Dyeable Polypropylene Fibers via Nanotechnology

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ABSTRACT: Polypropylene (PP) nanocomposites with three different clay loadings were prepared by solution mixing technique. The solution-mixed nanocomposites were extruded to fibers using a single screw extruder. The PP nanocomposite fibers obtained were uniformly dyed with three distinct disperse dyes at different levels of shade. The enhanced dyeability of PP nanocomposite fibers was characterized by spectrophotometric measure- ments. Satisfactory wash, light and crock fastness results were also achieved. Mechanical properties and degree of crystallinity of nanocomposite fibers with different clay loadings were also investigated. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 706–711, 2007

Key words: nanocomposite; polypropylene; montmorillon- ite; dyeability

INTRODUCTION

Polypropylene (PP) is a versatile and widely used synthetic polymer. Because of the low cost, high strength, high toughness, and resistance to chemi- cals, PP fibers find a broad spectrum of use in the industrial and home furnishing sectors. However, they do not enjoy comparable popularity in the apparel sector of the textile industry, one of the main reasons being lack of dyeability. The reasons for its inability to be colored by conventional dyeing techniques used for other synthetic fibers are its high crystallinity, non-polar nature, and lack of func- tional group to hold dye molecules.[1] Most of the commercially available PP fibers are colored by mass pigmentation.[2] Though the process produces deep and stable colors and is economical for long run pro- ductions, it suffers due to the limited number of shades available and it is not applicable in textile dyeing and printing operations. Several approaches, including modification of the fiber, use of new colo- rants and use of dye receptors in the unmodified fiber, have been tried to improve dyeability but prac- tically no lasting success has been achieved.[1–7]

Polymer Layered Silicate (PLS) nanocomposites exhibit outstanding improvement in material proper- ties as compared to neat and conventional micro/ macro-composites. These enhancements in properties include reinforced mechanical properties, better ther- mal resistance, reduced gas permeability, improved solvent resistance, and enhanced ionic conductivity, etc.[8] Montmorillonite, a clay mineral, is the most widely used filler for preparing PLS nanocomposites. Exchanging the inter-laminar cations with organic cations can alter surface chemistry of montmorillon- ite clays. It has been observed that by incorporating modified montmorillonite in the polymer matrix improved dyeability can be achieved.[9] In this research, we investigated the dyeability of PP fibers filled with nano-sized organically modified montmo- rillonite clay particles.

EXPERIMENTAL

Materials

Isotactic PP pellets were supplied by Philips Sumika Polypropylene Company, Houston, Texas. Nano- clay, Cloisite-15A was supplied by Southern Clay Products, Texas. It is a natural montmorillonite modified with, dimethyl dihydrogenated tallow qua- ternary ammonium ion, a quaternary ammonium salt. Xylene (used to dissolve PP) was obtained from Pharmco Products, Connecticut. In order to enhance the interaction between nano-particles and polymer a titanium coupling agent was used. Ken-react LICA 12, chemically, Titanium IV neoalkoxy tris (diiso- octyl) phosphate-O, was obtained from Kenrich Petrochemicals, New Jersey.

Preparation of nanocomposites

Nanocomposite fibers were prepared by solution mixing followed by melt spinning. Various clay con- centrations were added, namely 2%, 4%, and 6% on the weight of polymer. Since the clay particles as obtained existed as micrometer range assemblies,[9] ball milling and ultrasonication were used to reduce

