardancy of PANI.

At higher (0.50 g) amount of clay, the degradation of PANI was observed at 475°C. This value is very close to pure PANI (478°C). In the present system the added clay increased the degradation temperature to 582°C and with 44% weight residue remain at 700°C.

Intrinsic Viscosity (I.V.)

Pure PANI showed higher I.V. value (0.37 dL/g) than the polymer nanocomposites (Table 1). Increasing the amount of clay decreased the I.V. of polymer-nanocomposites. This is due to the restriction of interaction of anilinium radical cations by the added clay.

Mechanism

The mechanism of ANI polymerization was well explained in earlier publications [17,18]. It is known, that the free radical reactions proceed through three steps, namely initiation, propagation, and termination.

TABLE 1 I.V. Value of Polymer and Its Nanocomposites

Sl. No.	Sample	IV (dL/g)
1	PANI	0.37
2	PANI + 0.1 g Clay	0.36
3	PANI + 0.2 g Clay	0.34
4	PANI + 0.3 g Clay	0.31
5	PANI + 0.5 g Clay	0.27
6	PANI + 0.6 g Clay	0.25

Initiation

$\text{Clay} + \text{ANI} + \text{PDS} \Longleftrightarrow \text{Composite } C_1$
$C_1 \longrightarrow 2SO_4^{-0}(R^0) + \text{ANI} + \text{Clay}$
$R^0 + \text{ANI} \longrightarrow \text{ANI}^{+0}$

Propagation

$2\text{ANI}^{+0} \longrightarrow \text{Dimer}$
$\text{Dimer} + R^0 \longrightarrow \text{Dimer}^{+0}$
$2\text{Dimer}^{+0} \longrightarrow \text{Tetramer}$
$\text{Tetramer} + R^0 \longrightarrow \text{Tetramer}^{+0}$
$2\text{Tetramer}^{+0} \longrightarrow \text{Octamer}$
$\text{Octamer} + R^0 \longrightarrow \text{Octamer}^{+0}$
$2\text{Octamer}^{+0}\ \text{-} \longrightarrow \text{Oligomer}$
$\text{Oligomer} + R^0 \longrightarrow \text{Oligomer}^{+0}$
$\text{Clay} + \text{ANI} \cdot \text{HCl} \longrightarrow \text{Clay-ANI (ANI modified Clay)}$
$\text{Clay-ANI} + R^0 \longrightarrow \text{Clay-ANI}^{+0}$
$\text{Clay-ANI}^{+0} + \text{ANI}^{+0} \longrightarrow \text{Clay-dimer}$
$\text{Clay-dimer} + R^0 \longrightarrow \text{Clay-dimer}^{+0}$
$\text{Clay-dimer}^{+0} + \text{Dimer}^{+0} \longrightarrow \text{Clay-Tetramer}$

$\text{Clay-Oligomer} + R^0 \longrightarrow \text{Clay-Oligomer}^{+0}$

Termination

$2\text{Oligomer}^{+0} \longrightarrow \text{Polymer (PANI)}$
$\text{Clay-Oligomer}^{+0} + \text{Oligomer}^{+0} \longrightarrow \text{Clay-Polymer (Clay-PANI)}$

Here direct intercalation of PANI into clay is not possible due to lengthy chain of PANI, poor solute–solute (clay and PANI), and solute-solvent interaction and very low polymerization induction period of ANI. From these reactions one can come to a conclusion that ANI can intercalate into clay platelets and cannot exfoliate the clay platelets. From an earlier report the authors propose a unimolecular termination reaction (because of first order dependence of R_p on M, I and amount of fiber). Moreover, the mutual coupling of PANI is forbidden due to first order dependence of R_p on the weight of clay. Thus the aforementioned mechanism clearly explains the experimental results obtained.

CONCLUSIONS

PANI-clay nanocomposite was successfully synthesized by an in-situ polymerization method. The R_p decreased with increase amount of clay. The decrease in % yield supports the aforementioned statement. The FTIR spectrum confirms the presence of nano-sized clay particles in the polymer nanocomposites. Due to crosslinking reaction the DSC could not run successfully. AFM confirms the strong interaction between clay and PANI with spherical morphology. Polymer-nanocomposites showed higher conductivity value than the pristine polymer. Polymer-nanocomposites showed a high flame retardant behavior. I.V. of polymer–nanocomposites were decreased by an increase of the amount of clay.

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