Synthesis of a biodegradable polyacrylonitrile/sodium silicate nanocomposite fire retardant

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Polyacrylonitrile (PAN)/Sodium silicate (SS) nanocomposite was synthesized via non-conventional emulsifier free emulsion method using an *in situ* developed transition metal complex Cu(II)/EDTA taking potassium monopersulfate (KMPS) as initiator, with a novel motive of converting hydrophobic homopolymer PAN into hydrophilic nanocomposite by the inclusion of SS to the homopolymer. The formation of the PAN/SS nanocomposite was confirmed by infrared spectra (IR). Furthermore, as evidenced by transmission electron microscopy (TEM), the composite so obtained was found to have nano scale structure. X-ray diffraction (XRD) was carried out suggesting that the silicate layers were exfoliated or intercalated during the polymerization process. An increase in the thermal stability for the developed nanocomposite was recorded by thermogravimetric analysis (TGA). The combustion behaviour has been evaluated using oxygen consumption cone calorimeter and the nanocomposite exhibited good fire retardancy. The PAN/SS nanocomposite was found to be biodegradable as tested by sludge water and further confirmed by scanning electron microscopy (SEM).

Keywords: Emulsifier-free emulsion, Nanocomposite, Fire retardant, Biodegradation

A new class of composite materials known as polymer layered silicate nanocomposites[1] (PLSNs) are emerging as the most significant and new breed of composite materials due to their extensively enhanced mechanical[2,3], thermal[4-6], non-flammable[7] properties. Unlike to a virgin polymer or conventional macro and micro composites, the improvement in properties of PLSNs are remarkable, including high moduli[8], decreased gas permeability[9], increased biodegradability of polymers[10,11], increased strength and heat resistance[12] and fire retardancy[13,14]. This nanoscopic dispersion is achieved by using layered silicates. The study of PLSNs has become even more attractive by recent demonstrations of their flame retardant properties, namely a significant decrease in the peak heat release rate (PHRR), a change in the char structure, and a decrease in the rate of mass loss during combustion in a cone calorimeter[14].

There are already various methods of improving fire retardancy of polymers as required in many applications for safety considerations. The substances used for preparation of fire retardants are: bromine[15], phosphate[16], antimony[17], nitrogen[18], graphite[19], silicate[4,14] etc. However, some degrees of these methods are limited with respect to environment requirements and performance of polymers. PLSNs are believed to be a new promising approach in fire retardannt[20] due to their great potential in forced flaming conditions, for instance, the reduction of the flame spread and fire propagation. The most dominant mechanism in their improved fire retardant properties is the accumulation of clay layers at the combusting surface of the condensed phase serving as a barrier to O_2 supply and the pyrolysis gases[3,14,21,22].

Further, study on green polymeric materials which avoid the use of any toxic or noxious components in their manufacture and could be naturally biodegradable, are in demand, as they reduce the hazardous effect of plastics and other polymeric compounds on environment. In previous paper[23], the preparation of nanocomposites with various improved properties by emulsifier free emulsion technique has been reported. Here, the preparation of PAN/SS nanocomposites is described, which are characterized for their improved properties including flame retardancy and biodegradability.

Experimental Procedure
Material
Monomer, acrylonitrile (AN) from E Merck India, was purified as reported earlier[16]. Sodium silicate was a gift solid granular sample (CAS 1344-098, Batch

No. - 2023BB H_2O-1) from PQ Corp. Maastrichat, Netherlands. The initiator, potassium monopersulphate (KMPS) from Acros, USA and all other reagents were from E Merck India (AR grade) and were used after purification by standard techniques.

Synthesis of PAN/SS nanocomposites

PAN, PAN/SS nanocomposite were prepared via emulsifier free emulsion polymerization strategy as per previous reports[10,14,23] by taking distilled acrylonitrile dispersed in deionised water via stirring with *in situ* developed $CuSO_4$ (0.1 M)/EDTA (0.1 M) complex. Silicate solution, prepared on a weight percentage basis, was added and the mixture was slowly heated to 45ºC followed by addition of KMPS (0.1 M) dissolved in water. Polymerization was carried out with stirring (400 to 600 rpm) for 3 h. Polymerization was terminated by addition of a 0.1 M solution of ferrous ammonium sulphate solution. The coagulated products were purified by washing with distilled water and alcohol, then dried at 40ºC in vacuum oven till a constant mass was obtained.

