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Dope dyeing of polyacrylonitrile filaments with Ratanjot

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Dope dyeing of polyacrylonitrile (PAN) filaments with Ratanjot extract as a colouring additive has been studied. The rheological properties of dope solution are investigated through Brookfield viscometer. The dope solution shows both shear thinning and shear thickening behavior. Different concentrations of Ratanjot extract ranging from 0.25 % to 1% (w/w) are incorporated in PAN dope solution (20% w/v) and filaments are spun on laboratory wet spinning machine using dimethyl formamide as solvent and water as non-solvent. The filaments are characterized for their mechanical, morphological, fastness and antibacterial properties. The colour obtained on acrylic filament is found to be magenta. With the increase in Ratanjot extract concentration the tensile strength of filament increases. The scanning electron micrographs of Ratanjot incorporated filament shows hollow structure with circular cross-section. The dope dyed filament shows excellent wash fastness properties and very little antibacterial activity.

Keywords: Antibacterial property, Acrylic filament, Dope dyeing, Ratanjot, Rheology

1 Introduction

Conventionally, the dyeing of polyacrylonitrile filaments is carried out with synthetic cationic dyes using exhaust method. The co-monomers containing sulphate, sulphonate or carboxylate groups facilitate the dyeing of polyacrylonitrile filament with cationic dyes. Growing consciousness about organic value of ecofriendly products has generated renewed interest of consumers towards use of textiles dyed with ecofriendly natural dyes. Natural dyes are mostly used to dye natural filaments, like cotton, wool, silk, jute, etc. But very little information is available on dyeing of synthetic filament like acrylic with natural dyes. Natural dyes have similar structure to that of disperse dye and therefore it is possible to dye nylon, polyester and acrylic filament at high temperature[1] or by using carrier [2]. Recently, polyacrylonitrile filaments are dyed with natural dyes such as indigo[3], berberine[4], curcumin and madder[5]. It has been shown that lecuo vat acid molecule of indigo dye exhausts well on polyacrylonitrile filament in the 5.5-6 *p*H range[3]. Berberin (yellow dye), natural origin cationic dyes, has been applied on acrylic filaments through exhaust method[4]. Shishtawayet *et al.*[5] have dyed modified acrylic filament with curcumina and madder natural dyes using exhaust method along with mordant and ferrous sulphate.

Ratanjot (*Arnebia nobilis*) a natural source of red dye has traditionally been used as a food colourant, in cosmetic formulations and pharmaceutical preparations. Ratanjot gives appealing red colour to food stuff, oils and fats. The major constituents of Ratanjot extracts are naphthoquinones. Plant dyes rich in naphthoquinones such as lawsone from henna, juglone from walnut and lapachol from alkanet are reported to exhibit antibacterial and antifungal activities[6, 7]. The root bark of *A. nobilis* is reported to have several biological properties such as antibacterial, antifungal, antiviral, antitumor, antioxidant, radical scavenging and antithrombotic activity[8, 9]. Bairagi and Gulrajani[10] have reported that the Ratanjot extract behaves as disperse dye and have affinity for hydrophobic filaments such as nylon and polyester. Anjali *et al.*[11] have dyed various textile substrates such as cotton, wool, silk, nylon and acrylic with hexane extract of Ratanjot using exhaust dyeing method. The dyed polyester shows pink colour, nylon shows blue and all other substrate acquire purple colour under similar dyeing conditions. Recent study of Anjali *et al.*[12] shows that the naphthoquinone colourants of *A. nobilis* can be used to impart antibacterial properties to textiles. The dye and its components showed excellent antibacterial activity against both *S. aureus* and *E. coli.* Among the fabrics dyed with 5% shade of crude dye and alkannin

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β, β-dimethylacrylate, wool, silk and acrylic show 100% activity against both microbes.

Dyeing with natural dyes has some limitations, such as they are less permanent, more difficult to apply, have less wash fastness and require the use of mordant. Apart from that, natural dyes require huge amount of water for dyeing by exhaust method. The dope dyeing method has a potential to minimize the consumption of mordant, water and associated environmental problems. Since the colouring agent is entrapped between the polymer chains during the spinning process, dope dyed filaments show very good wash and light fastness.

In the present study, dope dyeing of polyacrylonitrile filament is carried out using Ratanjot extract as colouring additive. The rheological properties of dope solution are investigated. The coloured filaments are spun on wet spinning machine and characterized for mechanical, morphological, fastness and antibacterial properties.

