

CHAPTER VII

EFFECT OF DRAW RATIO ON MECHANICAL AND DYE-ABILITY OF POLYPROPYLENE—ORGANOCLAY NANOCOMPOSITE FIBER

7.1 Abstract

Polypropylene is a thermoplastic polymer used in a variety of applications, including food packaging and textiles. However, polypropylene presents some drawback on dye-ability due to the non polar aliphatic structure and high crystallinity. In this work, dye-able polypropylene fibers were prepared by adding organoclay into the polymer to act as the dye sorption part. The organoclay was made of bentonite modified with a cationic surfactant—(Methyl di-[(partially hydrogenated) tallow carboxymethyl]-2-hydroxyethyl ammonium methylsulfate) — which functions as an active site for interacting with the dye molecules. In addition to that, due to its small size and larger surface area, the clay becomes a good sorbent. The Surlyn[®] ionomer is used as a compatibilizer between the organoclay and the PP. The result of dye uptake clearly shows that PP/organoclay nanocomposite fiber can absorb dye better than the unfilled fiber. Moreover, increasing the draw ratio causes the fiber to gain higher dye uptake due to a reduction of the cross section of the fiber. Higher mechanical properties were also obtained due to the increased crystallinity.

7.2 Introduction

The polypropylene (PP) is famous in the textile industry because of its outstanding physical, chemical, and mechanical properties. However, the fiber is not dye-able with existing classes of dyes because of the hydrocarbon nature and the lack of polar sites in the molecular structure. Although mass pigmentation is the most widely accepted method of coloration of the PP fiber, attempts have been made to make the fiber dye-able by chemical treatment; for example, through bromination of the fiber (1), blending with another polymer containing polar groups (2), reactive blending during melt extrusion (3), or by graft copolymerization of an appropriate monomer into the fiber. The recent method for producing dye-able polypropylene fiber is by adding nanoparticles (sodium bentonite) into the polymer to act as dye

sorption (4). The improvement of dye-ability by chemical reaction requires chemical reactivity in the polymer structure, which is not necessary through the use of nanoparticles. And because their small size gives the large surface area necessary for a good sorbent, nanoparticles can be used to improve the dye-ability in polypropylene. Preferences are given to nanoclay because of its common availability at good quality and low price. Moreover, induced nanoparticles can enhance the physical and thermal properties of polymer (4). In this paper, we use organo-modified clay to improve the dye-ability of polypropylene. Organo-modified clay was prepared by mixing sodium bentonite with cationic surfactant—(Methyl di-[(partially hydrogenated) tallow carboxymethyl]-2-hydroxyethyl ammonium methylsulfate) — which functions as an active site for interacting with the dye molecules. In this study, sodium ionomer was used as a compatibilizer because at high shear rate, for LDPE high content, the viscosity of PA6/LDPE blends with sodium ionomer is equal to PA6/LDPE blends with lithium ionomer. Only two samples, neat PP and organo-modified PP nanocomposite with compatibilizer, were studied with respect to the effect of high elongational strain rate (draw ratio) on thermal, mechanical properties and dye-ability of the fiber with various types of dye (i.e. acid dye, basic dye, and direct dye). No comparison between organo-modified clay PP nanocomposite with or without the compatibilizer were studied.

7.3 Experimental

7.3.1 Materials

The polypropylene (MFI 11 dg/min) was obtained from IRPC Co., Ltd. Thailand under the trade name polypropylene NK1126. Clay Commercial sodium activated bentonite Mac-Gel[®] (GRADE SAC), Na-BTN, with a cationic exchange capacity (CEC) of 50 meq/100 g clay, was supplied by Thai Nippon Co., Ltd. Thailand. Methyl di-[(partially hydrogenated) tallow carboxyethyl]-2-dihydroxyethyl ammonium methyl sulfate (DOEM) was received from Union Compound Co., Ltd. Sodium-neutralized ethylene-co-methacrylic acid, Surlyn[®] PC350 (4.5 MFI, 15.2 wt% methacrylic acid, 1.99 wt% sodium and ~40% neutralization level), was purchased from DuPont Co., Ltd. The acid dye was Lanaset Red 2B from Chiba Co.,

7.3.2 Equipment

7.3.2.1 *Thermogravimetric Analysis (TGA)*

The samples were analyzed by TGA using a Perkin-Elmer Pyris Diamond TG/DTA instrument under N₂ flow of 200 ml/min. The heating process was conducted from 30 to 900°C at a rate of 10°C/min.