Characterization

The IR spectra of SS, PAN and PAN/SS nanocomposite, in the form of KBr pellets, were recorded with Perkin-Elmer model Paragon-500 FTIR spectrometer in the range 400-4000 cm^{-1}. The interaction of PAN into the silicate layer was confirmed by using a XRD monitoring diffraction on Philips PW-1847 X-ray crystallographic unit equipped with a Guinier focusing camera CuK_2 radiation. Nanoscale structure of PAN/SS was investigated by means of TEM (H-7100 Hitachi Co), operated at an accelerating voltage of 100 Kv. Thermal properties were measured by using a Shimadzu DTA-500 system. It was carried out in air from room temperature to 600ºC at a heating rate of 10ºC/min.

The fire performance of the PAN/SS nanocomposite was evaluated in a horizontal orientation using a Cone Calorimeter[21] in accordance with the procedure[22] outlined in AS/NZS 3837:1998, which was based on ISO 5660-1:1993, with dimensions $100 \times 100 \times 4$ mm^3 at a heat flux of 35 kWm^{-2}. All the specimens were tested in triplicate using a retaining frame with data collection intervals of 5 s. The Cone Calorimeter measures fire-relevant properties such as heat release rate (HRR), mass loss rate and smoke production rate among others. Heat release rate, in particular, peak HRR has been found to be the most important parameter to evaluate fire safety.

The activated sludge water was collected from tank receiving toilet and domestic wastewater. The sludge water contains many microorganisms (bacteria, fungi, yeast, etc.) responsible for the biodegradation of waste materials. The sludge was collected[24] in a polypropylene container, which was filled completely and then fully closed. Then the wastewater was brought to the lab immediately. After settling for about 1 h, the total solid concentration was increased to 5000 mg/L. The activated sludge water and a polymer sample (0.2 g) were incubated together in a sterilized vessel at room temperature (28±2ºC). Duplicate samples were removed at time intervals for biodegradation study via weight loss. Vessels containing polymer samples without sludge water were treated as control[25,26].

Results and Discussion

From the series of experiments, it was found that the PAN was inserted into gallery structure of silicate by the catalytic action of Cu(II)/EDTA complex. The complex initiating system helps to stabilize the emulsion latex to high conversion level in the absence of added emulsifier (Table 1). The initiation is a surface catalysis with adequate energy transfer from the complex to the initiator KMPS, resulting in a complex initiation mechanism deviating from a simple path of decomposition. The concerted

Table 1—Effect of variation of concentration of AN/KMPS/SS at constant time 180 min, temperature 45°C [$CuSO_4$] = 10×10^{-2} mol.dm^{-3} and [EDTA] = 10×10^{-2} mol.dm^{-3} on the % of conversion

Polymer Code	[AN] mol.dm^{-3}	[KMPS] x 10^{-2} mol.dm^{-3}	[SS] wt%	Conversion (%)
S_1	0.759	15	10	48.6
S_2	1.51	15	10	68.9
S_3	2.27	15	10	87.4
S_4	3.03	15	10	84.2
S_5	3.79	15	10	78.9
S_6	2.27	5	10	62.4
S_7	2.27	10	10	78.5
S_8	2.27	15	10	87.4
S_9	2.27	20	10	82.5
S_{10}	2.27	25	10	80.6
S_{11}	2.27	15	0	84.5
S_{12}	2.27	15	5	87.3
S_{13}	2.27	15	10	87.4
S_{14}	2.27	15	15	86.7
S_{15}	2.27	15	20	85.9
S_{16}	2.27	15	25	84.8

generation-consumption criterion is the driving force in the complex catalyzed peroxide and vinyl polymerization.

FTIR absorption peaks for SS, PAN and PAN/SS nanocomposite are shown in Fig. 1. The peak at 1360 cm^{-1} is due to = CH$_2$ bending and 1453 cm^{-1} is due to the scissoring vibration of terminal methylene group. The stretching vibration of – C Ξ N and vinyl C–H of the composite showed peak at 2245 cm^{-1} and 2935 cm^{-1} respectively. The peak at 2956 cm^{-1} is due to antisymmetric >CH$_2$ stretching. The absorption peaks at 700-1079 cm^{-1} are due to the Si–O–Si linkage (Fig. 1c) which are absent in Fig. 1a and 1b, indicating the presence of silicate in the PAN/SS nanocomposite matrix.

