

Synthesis, characterization and Thermal Degradation Studies of Acrylic Based nanocomposite Polymeric materials

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Abstract- Acrylic based polymeric nanocomposites have been synthesized with the incorporation of sodium montmorillonite and surface modified nanoclay to the extent of less than 1 wt% via in-situ intercalation method using N₂ gas as an inert media. The synthesized samples were characterized by X-Ray Diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). The XRD analysis shows that diffraction peaks in the low angle region are absent which indicate that the d-spacing of ordered intercalated and ordered delaminated nanocomposites has not been achieved but the diffraction peaks has been shifted to larger 2-theta values which is an indication to the fact that disordered nanocomposites has been synthesized due to changes in the structure of the layers of the clay. But diffraction peaks of surface modified MMT and simple MMT has been shifted to lower angles in polymer and co-polymer nanocomposites, an indication to intercalated composite. In all the XRD graphs of pure polymeric substances and PNC'S, the peaks associated with [010] plane of a hexagonal structure which appeared at 2θ values of ~17° confirm the crystalline structure of polyacrylonitrile. The diffraction angles at 29° in pure polyacrylonitrile indicate the pre-graphitic type structure having a bragg's plane of [300].

Keywords---Montmorillonite Clay (MMT), Polyacrylonitrile, Nanocomposite, Intercalated composite.

I. INTRODUCTION

The majority of the research has been focused on polymers/nano material composites for example polystyrene (PS) [1], polypropylene (PP), epoxy resins [2] polyamides, poly vinyl chloride [3] and polyurethane [4], polyacrylonitrile [5], polyacrylic acids [6] and many others. Polymer composites having ferrites in their layers are taking place of orthodox ceramic magnetic polymeric composites because of their mould ability and reduction in cost. They are also potential materials for microwave absorbers, sensors and other aerospace applications.

These stretchy magnets or rubber ferrite composites are promising by the assimilation of magnetic nanoparticles. Several synthetic approaches have been made practical to the preparation of zero valent metal-polymer nanocomposite [7, 8]. Many polymer thin films, containing noble metal nanoparticles, have been prepared by reducing polymer metal chelatefilms such as PANi/Au, PVA/ Ag [9]. In the last decade many of clay mineral deposits have been tailored using organic salts and metals such as Ni, Zn and Cu. The synthesis of exfoliated polystyrene/clay nanocomposites has also been reported. A reactive cationic surfactant was synthesized and ion exchanged with sodium ions in MMT by different other ions which specify startling properties to the polymers. The exfoliated polystyrene/clay nanocomposites were prepared by dispersing the nanoclay into the monomer via sonication followed by free radical polymerization [10].

II. EXPERIMENTAL

All chemicals were of analytical grade and used without further purification or process throughout this study. Deionized water was used for preparation and dilution of reagents and samples. All monomers were purified to remove inhibitor before they were used using the prescribed procedure in literature [11]

2.1. Synthesis of pure polyacrylonitrile-co-polyacrylic acid: (in-situ intercalation)

Copolymerization of polyacrylonitrile (AN) with acrylic acid (AA) were carried out in a two necked glass reactor, using mixture of deionized water and DMF as a reaction medium at 60° C, under pure nitrogen atmosphere. The total weight of H₂O and DMF was 3 times greater than that of the monomers. AIBN (1 % wt on the basis of the monomers) was used as initiator. [61] Poly (AN-AA) copolymer was synthesized by mixing 2 ml pure acrylic acid (10% wt) and 18 ml (90% wt) of pure acrylonitrile. The reaction was preceded at room temperature (40°C) for about one hour. Temperature was increased to 60°C with the interval of 5°C after every hour. After half an hour, the temperature was maintained to 60°C, white coloured crystalline sample was obtained. Copolymer were washed with excess of distilled water and filtered and dried in oven at 50° C overnight. Calcium chloride was further used to make the sample free from moisture. Synthesis of PAN/S.M.MMT (surface modified nanoclay) nanocomposite: (in-situ intercalation) according to the procedure [12].

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2.2. Synthesis of PAN/MMT(K-10 powder) composites: (in situ process)

In this synthesis required amounts of Na-MMT (less than 1% of the monomer weight) was taken in a conical flasks with 20 ml of inhibitor free acrylonitrile and montmorillonite (MMT) were dispersed in the monomer via stirring and ultrasonication. The monomer was taken in two neck glass reactor in which inert media was pre-established. The monomers were purged with N₂ gas, mixed with required quantity of AIBN and reaction was preceded 40°C for one hour on the constant temperature heating plate device. This glass reactor was placed in water baths at 45°C for one hour. Temperature was increased regularly in regular intervals of time to 60°C. After some time, the temperature was maintained at 60°C, thick material appeared which the required product was.

III. RESULT AND DISCUSSION

The FTIR studies of pure sample of polymer and then incorporated with montmorillonitrile clay MMT in various combinations confirms the IR bands are in well agreement with formation of polymers and their characteristic spectra bands are present. In case of copolymers of Poly(acrylonitrile – Acrylic acid) PAN-co-PAA the characteristic bands of both constituents are present. In case of PAN –co-PAA/S.M. MMT (surface modified nanoclay composite, The FTIR band at 532 cm⁻¹ is due to -C≡N. Absorption bands at 1652 cm⁻¹ are due to the hydrolysis of acrylonitrile unit during the polymerization process. The strong band appears at 2243 cm⁻¹ is assigned to nitrile functional group (-C≡N) group.