7.3.2.2 *Differential Scanning Calorimeter (DSC)*

The crystallization and melting behaviors of the PP/organoclay nanocomposites were measured with a Perkin-Elmer DSC 7 analyzer. The heat flow and temperature of the instrument were calibrated with the standard material, indium. Nitrogen was consistently purged into the equipment during the scan to prevent the thermal degradation of the specimens. During the crystallization experiment, the specimens were first melted at 200°C, and then cooled to room temperature at 10°C/min rate. The specimens were subsequently heated at 10°C/min for the corresponding melting behavior investigations.

7.3.2.3 *Twin Screw Extruder*

The PP/organoclay nanocomposites were prepared by a Collin D-8017 T20 twin screw extruder with an L/D ratio of 30 and 25-mm-diameter. Operating temperatures were maintained at 80/160/180/190/200/210°C with a screw speed of 50 rpm. Composites were made in a 2-step process: first the sodium ionomer and organoclay were extruded together as a 50/50 master batch, then the PP, and an appropriate amount of the 50/50 master batch mix was extruded together in composition of PP 81 wt%, Na-EMAA6 wt% and organoclay 5 wt%.

7.3.2.4 *Centrifugal Ball Mill*

The dried sediments were ground by FRITSCH Peluerisette 6 Centrifugal Ball Mill with a rotational speed of 450 rpm in forward and reverse milling directions for 1 hr. The particle size of the powder was less than 44 μ m.

7.3.2.5 UV-Visible spectrophotometer (Shimadzu)

The dye uptake (g/g fiber) was determined by a UV-Visible spectrophotometer. The difference between the absorption of the initial and final dye solution was reported as the dye uptake value.

$$\text{Dye uptake} = \text{initial dye concentration} - \text{final dye concentration}$$

7.3.2.6 Melt spinning machine

Polypropylene-organoclay nanocomposite fiber was prepared by melt spinning machine. The as-spun filament was collected at a extruder speed of 1.68 m/min and drawn at 190°C. The fiber was drawn with different speeds 15.3, 26.5, 36.6, and 47.6 m/min.

Table 7.1 Draw ratio of fiber

Roller speed (rpm)	Roller speed (measure) (m/min)	Draw ratio*	Cross section of fiber(mm ²)
30	15.3	9.1	0.0132
50	26.5	15.7	0.0132
70	36.6	21.8	0.0095
100	47.6	28.3	0.00636

*Draw ratio = Roller speed/Extruded speed

(Extruder speed = 1.68 m/min)

7.3.2.7 Dyeing machine DAELIM Starlet model DL-6000

The 5 g. fibers were dyed with acid, basic, disperse, and direct dye 250 ml. Each sample was put in the dye pot and placed in a dyeing machine (DAELIM Starlet model DL-6000). The temperature was raised to 50°C for 30 minutes and then raised to 100°C. The temperature was then kept constant at 100°C for 60 min. and was then decreased to 50°C. The fiber was washed with water for 30 min at room temperature and wash with tap water for 1 min. The initial dye concentration is 0.1 g/L.

7.3.2.8 Universal Testing Machine

The polypropylene-organoclay nanocomposite fibers were tested mechanical properties with an Instron Universal Testing 4206 by follow ASTM D3822-01. The crosshead speed was 270 mm/min. The linear density of the polypropylene fibers ranged from 1.85×10^5 to 6.58×10^6 tex, depending on draw ratio from 15×10^3 to 47.6×10^3 . The gauge length was 20 mm. Each sample was tested 10 times.

7.3.2.9 X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) was used to observe the d-value of organoclay and to investigate the crystal structure of fiber nanocomposites. X-ray diffraction patterns were measured on a Rigaku Model Dmax 2002 diffractometer with Ni-filtered Cu K_{α} radiation operated at 40 kV and 30 mA. The powder samples were observed on the 2θ range of 1 to 40 degree with scan speed 2 degree/min and scan step 0.02 degree.