The structure and apparent interlayer spacing (d-spacing) of the PAN/SS nanocomposites prepared via *in situ* intercalation have been detected by X-ray diffraction. Figure 2 shows the XRD patterns for the SS and the nanocomposites. The d spacing of SS has been calculated to be 1.54 nm from a diffraction peak at $2\theta = 6.4°$ using Bragg function. The SS free S$_{11}$ shows no diffraction peak in the 2θ range from 1 to 10°, indicating that the polymer has no ordered structure in this dimension range. The diffraction peak of the SS is absent in the X-ray diffraction spectrum when the SS content reaches 5 wt % for S$_{12}$. This suggests that the SS layers are highly disordered in the nanocomposite powders. In the cases of S$_{13}$ and S$_{14}$ powders, the diffraction peaks in the XRD patterns reveal an intercalated structure with the d-spacing values of about 3.0 and 2.6 nm. This indicates that the layered SS is delaminated in the aqueous medium by the PAN polymer when the SS content is relatively low, whereas the intercalated structure of SS in polymer matrixes is dominant when the SS content is higher than 10 wt%. This phenomenon accords with the conclusion drawn by Ray *et al.*[27] about the dependence of the nanocomposite structure (exfoliated or intercalated) on the silicate content.

TEM studies are necessary to verify the extent of delamination and exfoliation achieved[27]. Figure 3 presents the TEM images of S$_{12}$ and S$_{13}$ samples. In Fig. 3 the SS layers are well dispersed in the PAN matrix. Although the SS layers still retain their orientation to some degree, the SS tactoids are highly delaminated into some thin lamellas by PAN with a dimension of about 1~2 nm in thickness. When the SS content is up to 10 wt%, the layered structure of the
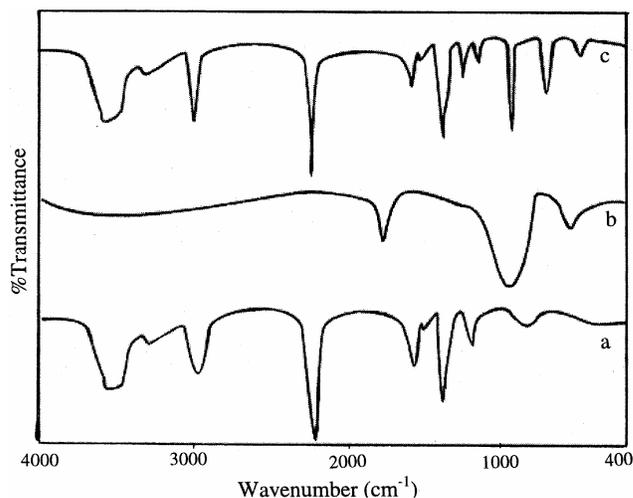

Fig. 1—FTIR of (a) PAN, (b) SS and (c) PAN/SS (S$_{13}$) nanocomposite.

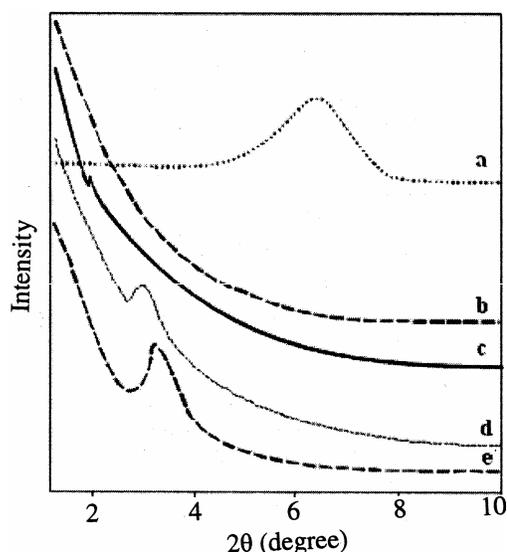Fig. 2—XRD of (a) SS, (b) PAN (S$_{11}$), (c) PAN/SS (S$_{12}$), (d) PAN/SS (S$_{13}$) and (e) PAN/SS (S$_{14}$) nanocomposites.

