Effect of Montmorillonite Clay on the Properties of PAN Filaments

Mohd Rahim[#1], Moksh Prasad[#2],Samarth Gandhi[#3],Roli Purwar[#4]

Discipline of Polymer Science & Chemical Technology, Department of Applied Chemistry, Delhi Technological University, Shahbad Daulatpur, Main Bawana Road, Delhi-110042, India

Abstract

In this study, Polyacrylonitrile (PAN)/ clay nano composite filaments were prepared by adding Montmorillonite clay using wet spinning technique with clay content ranging from 0-5%w/w. The rheological properties of PAN/clay dope solutions were evaluated. The dope solution showed shear thinning behaviour. The viscosity of the dope solutions was found to be 184 Centipoise. The fineness obtained ranges from 400 dtex to 5933 dtexfor undrawn and 256 dtex to 1122 dtex for drawn filaments. The thermal properties of the filaments were evaluated through DSC and TGA. The crystallinity of filaments is evaluated using X Ray Diffraction. The incorporation of clay resulted in enhancement of thermal degradation property of the filaments. The filaments were dyed with cationic dye Rhodamine B using exhaust dyeing method. The addition of clay enhanced the dye uptake properties of filaments.

Keywords - *Polyacrylonitrile, nano composite, Montmorillonite Clay, Rhodamine B.*

I. INTRODUCTION

Polyacrylonitrile (PAN) is a semi crystalline synthetics organic polymer resin, with the linear formula $(C_3H_3N)_n$. It is an all-rounder polymer utilized in a large variety of products including hollow fibres for reverse osmosis, oxidized PAN fibres, ultra-filtration membranes, and fibres for textiles. But PAN fibres also have some drawbacks, for example low thermal stability[1], a susceptibility to degradation upon exposure to heat, and poor dyeability in pure PAN. They don't offer protection against gleaming heat; hence, attempts are under way to modify them. PAN ignites effortlessly and burns intensely. Poisonous hydrogen cyanide will be liberated accompanied by fumes, which seriously limits its wider uses. Protective clothing in case thermal dangers[2] are required for many situations in industry, in public undertakings, and in military uses.Pure PAN is not dyeable[3]. Dyeing in PAN is made possible by copolymerization with reactive groups[4]. Usually it is made up of 89–90% acrylonitrile, 4–10% non-ionic co-monomer such vinyl acetate and about 1% ionic co-monomer carrying a sulphonate (SO_3H) or organosulphate (OSO_3H) group[5].

Acrylic fibres are utilized mainly in the home textile and decoration sectors in inclusion to the garment sector, especially for knitted merchandise. These areas of uses are becoming increasingly crucial in terms of fire-proofing regulations. It is prone to degradation well below its melting point, because it undergoes particular exothermic reactions. Thermal properties of polymers are improved by incorporating flame retardants and heat stabilizers. Researches have shown that clay in general is an excellent flame retardant[6].

In this project we have made an attempt to investigate the effect of montmorillonite clay on thermal and dyeability properties of PAN fibres synthesized using wet spinning technique for more industrial applications. The purpose of selecting Montmorillonite Clay is that it is naturally occurring and can enhance the thermal properties as well as dyeability properties. Montmorillonite Clay is a monoclinic translucent hydrophilic clay belonging to the smectite group. Its chemical formula is $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$. It is highly thermally stable on its own. Also, it is identified as having substantial octahedral charge because of its cation swapping capacity which is due to isomorphous exchange of Mg for Al in the middle alumina plane. This property will help improve dyeability properties of PAN fibres because of the presence of ionic charges which interact with anions/cations of dyes[7].

II. MATERIALS AND METHODS

A. Materials Used

N,N'-Dimethylformamide (DMF) was procured from Merck. Polyacrylonitrile (PAN) Powder having molecular weight of 1,50,000 was obtained from Otto Chemie Pvt. Ltd. Montmorillonite Clay (MMT) having surface area ranging from 220-270 m^2/g was acquired from Sisco Research Laboratory (SRL).Sanolin Rhodamine B 02 dye was bought from Clariant Chemicals India.