7.4 Results and discussion

7.4.1 Dispersion and distribution of organo-modified clay in PP matrix

Scanning Electron Microscope/Energy Dispersive using X-Ray analysis (SEM-EDX) was used to probe the dispersion and distribution of the organo-modified clay in the PP matrix. The addition of sodium ionomer in the PP matrix improves the dispersion and distribution of organoclay in the PP matrix, as shown in Figure 7.1. This is because organo-modified clay can disperse in polar part of the sodium ionomer, which sodium ionomer is able to disperse in the PP matrix.

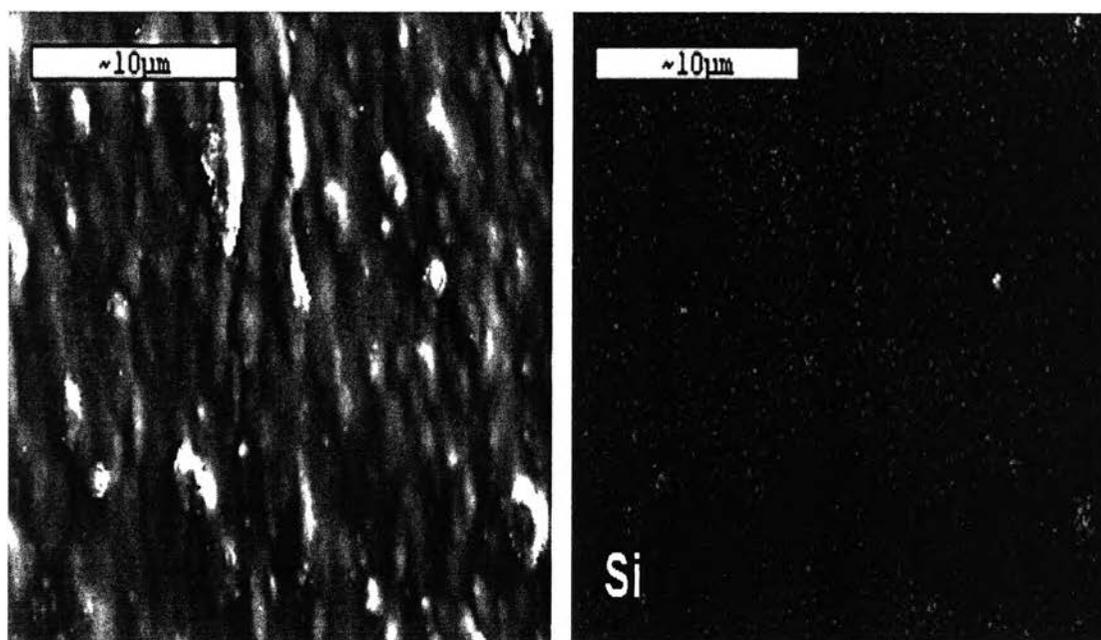


Figure 7.1 Morphology of 81%PP/6%Surlyn/5%organoclay A) SEM picture, B) Silica mapping.

7.4.2 Effect of organo-modified clay on PP crystallization

Figure 7.2 showed the XRD patterns of the crystal structure of organo-modified clay PP nanocomposites fibers at different draw ratio. The peak at 6.12° represented the organo-modified clay. The interlayer spacing for the fiber was 1.45 nm, which was calculated by the Bragg equation. It was shown that polypropylene can penetrate the organoclay layer. Moreover there is no change in the peak positions of polypropylene crystal, ($[\alpha 110]$, $[\alpha 040]$, $[\alpha 130]$, $[\alpha 111]$, and $[\alpha 060]$), so that adding organoclay in the PP matrix does not affect to the crystal structure of the PP. In line with the DSC data, the crystal size of the $[\alpha 040]$ plane of polypropylene crystal for organo-modified PP nanocomposite fibers increased with increasing the draw ratio and then decreased at draw ratio of 21.8 to 28.3.