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the particle size and the particle size distribution. Ball milling of supplied clay was done in a Thumbler's tumbler using 3 mm diameter glass balls in a 5.5 inches in length and 2.5 inches in diameter glass bottle. The weight ratio of balls-to-clay particles in the tumbler media was 100:2.5 and the milling was done for 24 h. The milled particles were then dispersed into xylene followed by ultrasonication for one hour to disaggregate the clumps. The ultrasonication was done using 750-watt ultrasonic homogenizer obtained from Cole Parmer Instrument Company. The ultrasonication parameters were 90% amplitude, 8-second pulse on and 4-second pulse off. To the mixture (xylene +clay), 0.4 wt % (on the weight of the polymer) of titanate coupling agent was added and ultrasonication was continued for another hour. PP pellets were then added to the mixture. The system was heated on a hot plate and the temperature was gradually raised to the boiling point of xylene (140°C) to get PP pellets dissolved. Further ultrasonication was done to homogenize the mixture. The remaining xylene was allowed to evaporate at its boiling point until the nanocomposite solidified. Subsequently, the nanocomposite was mechanically crumbled and dried in an oven at 70°C to remove any traces of xylene. The melt spinning of solution mixed nanocomposites was carried out in a single screw Sterling Extruder. The fiber extrusion was done using a 30-spinneret fiber die and following extrusion parameters:

1. Temperature of different zones: 163 °C (Hopper), 185°C, 185°C, 191°C, 191°C, and 191°C (Spinneret)
2. Screw speed: 8 rpm
3. Material throughput: 4.8 g/min
4. Spinneret diameter: 0.5 mm
5. Winding speed: 31 m/min
6. Draw ratio: 4
7. Drawing temperature: 100°C.

Disperse dyeing of nanocomposite fibers

The prepared nanocomposite fibers and neat PP fibers were disperse-dyed at 2%, 4%, and 6% depth of shade. For comparison, commercially available polyester fibers (Dacron®) were also dyed under the same conditions as those for nanocomposite fibers. Dyeing was performed using Ahiba Polymat laboratory dyeing machine. Three types and three shades of disperse dyes were used: C.I. Disperse Yellow 42, C.I. Disperse Red 65, and C.I. Disperse Blue 56. All the disperse dyes were obtained from Ciba Specialty Chemicals. The dyeing method and dye recipe for disperse dyeing was the same as conventionally used for dyeing of polyester fibers. The liquor to material ratio was 20 : 1. The dye powder was added to

the dye bath according to percentage depth of shade required. The quantities of other auxiliaries were 1 g/L of 80% acetic acid, 2 g/L of dispersing agent (Irgasol DAM, Ciba), and 2 g/L of leveling agent (TRYFAC 5553 (610-K), Cognis). Dyeing was performed by raising the temperature of dye bath from 40°C to 130°C at the rate of 1.5°C/min, holding at this temperature for 60 min and then cooling the bath to 60°C at the rate of 3°C/min. The dyed samples were then rinsed in distilled water for 5 min followed by reduction clearing. Reduction clearing was done at 60–70°C for 10 min in a solution of 6 ml/L, 30% caustic soda, and 4 g/L hydrosulphite at a liquor ratio of 40 : 1. The samples were then rinsed in cold running water followed by neutralizing with acetic acid and once again rinsed for 5 min in cold running water.

Spectrophotometric measurements

Color arises in the dyed material as the result of selective absorption of radiation within the visible region of the electromagnetic spectrum. It has been recognized that a relationship exists between the hue of sample observed and the wavelength regions over which the absorption of light is strong, although the color is actually determined by the spectral energy distribution of the radiation reflected from a colored opaque sample.

Reflectance value of the dyed samples including nanocomposite fibers and controls were obtained using Macbeth Color Eye 2040 spectrophotometer. In order to standardize the measurements and to eliminate the effect of black background on the reflectance values, a white background was used. The depth of shade of the tested samples was assessed by determining the K/S value using the Kubelka-Munk equation. The K/S values were calculated using reflectance at maximum absorption wavelength (λ_{max}) and were used as color yields for dyed PP composites. The Kubelka-Munk equation is given as:

$$K/S = \frac{(1-R)^2}{2R} \qquad (1)$$

where K is the absorption coefficient, S is the scattering coefficient, R is the reflectance at maximum absorption wavelength.