B. Preparation of Dope Solution and evaluation of its Rheological Properties

Dimethylformamide was poured into 4 beakers (180 ml each). 0%, 1%, 3%, 5% w/w Montmorillonite clay was added w.r.t Polyacrylonitrile. The solutions with clay were stirred followed by sonication for 30 min. 20g PAN powder was weighed and separated 4 times.

Dope solutions were prepared by stirring it continuously at 70°C and it was kept covered for at least 2 days for stabilization. Brookfield (DV-II) pro viscometer was used to study the rheological properties of the dope solution.

C. Wet Spinning Extrusion of PAN Fibre

Dope solution was preheated up to 25°C and poured into the dope tank of a wet spinning machine (Tex Lab India) having 0.5 mm as spinneret hole size. The Dope solution went through the machine and passed through the spinneret to reach coagulation bath which consisted of water and DMF in the ratio of 9:1 and had a temperature of 0°C. After that, it was drawn to other washing baths and winded by multiple rollers. When the filaments were slightly dried out and heat set to stabilize their structure[8].

D. Test Performed

1) Fineness Measurement:

Fineness of fibres was calculated by weighing 1m fibre sample and applying unitary method[9].Formula used:*Fineness = Weight of 1m Fibre in g × 10000.*

2) Exhaust Dyeing:

A 50-ppm Rhodamine B (Fig. 1) dye solution was prepared by keepingfibre: water ratio being 1:100.The fibre was immersed in the dye solution at 90°C for 30 min with constant stirring for 30 min. After dyeing was finished, each dyed specimen was left to cool to ambient temperature and after which the fibre was removed and water was added to balance out the volume. A sample of this solution was diluted 20 times and tested under UV Visible spectrophotometer.

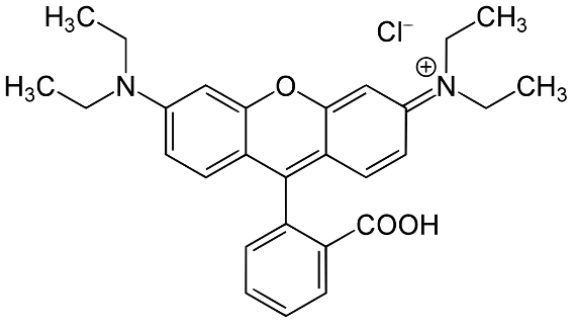

Figure 1: Structure of Rhodamine B

3) Rhodamine B and Standard Curve:

Dye adsorption was characterised by using Agilent Cary 300 UV-Vis Spectrophotometer. A standard curve of Rhodamine B Dye was prepared by using solutions of concentrations 1, 2, 3 and 4ppm and the equation for the curve was found to be y = 0.2421x in accordance with Beer-Lambert Law. λ_{max} was found to be 546nm.

4) Tests for Thermal properties:

Thermal gravimetric analysis was performed on the Perkin Elmer TGA 4000 System, 100-240V/50-60Hz with temperature ranging from 30°C-900°C, heating rate 10°C/min and sample weight 5 mg under N_2 atmosphere. Differential Scanning Calorimetry was performed on the Perkin Elmer DSC 4000 System, 100-240V/50-60Hz with temperature ranging from 0°C-290°C, heating rate 10°C/min and sample weight 5 mg under N_2 atmosphere.

5) XRD:

The X-ray scans were performed with a Siemens type-F, X-ray diffractometer (Bruker D S Advanced, Germany). The X-ray source was Cu Kα radiation (40 kV, 30 mA and λ=1.5 Å). The samples were mounted on aluminium frames and scanned from 5 to 70° (2θ).

6) UV Visible Spectroscopy:

10ml Rhodamine B dye solutions were prepared of concentrations 1, 2, 3 and 4 ppm. These samples were used to find the Absorbance Concentration Characteristics and a standard curve of dye was plotted. UV Visible Spectroscopy was performed on dye solutions to know the peak wavelength and absorbance. Agilent Cary 300 UV-Vis was used for testing with sample volume of 3ml and distilled water as reference over a range of 200-800nm.