2 Materials and Methods

2.1 Materials

Polyacrylonitrile powder was kindly supplied by Techno Orbital Ltd, Kanpur, India (molecular weight 170KDa). Reagent grade dimethyl formamide (DMF) (Fischer Scientific) and chloroform (Merck) were used. Root of Ratanjot (*Arnebia nobilis*) was procured from local market of Delhi. Distilled water was used as nonsolvent. Ratanjot extract was obtained by soaking the fine chopped roots of Ratanjot into chloroform for 48 h. After that, the solution was filtered and distilled to obtain solid Ratanjot extract.

2.2 Methods

2.2.1 Preparation of Dope Solution and Evaluation of its Rheological Properties

Dope solution was prepared by dissolving polyacrylonitrile polymer (20% w/v) in DMF. The Ratanjot extract was added in dope solution under constant magnetic stirring at 40-45°C. Different dope solutions were prepared by varying the amount of Ratanjot extract ranging from 0.25 % to 1% (w/w). Dope solution without Ratanjot extract was considered as blank.

The rheological properties of dope solution were evaluated through Brookfield (DV-II) pro viscometer.

2.2.2 Wet Spinning of Polyacrylonitrile Filaments

Filament spinning was carried out on a laboratory scale wet spinning machine (Tex Lab India) having spinneret hole size of 0.5 mm. The dope solution temperature was kept at 80°C. Water was used as non-solvent and the temperature of coagulation bath was kept at 10°C. The dope solution was passed through the spinnerette which was immersed in coagulation bath having mixture of water and DMF (90:10). After keeping in coagulation bath the filaments were drawn and washed in a subsequent bath. The jet stretch ratio was kept 1 and the draw ratio was kept 1.8. After wet spinning, filaments were drawn to its maximum draw ratio (4 - 5) and heat set on laboratory drawing machine to stabilize its structure.

2.2.3 Test Methods

Mechanical Testing

The mechanical properties of the filaments were determined by universal testing machine (Instron 3369) using ASTM D 2101 with crosshead speed of 6 mm/min and gauge length of 75 mm.

Colour Measurement

The colourimetric values of filaments were obtained on Gretag Macbeth colour-eye 7000 A spectrophotometer using CIE lab software with 10° observer.

Scanning Electron Microscopy

Structural morphology of filaments was studied under scanning electron microscope (SEM) (Model: S3700N HITACHI). For cross-sectional structure, samples were cut with sharp blade. Samples are sputter coated by a thin layer of ultrafine gold for 30 s.

Fastness Testing

The wash fastness of the dyed samples was measured in Laundrometer as per the ISO 105-C06:1994 specifications.

Assessment of Antibacterial Activity of Dope Dyed Filaments

Staphylococcus aureus (NCIMB-17) and *Escherichia coli* (NCIMB-1) used in this study were obtained from culture collection of Department of Bio-Chemical Engineering and Bio-Technology, IIT Delhi India. Luria Broth (Himedia) was used to maintain the liquid culture and agar agar was used to maintain the solid culture on the sterile petri dish. The antibacterial activity of dope dyed filament (1% w/w Ratanjot) was evaluated using AATCC 100 method. Filament samples (dyed and undyed) weighing 0.1 g each was placed in 100 mL conical flask containing 20 mL Luria broth solution. Twenty microletre of the test organism with the count of 10^6 CFU/mL was then inoculated. The flasks were incubated at 37°C for 24 h.

Serial dilutions of the liquid were made in sterilized water. Dilution of 10^{-4}, 10^{-5}, and 10^{-6} were used for colony counting. The diluted liquid (20 μL) was spread on an agar plate and the plates were incubated at 30°C for 24 h. After incubation, the bacterial colonies were counted. The antibacterial activity was calculated using following equation.

$$\text{Antibacterial activity (\%)} = (A-B)/A \times 100$$

where A is the number of colonies in the control sample; and B, the number of colonies in the dope dyed filament sample.

3 Results and Discussion

Dope dyeing of polyacrylonitrile filament is carried out using Ratanjot extract as colouring additive. The rheological properties of Ratanjot incorporated dope solution are first investigated. The coloured filaments are spun on wet spinning machine and characterized.

3.1 Rheological Properties

The rheological properties of the dope solution are measured out using Brookfield viscometer. Rheology is the study of the deformation and flow of matter. Viscosity has crucial role in setting up the process parameters for filament spinning. Viscosity of the dope solution depends upon concentration of polymer, temperature and shear rate. The polymer concentration (20% w/v) and Ratanjot concentration (1% w/w) have been taken for this study. This was the maximum concentration of polymer which we were able to handle in laboratory wet spinning machine. The study on the effect of temperature on viscosity at constant shear rate of 5 s^{-1} shows that viscosity of dope solution decreases with increase in temperature. The viscosity of dope solution was 3000 centipoise at 40°C which reduced to 1500 centipoise at 80°C. As the temperature increases, the time of interaction between neighbouring molecules of the polymer solution decreases because of the increase in velocities of individual molecules. The intermolecular force appears to decrease and so does the bulk viscosity. In the polymer solution the cohesive forces between the molecules predominate the molecular momentum transfer between the molecules. When the polymer solution is heated the cohesive forces between the molecules reduce thus the forces of attraction between them reduce, which eventually reduces the viscosity of the liquids[13]. Based on this study we have kept 80°C as dope solution temperature in wet spinning machine.