Colorfastness

To evaluate the color fastness of dyed fibers to laundering, AATCC Test Method 61, Test No. 2A was performed. This is an accelerated test designed for evaluating the color fastness of textiles that are expected to withstand frequent laundering. The color
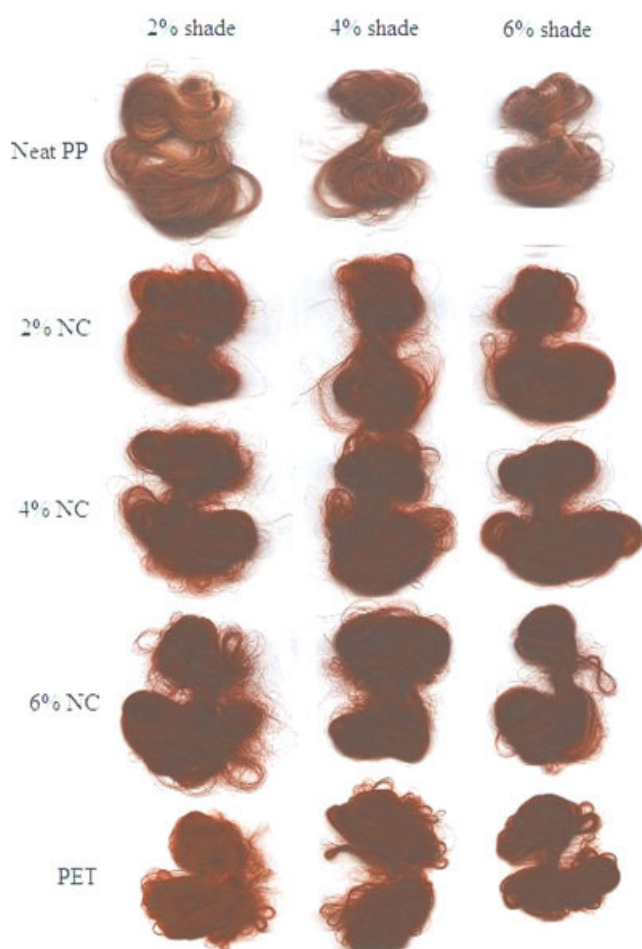
Figure 1 Scanned images of PP fibers (nanoclay modified and unmodified) and PET fiber samples dyed with C. I. Disperse Red 65 (nanoclay add-ons are shown in % NC, and dye concentrations are shown in % shade). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

loss resulting from the detergent solution and abrasive action of five typical home laundering are closely approximated by one 45-min test. Specimens are laundered under regulated conditions of temperature, alkalinity, bleaching and abrasive action.

When textiles are exposed to light, the light tends to destroy the coloring matter and results in ''fading'' of textiles. With the action of light, dyed materials change color – usually becoming paler and duller. The AATCC Test Method 16A is intended for determining the resistance of colored materials to the action of an artificial light source representative of natural daylight D_{65}. Principally, a specimen and a blue reference are exposed to artificial light under prescribed conditions. The color fastness to light is assessed by comparing the change in color of an exposed portion of specimen to the control masked portion of the test specimen or unexposed original material using AATCC Gray Scale for color change. Light fastness classification is accomplished by eval-

uation of specimens versus a simultaneously exposed series of AATCC Blue Wool Light-Fastness Standards.

To determine the action of rubbing on color of dyed nanocomposites, AATCC Test Method 8 was used to evaluate the amount of color transferred from the surface of PP nanocomposites fibers onto other substrates when rubbed against the substrate. Both dry and wet crock fastness were determined. All the colorfastness tests were performed on the neat PP and PP nanocomposites (2%, 4%, and 6% nanoclay) fibers dyed at 4% shade on the weight of fiber.