3.1. XRD Studies

The XRD diffraction pattern of polyacrylonitrile shows its crystalline structure. The XRD pattern of PAN nanoparticles reveals two diffraction peaks at $2\theta = 16.8^\circ$ and 29.8° and is in good agreement to literature [63]. In case of Polyacrylonitrile/surface modified MMT composite, the X-Ray diffraction pattern (figure 2) polyacrylonitrile / surface modified nanocomposite shows four peaks along the 2-theta range. The first peak at 17.1° corresponds to highly crystalline phase of polyacrylonitrile hexagonal structure. The second peak is at a diffraction angle of 29.8° which has been developed due to fabrication of MMT with d-spacing of 2.99Å . Actually diffraction peak of pure MMT at 34.8° having basal spacing of 2.5Å has been shifted to 29.8° . The increase in the d-spacing, shifting of diffraction peaks and comparison of the data to previous literature clearly confirm the exfoliated or intercalated structure of nanocomposite. In the very similar way the peak at 49° has been shifted to 44.89° .

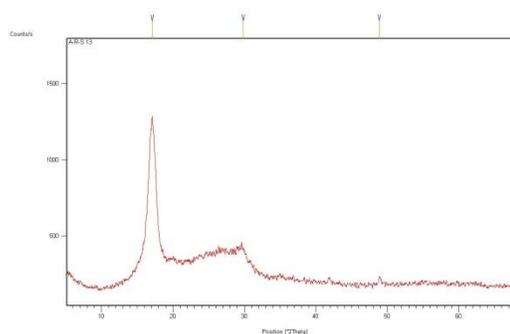


Fig.1. XRD pattern of PAN/ surface modified MMT (intercalated).

TABLE 1
CHANGE IN 2-THETA VALUES

Sr. no.	2-theta values of surface modified MMT (degrees)	Shifted 2-theta values in composite (degrees)	d-spacing of clay
01	19.75	19.02	Increased
02	34.87	29.82	Increased
03	54.33	48.89	Increased
04	61.77	50.54	Increased

The XRD pattern of pure PAN –co-PAA has been shown in the (figure 3). Three peaks are visible, first and second peak form a doublet structure has which shows that copolymer has been formed. This doublet peak is at a diffraction angle of 16.9° and 17.3° . The peak at 16.9° is for hexagonal crystalline polyacrylonitrile and the peak at 17.3° might be for polyacrylic acid [11]. The broad at 29° is due to stabilization of polyacrylonitrile nanoparticles within the amorphous polyacrylic acid

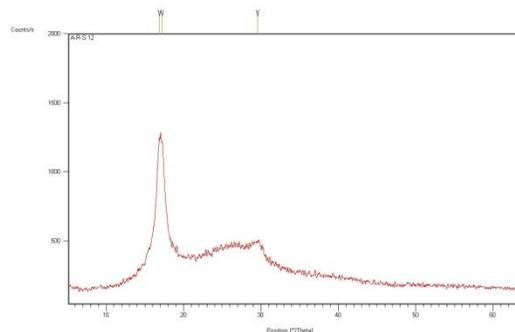


Fig.2. XRD pattern of PAN-co-PAA (pure)

3.2. TGA Studies

Thermogravimetric studies carried out in the temperature range of 50 - 650°C under nitrogen flow. TGA thermograph of PAA-co-PAN/ MMT composite show the one major weight loss beginning from 173°C and ending at 638°C . Once the degradation triggered it continue until the whole weight is lost, there are few small degradation stages which are overlapped are due elimination of small fragmented products due to chain scission. In the said copolymer of PAA-co-PAN/ MMT composite, the early stage of degradation is assigned to the primary oxidative reactions including dehydrogenation and cyclization and later stage of degradation corresponds to

secondary oxidative reaction leading to the evolution of HCN, CO₂, and CO. This has been observed that the acidic comonomer reduces the extent of cyclization reactions. The acidic comonomer promote the secondary oxidative reactions. This is probably due to the increase in the amorphous phase in the polymer by incorporation of the comonomer units (acrylic acid), which may provide greater opportunity for the molecules to come in to contact with air. A residue of about 6.7% was left beyond 650°C which was of the amorphous carbon and might be MMT.

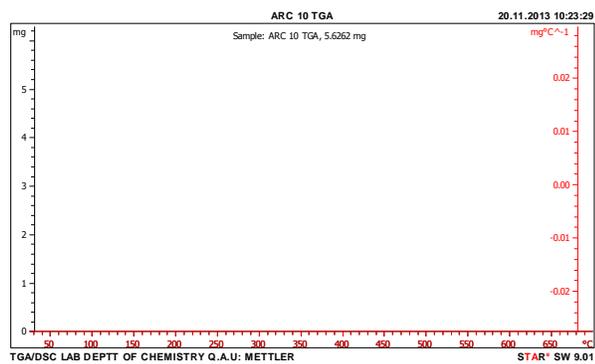


Fig. 3. TGA curve for PAA-co PAN /MMT nanocomposite

IV. CONCLUSION

Variety of polymers their copolymers synthesized with the incorporation of sodium montmorillonite and surface modified nanoclay in various combinations less than than 1 wt% via in-situ intercalation method under the continuous N₂ purging for inert atmosphere. The synthesized samples were characterized by X-Ray Diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA).

The XRD analysis shows that diffraction peaks in the low angle region are absent which indicate that the d-spacing of ordered intercalated and ordered delaminated nanocomposites has not been achieved but the diffraction peaks has been shifted to larger 2-theta values which is an indication to the fact that disordered nanocomposites has been synthesized due to changes in the structure of the layers of the clay. In all the XRD graphs of pure polymeric substances and PNC'S, the peaks associated with [010] plane of a hexagonal structure which appeared at 2θ values of ~17° confirm the crystalline structure of polyacrylonitrile. Crystalline size ranges and d-spacing values calculated by Scherrer's calculator have also been mentioned.

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