SS is generally intercalated in the polymer matrix. The d-spacing values increase from 1.4 nm for the pristine SS to a value ranging from 2 to 3 nm, which is in good agreement with the results from the XRD experiments. On the basis of the evidence from XRD and TEM, it is clear that the PAN/SS nanocomposites with a highly delaminated or intercalated structure have been successfully prepared via an *in situ* intercalation process in the neutral aqueous media without any special aid. Moreover, the results obviously suggest a high affinity between PAN and SS. It should be assigned to some kind of interaction, such as an electrostatic interaction and/or hydrogen bonding.
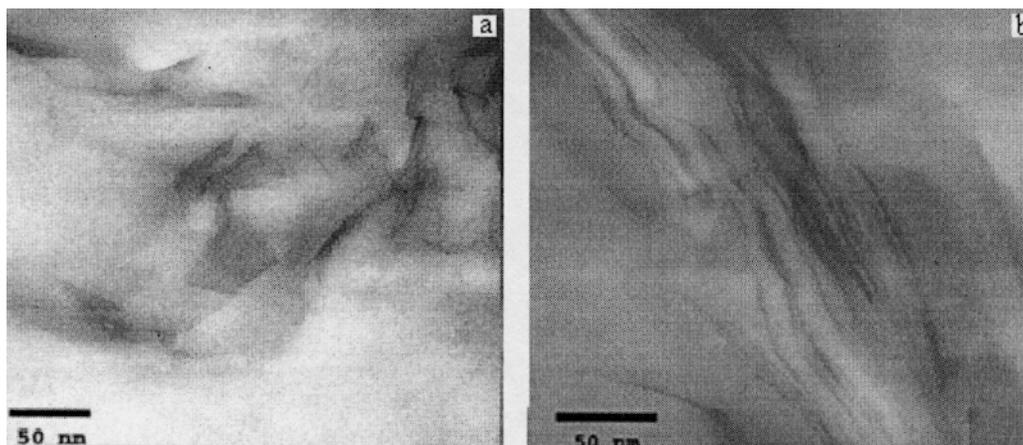
Fig. 3—TEM of (a) PAN/SS (S$_{12}$) and (b) PAN/SS (S$_{13}$) nanocomposites.

The thermal degradation of the nanocomposite materials have been evaluated by TGA as shown in Fig. 4. In contrast to PAN, the onset of decomposition for PAN/SS nanocomposite is shifted towards a higher temperature with increased clay content, indicating an enhancement of the thermal stability upon intercalation. The higher thermal stability of PAN/SS nanocomposite suggests that the generated silica-rich char is protecting the polymer from ambient oxygen, and reducing the rate of oxidative degradation in the composite materials[28] than that of PAN, which can be attributed to the nanoscale clay layers preventing out-diffusion of the volatile decomposition product. On the other hand, the inorganic part of the nanocomposite film almost did not lose its weight during the heating period.

The evidence for protective effect of layered silicate on the polymer systems is obtained by cone calorimetry. The cone calorimeter instrument provides a method for measuring the amount of heat, or energy, released from a material during combustion. Other parameters that are measured simultaneously include smoke, carbon dioxide and carbon monoxide generation, ignition behaviour and also mass loss.

From Fig. 5 and Table 2, it is observed that, the time to ignition of the polymer-clay nanocomposites were lower than virgin polymer i.e., time to ignition (TTI) for PAN/SS nanocomposite were less than virgin polymer due to the decomposition of SS clay at lower temperature, which is same as reported in previous studies[27,29,30].

Rate of heat released (HRR) is one of the most important parameters associated with the flammability and combustion of materials. The samples which have low value of HRR are better fire retardant than those with high HRR value. Even a small amount of silicate
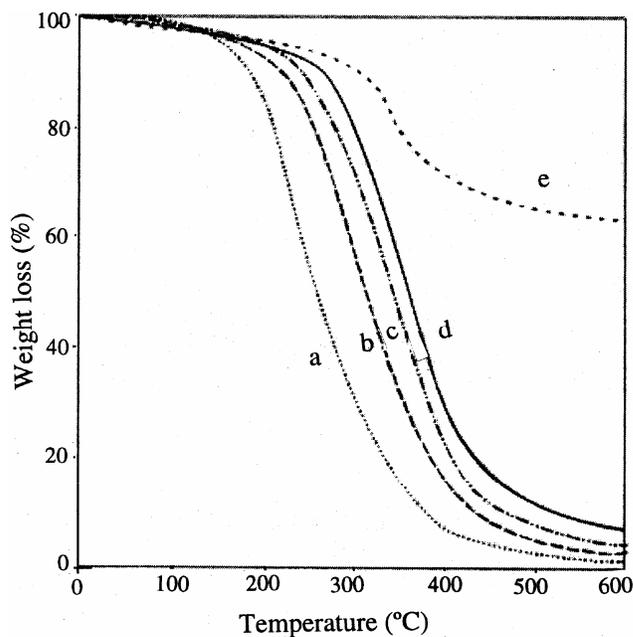

Fig. 4—TGA of (a) PAN (S$_{11}$), (b) PAN/SS (S$_{12}$), (c) PAN/SS (S$_{13}$), (d) PAN/SS(S$_{14}$) nanocomposites and (e) SS.