Differential scanning calorimetery

The DSC analysis was carried out using DSC Q1000 from TA Instruments (New Castle, DE). Nitrogen gas was used to provide an inert atmosphere. The sample pan and reference pan were heated to 220°C at the rate of 10°C/min.
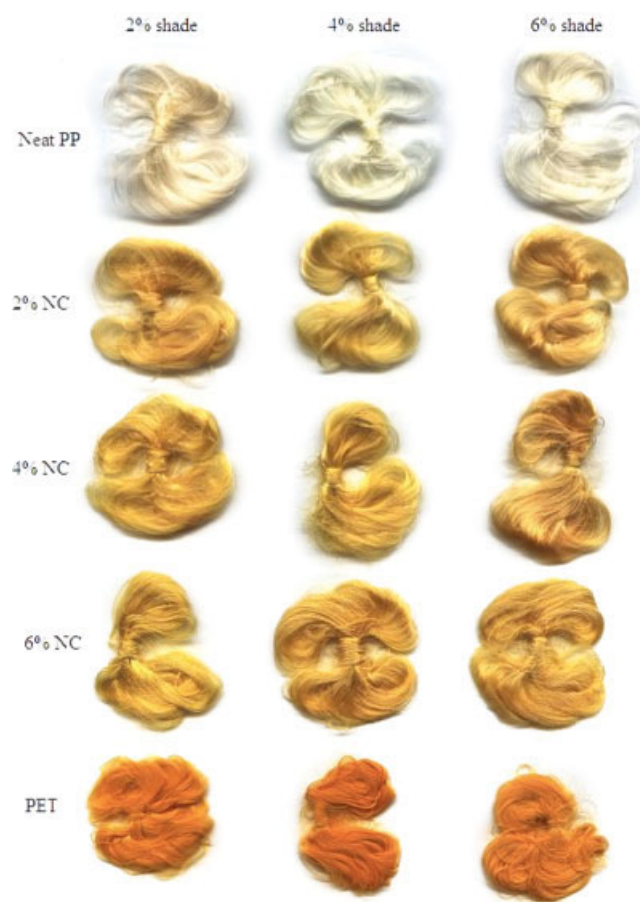

Figure 2 Scanned images of PP fibers (nanoclay modified and unmodified) and PET fiber samples dyed with C. I. Disperse Yellow 42 (nanoclay add-ons are shown in % NC, and dye concentrations are shown in % shade). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3 Scanned images of PP fibers (nanoclay modified and unmodified) and PET fiber samples dyed with C. I. Disperse Blue 56 (nanoclay add-ons are shown in % NC, and dye concentrations are shown in % shade). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
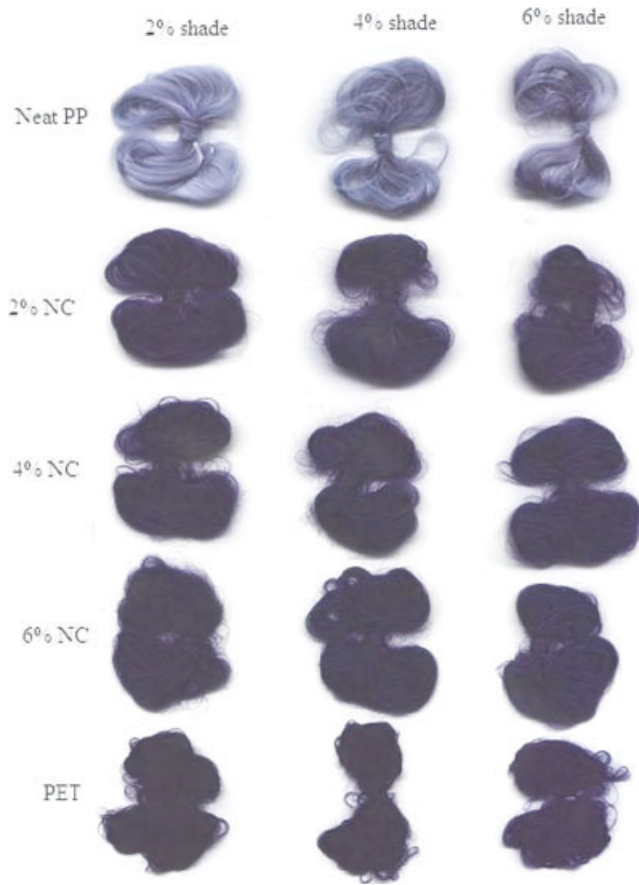
Tensile testing