The effect of shear rate on viscosity of the dope at constant temperature of 80°C is also studied and it is observed that with the increase in shear rate from 1 s^{-1} to 5 s^{-1}, the viscosity of the dope solution decreases from 2500 centipoise to 1500 centipoise. With further increase in shear rate, the viscosity of the dope solution increases. This shows that the dope solution first indicates shear thinning phenomenon up to 5 s^{-1} shear rate and above this shear rate, the shear thickening behaviour is observed.

3.2 Mechanical Properties

The mechanical properties of dyed and undyed wet spun filaments have been evaluated with universal tensile testing machine. The results are summarized in Table 1. The tenacity of undyed filament is 0.76 cN/tex. As the concentration of Ratanjot extract increases the tenacity of dope dyed filaments increases. The tenacity of filament with 1% Ratanjot concentration is found to be 3.35 cN/tex. Incorporation of Ratanjot extract enhances the filament tenacity fivefold. This may be due to the fact that Ratanjot being an organic moiety non soluble in water, immediately phase separated in water/DMF, which may promote the coagulation process of dyed filaments in water/DMF mixture. However, the tenacity of commercial available polyacrylonitrile filaments is in the range of 35-90 cN/tex, which is much higher as compared to Ratanjot dyed filaments.[14]

3.3 Morphological Properti*es*

The morphological properties of undyed and dope dyed filaments (1% Ratanjot) were characterized by scanning electron microscopy techniques. The longitudinal and cross-sectional structures of the filaments were analyzed. The SEM micrographs are shown in Fig. 1. The longitudinal view shows the smooth surface of the dyed and undyed filaments [Figs 1 (a) & (b)]. Figures 1 (c) and (d) show the cross-section of undyed and dope dyed filaments. It is observed that pure polyacrylonitrile filament shows porous and circular cross-section. The Ratanjot incorporated polyacrylonitrile filament shows hollow, semi-solid and circular structure. This indicates that the incorporation of Ratanjot modified the coagulation process[9,15,]. It may be due to high solubility of Ratanjot in the dope solution and non solubility in water. Formation of more solid structure as compared to undyed filament on incorporation of Ratanjot further supports the enhancement of tensile strength.

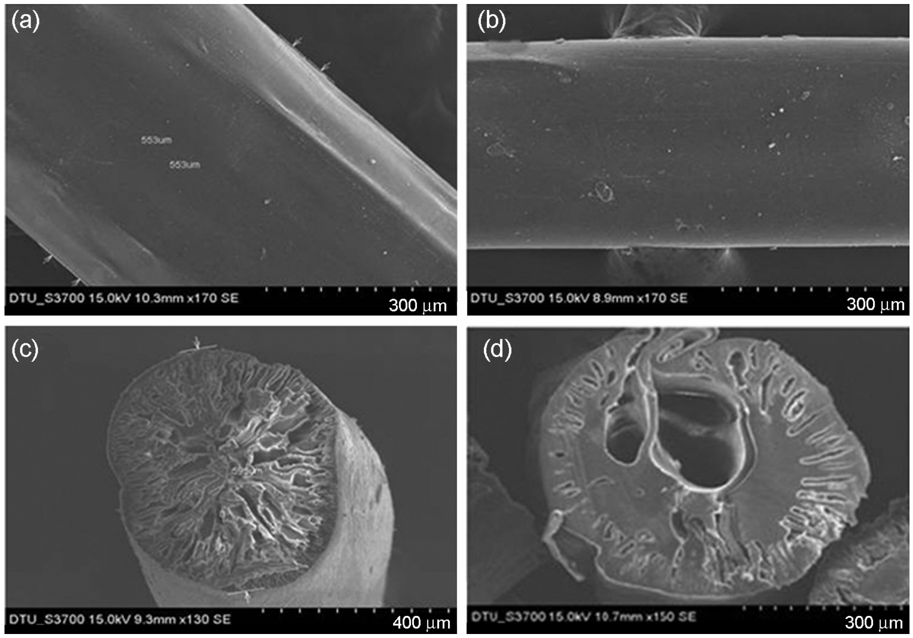

Fig. 1—SEM micrographs of undyed and dope dyed polyacrylonitrile filament (a) longitudinal view undyed, (b) longitudinal view of dope dyed, (c) cross-sectional view undyed, and (d) cross sectional view dope dyed