Table 2— Cone calorimeter data of PAN and PAN/SS nanocomposites

Sample	TTI (s)	PHRR (kW/m^2)	THR (Mj/m^2)	MLR (g/stm^2)	AvCO (kg/kg)	PkSEA (m^2/kg)
S$_{11}$	58±2	737± 13	65± 8	54± 4	3.9	184
S$_{12}$	52±2	546± 13	64± 6	53± 4	3.3	187
S$_{13}$	50±2	501± 13	63± 6	52± 2	3.1	189
S$_{14}$	49±2	476± 13	62± 4	51± 2	3.0	190

present in polymer decreased the HRR value of nanocomposites. From Fig. 5 and Table 2, it is clear that the HRR value of virgin polymer was more than any PAN/SS nanocomposite. Due to formation of char residue, which acted as a protective barrier by reducing the heat and mass transfer between the flame and hence the HRR value was normally lowered as explained by Gilman and Kashiwagi[31] and others[29,30]. Further, with increasing % of SS content in the polymer nanocomposites, the HRR values decreased as shown in Fig. 5 (b-d). The reduction of peak heat release rate (PHRR) (Δ) values was proportional to the fraction of clay present in the nanocomposite at very low concentrations[20]. But the rate of decrease of PHRR value was independent on % of SS present, an observation similar to the results of Gilman and Kashiwagi[31] and others[32]. In comparison, among the PHRR of exfoliated and intercalated polymer nanocomposites, the intercalated nanocomposite has high fire retardant properties.

The heat release capacity mainly depends on the maximum mass loss rate (MLR) and the heat of combustion of the decomposition products at that temperature. Therefore, the MLR is another factor that can determine the heat release rate. From the values of MLR included in Table 2, it is found that the MLR value of PAN/SS nanocomposite decreased with the presence of SS in the virgin polymer. The rate of mass loss from a polymer-silicate hybrid when exposed to heat, was significantly reduced compared with the pure polymer. The result was also correlated with those of Le *et al.*[33] and Lee *et al.*[34]. Additionally, several other parameters were measured simultaneously during the cone calorimetry experiments. These included measurement of the effective heat of combustion, specific extinction area (SEA) (smoke emission) and carbon monoxide and carbon dioxide emissions, which are given in Table 2.

For its commercialization and ecologically friendly nature, the biodegradation testings are carried out. Biodegradation by activated sludge is less in case of PAN than that of PAN/SS nanocomposites. The biodegradation is increased with increasing percentage of silicate (Fig. 6). From this observation, it is confirmed that the growth of microorganisms are more because of the presence of more hydrophilic silicate, and more water absorbency resulting in the more degradation i.e. more percentage weight loss of nanocomposite samples and the degradation is further confirmed by SEM (Fig. 7). The rupture surface of
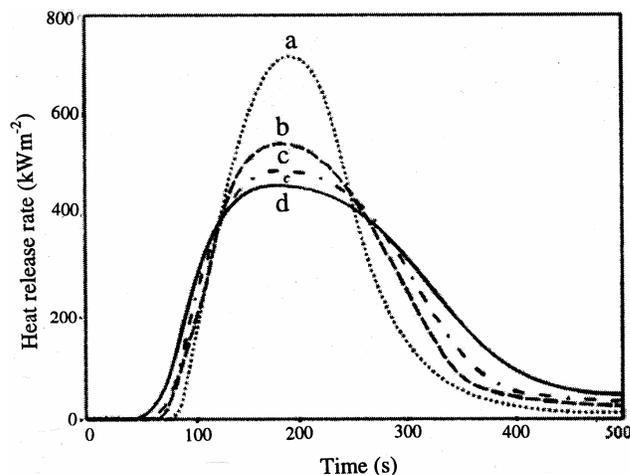