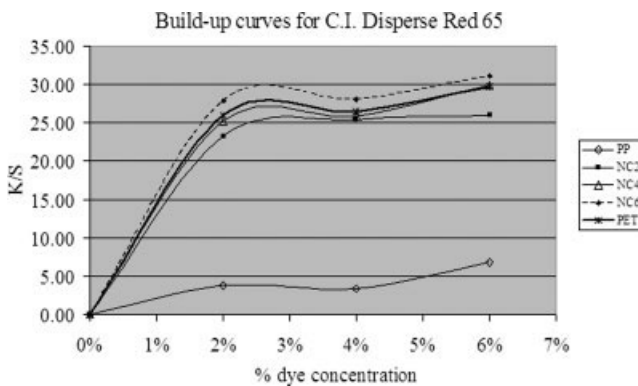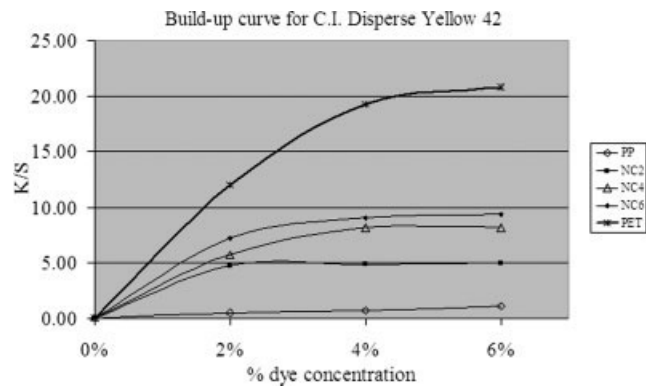The tensile testing of prepared nanocomposite fibers and neat PP fibers were done according to ASTM

Figure 5 Color build-up curves of C. I. Disperse Yellow 42 on PP fibers (nanoclay modified and unmodified) and PET fiber samples (K/S represents color build ups, and NC x represents nanoclay add-ons in x%).

Standard Test Method D 3822. Constant Rate of Extension (CRE) type tensile testing machine (Instron Tensile Tester) was used and the force-elongation curves were recorded at specified rate of extension (240% of initial specimen length/min). The test was performed for 20 specimens each of neat PP and nanocomposite fibers.

RESULTS

Figures 1–3 show the scanned images of the dyed samples. The build-up curves of disperse dyes are shown in Figures 4–6. The build-up curves are measured as K/S values with respect to increase in dye concentration in the dye bath. From the scanned images and build-up curves it is evident that a positive correlation exists between the clay add-on and the dye absorbed by the nanocomposites. However, with the increase in depth of the shade, i.e., by

Figure 4 Color build-up curves of C. I. Disperse Red 65 on PP fibers (nanoclay modified and unmodified) and PET fiber samples (K/S represents color build ups, and NC x represents nanoclay add-ons in x%).
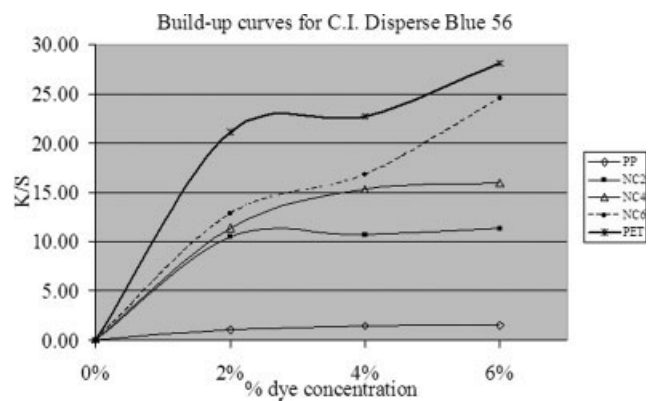

Figure 6 Color build-up curves of C. I. Disperse Blue 56 on PP fibers (nanoclay modified and unmodified) and PET fiber samples (K/S represents color build ups, and NC x represents nanoclay add-ons in x%).