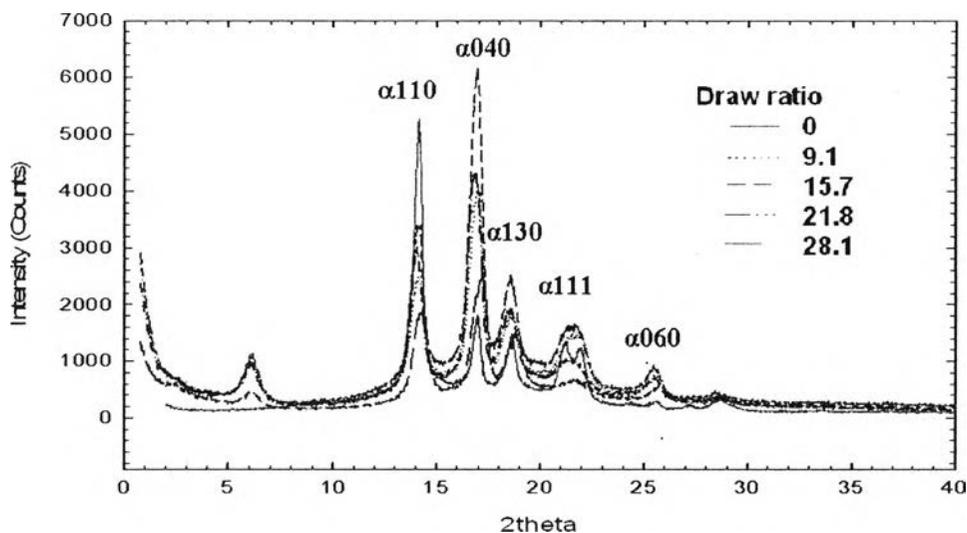


Figure 7.2 XRD of PP organo-modified clay nanocomposite fiber.

7.4.3 Melting and crystallization behavior

The melting and crystallization parameters determined from the DSC heating, and cooling scans of the pure PP and organo-modified PP nanocomposite fiber are presented in Tables 7.2, and 7.3 respectively. For neat PP fibers, increasing the draw ratio results in increasing T_m and crystallinity by 4 to 5 °C and 5 to 9 % respectively while the crystallization temperature almost unchanged. It should be noted that the change occurs clearly at 15.7 draw ratio, suggesting that the drawing force at this speed is strong enough to induce uniaxial orientation of the PP chains to align and pack in regular array, making bigger crystalline portion with bigger crystalline size.

For the organo-modified clay PP nanocomposite fibers, the orientation is also clear at the 15.7 draw ratio, which brings maximum crystallinity and melting temperature. Further drawing of the fibers at high speed results in a slight reduction of melting temperature and crystallinity. This suggests that within the fibers both components are well oriented in the draw direction at the 15.7 draw ratio. However, increasing the draw ratio may induce slippage of the polymer chain and the clay nanoplatelets. Besides the layered silicates occupy some spaces in the thin volume of the fiber, so both affect lead to an interrupting of the crystallization by obligating the crystal growth.

Table 7.2 Thermal properties of neat PP fiber

Drawing ratio	T _c onset (°C)	T _m onset (°C)	ΔH _m (J/g)	%Crystallinity	T _d (onset) (°C)	DTG
undrawn	118.43	156.49	69.37	33.19	430.80	455.41
9.1	117.70	153.96	59.06	33.21	425.20	445.84
15.7	118.92	157.47	72.12	38.72	430.60	454.32
21.8	117.08	158.38	77.91	41.88	427.00	452.83
28.3	118.65	158.38	78.59	42.25	427.50	453.92

Table 7.3 Thermal properties of organo-modified PP nanocomposite fiber

Drawing ratio	T _c onset (°C)	T _m onset (°C)	ΔH _m (J/g)	%Crystallinity	T _d (onset) (°C)	DTG
undrawn	118.12	156.47	59.60	32.04	437.90	458.10
9.1	118.29	156.40	59.82	32.16	435.80	456.00
15.7	118.92	157.47	70.52	37.21	436.50	457.40
21.8	117.37	156.81	67.78	36.44	437.20	457.40
28.3	118.10	156.32	68.55	36.85	435.10	457.10

7.4.4 Decomposition temperature

The decomposition temperature of neat PP and organo-modified clay PP nanocomposite fibers were investigated by TG-DTA. The decomposition temperatures, all found in neat PP and organo-modified clay PP nanocomposite fiber, at first increased with increasing drawing ratio and then reached the steady value. Introducing the organo-modified clay into the PP fiber causes the decomposition temperature to increase by 5–10°C and reaches the maximum decomposition temperature at high draw ratio; e.g. 15.7 draw ratio for neat PP fibers and 21.8 draw ratio for organo-modified clay PP nanocomposite fibers. Due to the heat transfer to the organoclay layer, the decomposition of the organo-modified clay PP nanocomposite fibers is more retarded by higher temperature than the neat PP fibers.