III.RESULTS AND DISCUSSION

A. Fineness

The fineness of undrawn fibres was found to be 1400, 2000, 5933 and 400 dtex for 0%, 1%, 3% and 5% clay concentration respectively. Similarly, the fineness of fibres after drawing was found to be 833, 667, 1122 and 256 dtex for 0%, 1%, 3% and 5% clay concentration respectively. Hence, fibres became after drawing.

B. Rheology

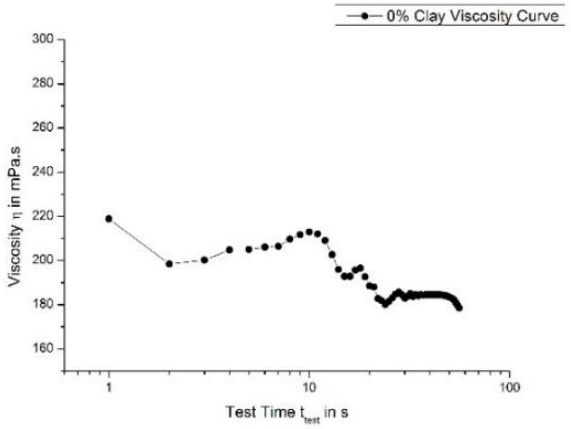

Figure 2: Viscosity curve of PAN with 0% Clay

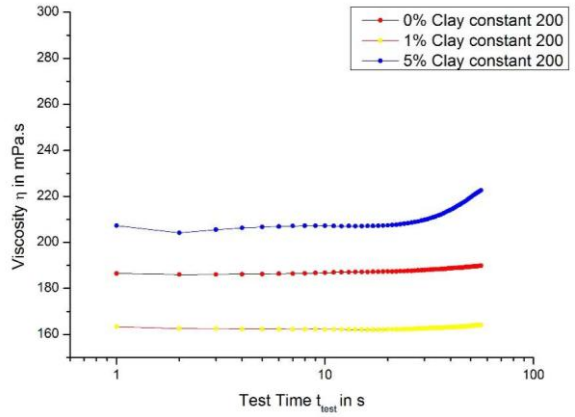

Figure 3: Viscosity-Time Characteristics of Samples

It has been observed that PAN solution without clay is stable and has a viscosity of 184 mPa.s. At room temperature and constant shear rate, as the concentration of MMT clay increases the viscosity decreases up to a certain level, after which increase in concentration increases the viscosity of PAN compared to neat PAN solution. The reason for this trend is increase in space between the polymer chains after addition of clay.

C. TGA

Two degradation peaks were observed, one at 290°C and one at 460°C. The weight % of filaments at 290°C was found to be 88.95%, 90.38%, 90.40% and 90.47% for 0%, 1%, 3% and 5% clay concentration. The weight % of filaments at 460°C was found to be 63.72%, 63.73%, 66.53% and 66.91% for 0%, 1%, 3% and 5% clay concentration. Similarly, the weight % of filaments at 600°C was found to be 55.96%, 56.53%, 58.13% and 59.29% for 0%, 1%, 3% and 5% clay concentration.

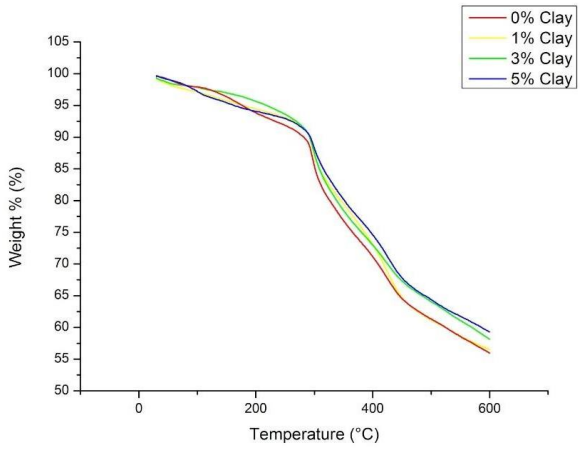

Figure4: TGA curve of PAN Fibres

As the concentration of clay is increased, the weight loss percentage is reduced with up to 1.52% at 290°C, 3.18% at 460°C and 3.34% at 600°C for 5% clay concentration. Hence, the fibres became thermally more stable after addition of Montmorillonite Clay.