Table 1— Mechanical, colourimetric and wash fastness properties of dope dyed polyacrylonitrile filament

[Wash fastness 4/5-5]

Ratanjot, %	Mechanical properties			Colorimetric values		
	Tex	Tenacity, cN/tex	Elongation - at-break, %	L	a*	b*
Parent fibre	5.1	0.76 (0.21)	10	90.38	-0.03	11.21
0.25	2.4	0.71 (0.46)	10	38.34	3.38	-2.675
0.50	2.7	0.78 (0.32)	8	37.03	1.53	-4.19
0.75	2.9	1.04 (0.76)	8	26.76	1.95	-3.48
1.0	3.2	3.35 (0.44)	7	22.45	2.08	-3.01

Values in parentheses show coefficient of variation (CV %).
L*, a* and b* values are represented in 3-D geometry. With each axis representing the significance of each value.

3.4 Colour Value

Gretag Mcbeth colour eye 7000A was used to compare the colour values of the dope dyed polyacrylonitrile filaments with Ratanjot. The filaments samples were pasted onto a strip of paper with a definite thickness width so that the paper through the sample is not visible. The width was chosen on the basis of the aperture of the colour eye 7000. Visually, the dope dyed filament shows magenta colour (mixture of red and blue). The colourimetric data of undyed and dope dyed acrylonitrile filament is shown in Table 1. The L* value shows that the lightness of the dyed samples decreases with the increase in concentration of Ratanjot extract in dope solution. The lightness of the sample is determined by the amount of light that the sample reflects. The undyed sample reflects most of the light (L*=90), as a result of which its lightness value is high. The sample containing 1% Ratanjot extract is the darkest out of all the samples having lowest L* (22) value. The undyed filament sample shows the zero a* value and positive b* value showing yellowish shade of the undyed filament. All the dope dyed filament samples show positive a* values corresponding to red and negative b* values corresponding to blue colour respectively. Therefore, the colour of Ratanjot dyed sample is mixture of blue and red. Anjali *et al*[11] have dyed acrylic fabric with Ratanjot extract using exhaust method. The colour obtained on the filament was found purple (mixture of blue and red).

3.5 Fastness Properties

The wash fastness rating of dope dyed filament is shown in Table 1. All the samples have shown excellent wash fastness with the rating 4-5 to 5. The good ratings of wash fastness is due the fact that the Ratanjot root powder is insoluble in water and it

Table 2—Antibacterial activity of dope dyed polyacrylonitrile filaments

Ratanjot %	CFU/mL × 10^5		Antibacterial activity, %	
	S .aureus	*E. coli*	*S.aureus*	*E. coli*
0	2.5	6.6	-	-
1	1.8	5	28	24

behaves like a pigment. High solubility of Ratanjot in dope solution gives uniform distribution of pigment in the filament. Similar results were obtained by Anjali *et al.*[11] when acrylic fabric was dyed with Ratanjot extract.

3.6 Antimicrobial Properties

The antimicrobial activity of dope dyed polyacrylonitrile filament (1% Ratanjot w/w) was evaluated by AATCC 100 method, using *S. aureus* and *E. coli* bacteria. The results are shown in Table 2. The dope dyed filament shows very little antibacterial activity against tested bacteria. This may be due to the fact that, we have conducted test with small quantity of filament (0.1g), which may not contain sufficient amount of Ratanjot to inhibit the growth of bacteria. Anjali *et al.*[12] have evaluated antibacterial activity of acrylic fabric dyed with Ratanjot. The fabric (5% shade) shows very good antibacterial activity. To make dope dyed antibacterial polyacrylonitrile filament, we need to increase the concentration of Ratanjot in dope solution.

4 Conclusion

The rheological properties of the dope solution are studied at constant temperature of 80°C and at constant shear rate of $5s^{-1}$. As the temperature increases the viscosity of dope solution decreases. The dope solution first shows shear thinning phenomenon up to 5 s^{-1} shear rate and above this shear rate, the shear thickening behaviour is observed. As concentration of Ratanjot increases, the tenacity of the dope dyed filament increases. The dope dyed filaments show smooth structure in longitudinal view and nearly circular, hollow, semi-solid structure in cross-section structure. The filament shows excellent wash fastness properties with purple colour. The dope dyed filament shows little antibacterial activity, which can be further enhanced by incorporating higher concentration of Ratanjot in dope solution.

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