Fig. 5—Heat release rate curve of (a) PAN (S_{11}), (b) PAN/(S_{12}), (c) PAN/SS (S_{13}) and (d) PAN/SS (S_{14}) nanocomposites.
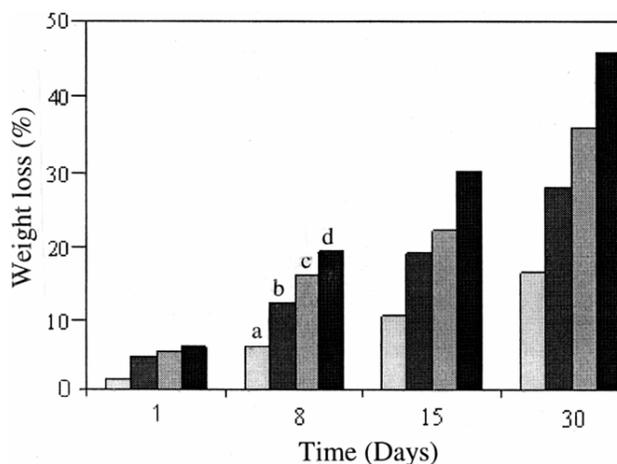

Fig. 6—Degradation via weight loss by bacteria (B. cereus) of (a) PAN (S_{11}), (b) PAN/SS(S_{12}), (c) PAN/SS (S_{13}) and (d) PAN/SS (S_{14}) nanocomposites.
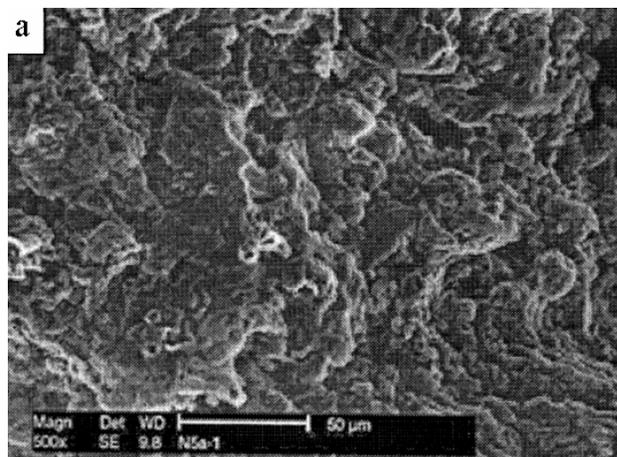

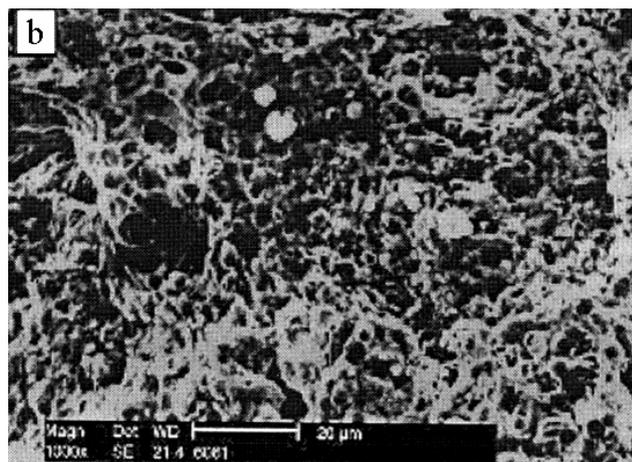Fig. 7a—SEM of PAN/SS (S_{13}) nanocomposites before biodegradation

Fig. 7b—SEM of PAN/SS (S$_{13}$) nanocomposites after biodegradation.

Fig. 7b, over the surface of the nanocomposite in Fig. 7a indicates the degradation of nanocomposite.

Conclusion

First and foremost, the synthesis of the PAN/SS nanocomposite by the non-conventional emulsion method avoids the use of added emulsifier thereby ruling out any chances of removal of surfactants or residual emulsifiers from the nanocomposite which indeed is a very complicated, costly and time consuming process. Secondly, the developed novel flame retardant nanocomposite PAN/SS exhibits significant properties thereby inducing hydrophilic character to the hydrophobic PAN matrix and most importantly, shows good biodegradability. Further, the potential nanocomposite is characterized by IR, XRD, TEM and SEM. The TGA exhibits higher thermal stability and Cone calorimeter gives better flame retardancy than homopolymer PAN. To conclude, as the synthesized nanocomposite is eco-friendly it may open the door for use as a good commercial fire retardants.

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