TABLE I
GSR and Staining Rate of C.I. Disperse Red 65

Sample	GSR	Staining on multifiber strip
		1	2	3	4	5	6	7	8
PP	4/5	5	5	5	3/4	4/5	5	5	5
2% NC	3/4	5	4	4/5	4	5	4/5	5	5
4% NC	4	5	4	4	4	4/5	4	5	5
6% NC	4	5	4	4	3/4	5	5	4	5

TABLE III
GSR and Staining Rate of C.I. Disperse Blue 56

Sample	GSR	Staining on multifiber strip
		1	2	3	4	5	6	7	8
PP	4/5	4	5	4	4/5	5	5	5	4/5
2% NC	4/5	4	5	4/5	3/4	4	5	5	5
4% NC	4	3/4	5	4/5	4	4/5	5	5	5
6% NC	4/5	4	5	4	3/4	4	4/5	5	4/5

increasing the dye concentration in the dye bath, the build-up curves tend to flatten. This represents the saturation of dye sites available in PP nanocomposites.

Another observation here is the effect of dye structure on the color yield of the nanocomposite fibers. For dyeing of the fibers with Disperse Red 65, a monoazo type of dye, values of K/S for the nanocomposite fibers were as high as for the polyester fibers. For Disperse Yellow 42, a nitrodiphenylamine type of dye, there was an improvement in the K/S values for nanocomposite fibers as compared to the neat PP fibers but the color yields for nanocomposite were not comparable to those for polyester fibers. While with Disperse Blue 56, E-type anthraquinone dyes, moderate improvement in the K/S values for nanocomposite fibers was observed; at higher depth of shade i.e. 6% for higher clay loading (6% on the weight of polymer) the values of K/S close to those for polyester fibers can be obtained. Thus, by properly selecting the dye structure higher color yield can be obtained for nanocomposite fibers.

Wash fastness of dye can be divided into two broad categories: (i) the fading or shade change of the sample on washing and (ii) the staining on adjacent fabrics. The results listed in Tables I–III show the gray scale rating (GSR) of change in color of dyed fibers after the test along with the stain rating on multifiber strip. The washed disperse dyed samples showed little or no change in color. Also there were no significant stains on multifiber strips except on the polyester.

Light fastness rating of disperse-dyes on neat PP and nanocomposite fibers is shown in Table IV. Disperse dyes conferred excellent light fastness results on PP nanocomposite fibers. After exposure to light,

no noticeable fading of disperse dyed PP nanocomposite fibers was observed.

Crock fastness results for the dyed neat PP and nanocomposite fibers are shown in Table V. Disperse-dyed nanocomposite fibers exhibited satisfactory crock fastness. The dry and wet crock fastness ratings observed did not differ considerably.

DSC results (Fig. 7) showed that the nanocomposite fibers are 2–4% less crystalline than the PP fibers. It can be argued that the improved dyeability of nanocomposite fibers is because of the decreased crystallinity. However, a 2–4% decrease in crystallinity in the crystallinity of nanocomposite fibers cannot be the only reason for their high color yields. The improved dyeability of nanocomposite fibers can be attributed to the addition of suitable additives like clay into the PP matrix because the dye-saturation values obtained were higher than those justifiably associated with purely solution mechanisms.[1] The clay-polypropylene system can be viewed as an assembly of a large number of fine, elongated fibrils of the additive embedded in the polymer matrix. The interphase area thus created represents high-energy surfaces and the dye molecule, in addition to forming the usual solid solution in the additive phase, would be prone to preferentially concentrate on these interphase high-energy surfaces.[1] The number of fibrils and the interphase between polymer and clay would increase as the compatibility of clay with PP and the relative amount of clay in the PP polymer increase. Thus, the color yield of nanocomposite fibers increases with increase in clay concentration. In addition, certain secondary forces such as van der Waals forces may be active between the disperse

TABLE II
GSR and Staining Rate of C.I. Disperse Yellow 42

Sample	GSR	Staining on multifiber strip
		1	2	3	4	5	6	7	8
PP	4	5	5	4	4	5	5	4/5	4
2% NC	4	5	5	4/5	4/5	5	5	5	4
4% NC	4/5	5	4/5	4	3/4	4/5	5	4	5
6% NC	4/5	5	5	4	4	4	5	4	4