D. DSC

Sample	Glass Transition Temperature (T_g) (°C)	Degradation Temperature (°C)
0% Clay	78.98	254.87
3% Clay	70.96	266.03
5% Clay	69.35	268.72

Table 1: DSC data of Samples

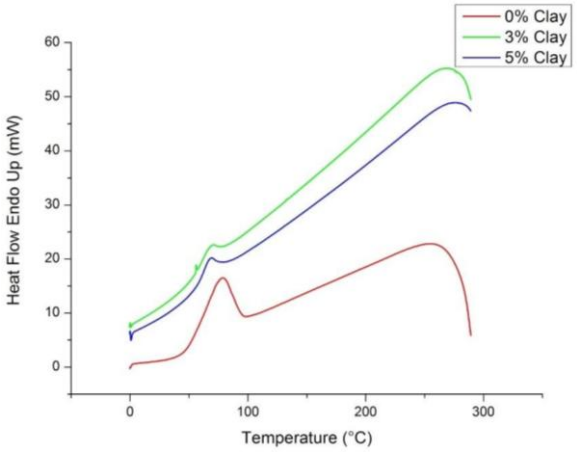

Figure 5: DSC curve of PAN Fibres

A peak was observed between 70-80°C which can be either due glass transition or vaporization of water. As observed from Figure 4, the weight loss percentage is less than 3% even at 100°C so this peak in the DSC curve is due to glass transition. As we are increasing the concentration of the montmorillonite clay, the glass transition temperature (T_g) decreases which results in increased stiffness at lower temperature[10]. It has been observed that increase in concentration of clay content shifts degradation temperature forwards means late degradation of our fibres which concludes that the fibres became thermally more stable.

E. XRD

Table 2: XRD data of Undrawn Fibres

Sample	Peak (°)	Crystalline Peak Area	Total Area	Crystallinity (%)
Undrawn 0% Clay	16.8	326.4	480.34	67.95
Undrawn 1% Clay	16.84	343.08	496.68	69.07
Undrawn 3% Clay	17.12	343.1	478.44	71.71
Undrawn 5% Clay	17.16	386.68	520.06	74.35

XRD is used to investigate the crystalline structure and molecular orientation of fiber materials. XRD of PAN shows that preferred orientations of the crystalline regions are aligned along the fiber axis. Increase in degree of orientation is observed as the draw ratio increases. Thus, clay can be responsible for increase of draw ratios of PAN fiber and tenacity [11].

Table 3: XRD Data of Drawn Fibres

Sample	Peak (°)	Crystalline Peak Area	Total Area	Crystallinity (%)
Drawn 0% Clay	17.12	330.10	444.04	74.34
Drawn 1% Clay	17.04	366.60	478.02	76.69
Drawn 3% Clay	17.16	391.02	494.12	79.13
Drawn 5% Clay	16.88	417.08	486.44	85.74

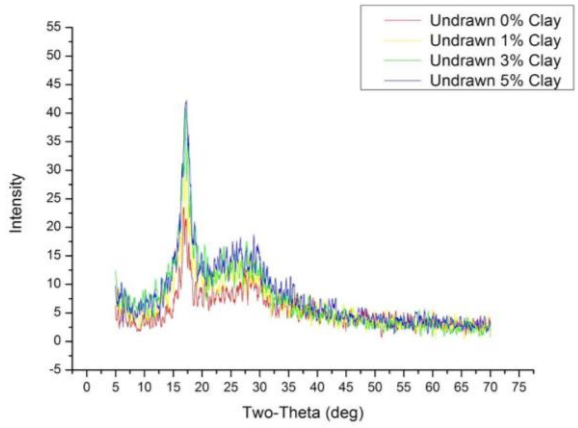

Figure 6: XRD curves of Undrawn Fibres

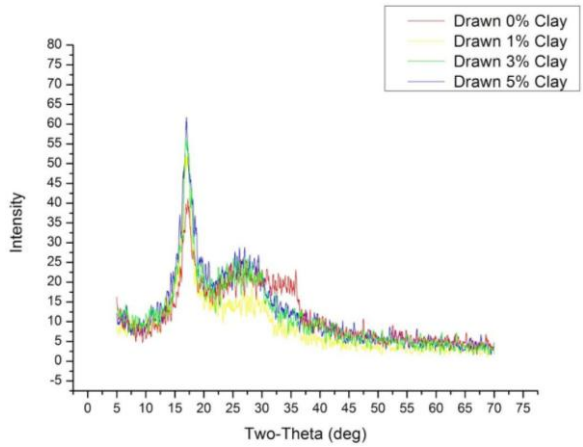

Figure 7: XRD curves of Drawn Fibres

The positioning between clay platelets is considered to suggest the degree of exfoliation/intercalation of clay platelets inside a polymer complex using X-ray crystallography[12].Fibreswithincreasedconcentration of Montmorillonite clay showed higher crystallinity. This is due to the fact that clay acts as a nucleating agent and creates numerous crystallization sites which increase the rate of crystallization[13]. Also, drawn fibres shows higher crystallinity as compared to undrawn fibres (Table 3).

Table 4: Crystallinity change after Drawing

Sample	% Increase in Crystallinity after Drawing
0% Clay	09.40
1% Clay	11.03
3% Clay	10.35
5% Clay	15.31

F. UV Visible Spectroscopy

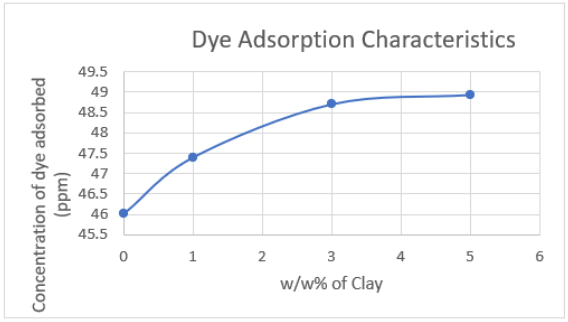

Figure 8: Dye AdsorptionCharacteristics

With regards to chemical composition, dyeability is ruled by the existence, firstly by presence of polar groups which link with water molecules and permit substrate swelling and, secondly by the presence of functional groups which attract dye molecules[14].It is observed that by adding MMT in PAN fibre the dye adsorption of fibre increases. At 5% clay concentration, 6.37% more dye is adsorbed by the fibre. The curve is steeper initially flattens with increases in clay concentration with only 0.47% increase between 3% and 5% clay concentration compared to 3.02% increase between neat samples and 1% clay concentration.

IV.CONCLUSION

In conclusion, effect of Montmorillonite Clay on thermal and dyeability properties of PAN Filaments was studied. Wet spun fibers were coagulated in water bath. The inward diffusion of water causes fiber solidification which leads to an irregular fiber shape and smaller PAN crystal size[15]. It is observed that an increase in clay content shifts degradation temperature forwards means late degradation of our fibres which concludes that our fibres become thermally more stable. Fibres with

increased concentration of Montmorillonite clay show higher crystallinity. This is due to the reason that MMT clay acts as a nucleating agent and accelerates the crystallinity with increase in clay content. Drawn fibres shows higher crystallinity as compared to undrawn fibres. It is observed that by adding MMT in PAN fibre the dye adsorption of fibre increases. There are two major possibilities for increase of dye uptake. First, there is ion exchange between clay and the dye or second, there is a surface negative charge on the clay platelets which attracts the cations in the dye.