TABLE IV
Light Fastness Rating of the Disperse Dyes

Sample	Dyes
	C.I Disperse Red 65	C.I. Disperse Yellow 42	C.I. Disperse Blue 56
PP	>6	5/6	6
2% NC	6	>6	6
4% NC	>6	>6	>6
6% NC	6	>6	>6

TABLE V
Crock Fastness Rating of the Disperse Dyes

| | Dyes | | | | | |
| | C.I. Disperse Red 65 | | C.I. Disperse Yellow 42 | | C.I. Disperse Blue 56 | |
Sample	Wet	Dry	Wet	Dry	Wet	Dry
PP	4	4/5	5	5	3/4	4
2% NC	4	4	5	5	4	4
4% NC	3/4	4	4/5	5	4	4
6% NC	3/4	4	4/5	4/5	3	3/4

TABLE VI
Mechanical Properties of Neat Polypropylene and Nanocomposite Fibers

| | Modulus (gf/den) | | Breaking stress (gf/den) | | Breaking strain (%) | |
Sample	Avg.	SD	Avg.	SD	Avg.	SD
Neat PP	9.89	1.79	2.72	0.11	109.2	12.23
2% NC	12.17	1.97	3.01	0.27	94.67	16.51
4% NC	12.69	2.08	3.28	0.35	90.68	21.38
6% NC	13.25	2.36	3.26	0.29	88.41	20.23

dye molecules and the clay particles, and the disperse dye molecules and the PP.

Table VI shows the mechanical properties of neat PP and nanocomposite fibers. The increase in modulus and breaking stress of the nanocomposite fibers as compared to neat PP fibers were up to 34% and 20% respectively. However nanocomposite fibers showed up to 19% reduction in the breaking elongation as compared to the neat PP fibers. The enhancement in mechanical properties is in accordance with the previous studies.[10,11] It is inferred that the reinforcement of polymer chains with clay platelets causes the increase in the modulus and the breaking stress of the fibers. However the reinforcement of PP with clay particles also causes restricted mobility of the polymer chains and leads to reduction in elongation-to-break of nanocomposite fibers. Another possible explanation for the decrease in elongation-to-break and improved modulus and breaking stress of nanocomposite fibers could be the increase in the

viscosity of extrudate with the increasing clay content and a concomitant increase in the orientation of extrudate.[12]

CONCLUSION

PP fibers could be made dyeable by incorporating nanoclay particles. As compared with neat PP fibers, improved and uniformly disperse-dyed nanocomposite fibers were observed. The dyed nanocomposite fibers exhibited satisfactory light, wash and crock color-fastness. Tensile testing of neat PP and nanocomposite fibers showed that the modification of PP with quaternary ammonium compounds exchanged clay increased the modulus and the strength of the resultant fibers. However, the nanocomposite fibers showed reduction in the breaking elongation as compared to the neat PP fibers.

Figure 7 DSC thermographs of PP fibers (nanoclay modified and unmodified) samples (NC *x* represents nanoclay add-ons in *x*%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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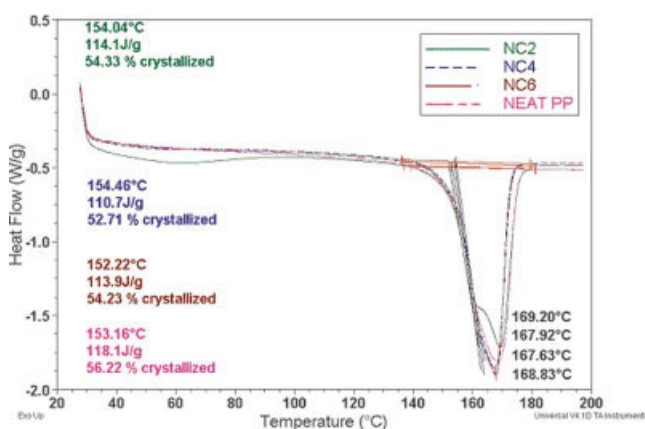12. Pal, S. K.; Gandhi, R. S.; Kothari, V. K. J Appl Polym Sci 1996, 61, 401.