REFERENCES

[1] P. Bajaj, A. K. Agrawal, A. Dhand, N. Kasturia, and Hansraj, "*Flame retardation of acrylic fibers: An overview,*" J. Macromol. Sci. - Polym. Rev., vol. 40, no. 4, pp. 309–337, 2000, doi: 10.1081/MC-100102400.

[2] A. Handermann and Z. Corporation, "*Zoltek Whitepaper Oxidized Polyacrylonitrile Fiber Properties , Products and Applications By Alan Handermann , Zoltek Corporation,"* no. September, 2017.

[3] S. Rosenbaum, "*Dyeing of polyacrylonitrile fibers: I. Rates of diffusion with malachite green and diffusion model,"* J. Appl. Polym. *Sci.*, vol. 7, no. 4, pp. 1225–1242, 1963, doi: 10.1002/app.1963.070070404.

[4] W. Virginia, "*Dyeing of Polyacrylonitrile Fibers doubtedh data . Tlii* ," pp. 52–60.

[5] R. Paul and E. Genescà, "*The use of enzymatic techniques in the finishing of technical textiles,*" *Adv. Dye. Finish. Tech. Text.*, pp. 177–198, 2013, doi: 10.1533/9780857097613.2.177.

[6] J. M. Lopez-Cuesta, *Flame Retardancy Properties of Clay-Polymer Nanocomposites*. Elsevier Inc., 2017.

[7] M. Shahidi, S. Wiener, J. Ghoranneviss, "Surface modification methods for improving the chemical modification of fabrics," *Eco-Friendly Text. Dye. Finish.*, 2013.

[8] *Manufactured Fibre Technology*. 1997.

[9] P. K. Hari, "*Types and properties of fibres and yarns used in weaving,"* Woven Text. Princ. Technol. Appl., pp. 3–34, 2012, doi: 10.1533/9780857095589.1.3.

[10] K. E. Smith, S. S. Parks, M. A. Hyjek, S. E. Downey, and K. Gall, "*The effect of the glass transition temperature on the toughness of photopolymerizable (meth)acrylate networks under physiological conditions,*" *Polymer (Guildf).*, vol. 50, no. 21, pp. 5112–5123, 2009, doi: 10.1016/j.polymer.2009.08.040.

[11] Yan-Xiang Wang, Cheng-Guo Wang, Yu-Jun Bai and Zhu Bo, "*Effect of the Drawing Process on the Wet Spinning of Polyacrylonitrile Fibers in a System of Dimethyl Sulfoxide and Water*"J. Appl. Polym. Sci., vol. 104, no. 2, pp. 1026-1037, 2017, doi: 10.1002/app.24793.

[12] I. Özen, *"Enhanced dyeability of poly(ethylene terephthalate)/organoclay nanocomposite filaments,*" *Color. Technol.*, vol. 131, no. 6, pp. 464–473, 2015, doi: 10.1111/cote.12179.

[13] N. Fanegas, M. A. Gómez, C. Marco, I. Jiménez, and G. Ellis, "*Influence of a nucleating agent on the crystallization behaviour of isotactic polypropylene and elastomer blends*," *Polymer (Guildf).*, vol. 48, no. 18, pp. 5324–5331, 2007, doi: 10.1016/j.polymer.2007.07.004.

[14] Z. Yang, H. Peng, W. Wang, and T. Liu, "*Crystallization behavior of poly(ε-caprolactone)/layered double hydroxide nanocomposites," J. Appl. Polym. Sci.*, vol. 116, no. 5, pp. 2658–2667, 2010, doi: 10.1002/app.

[15] J. Hao, F. An, Y. Yu, P. Zhou, Y. Liu, and C. Lu, *"Effect of coagulation conditions on solvent diffusions and the structures and tensile properties of solution spun polyacrylonitrile fibers,*" *J. Appl. Polym. Sci.*, vol. 134, no. 5, pp. 1–9, 2017, doi: 10.1002/app.44390.