7.4.3 Mechanical Properties

The Young's modulus of PP fibers and organo-modified clay PP nanocomposite fibers at various draw ratios are shown in Figure 7.3. By increasing the draw ratio, Young's modulus tends to increase. In addition to that, the Young's modulus of organo-modified clay PP nanocomposite fiber is much higher than the neat PP. Looking at the DSC result, the crystallinity of organo-modified clay PP nanocomposite fibers at draw ratios of 21.8 and 28.3 are lower than neat PP. However, the Young's modulus of organo-modified clay PP nanocomposite fibers is higher than neat PP, suggesting that elongational force is attributed to the reinforcement of layer silicates. By adding the compatibilizer and the organoclay, the blend has a higher Young's modulus because the force can be transferred from the polymer matrix to the organoclay. In addition to that, the compatibilizer helps the organoclay to have good dispersion in the blend system, which allows force to dissipate (6).

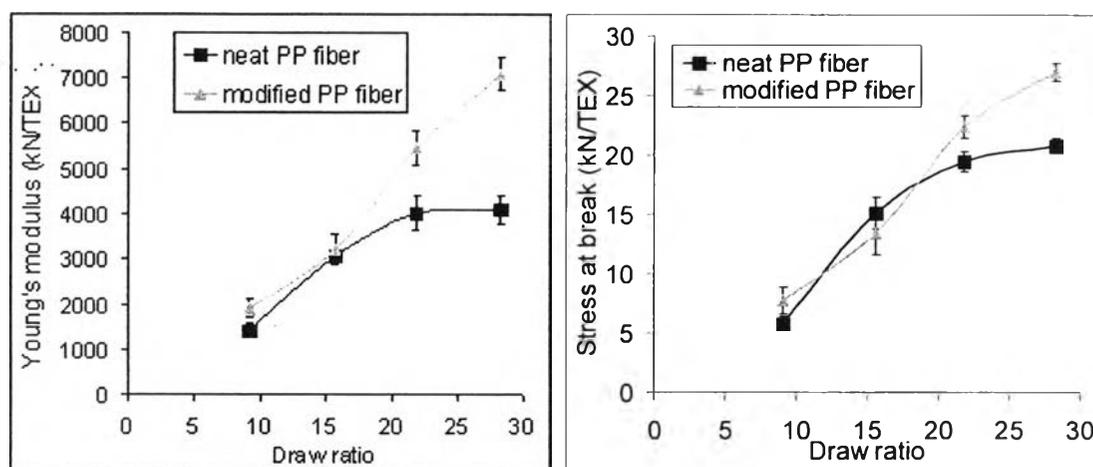


Figure 7.3 Young's modulus of materials. **Figure 7.4** Tensile strength of materials.

Figure 7.4 shows the tensile strength of neat PP and organo-modified clay PP nanocomposite fibers. The results of tensile strength are the same as for the Young's modulus; i.e. the organo-modified clay PP nanocomposite fibers have

higher tensile strength than the neat PP fibers because the force can be transferred from the polymer matrix to the organoclay.

Percent strain at break is shown in Figure 7.5. By increasing the draw ratio, the polymer has low % strain at break due to a higher draw ratio, which gives higher crystallinity. The chain movement relates to the crystalline and amorphous parts. If the polymer has more amorphous parts than crystalline parts, the percent strain at break is high because the chains of PP move easily. Comparing the neat PP with the organo-modified clay PP nanocomposite fibers, adding compatibilizer given organo-modified clay PP nanocomposite fiber has more % strain at break at high drawing ratio because the neat PP fibers have higher crystallinity than organo-modified clay PP nanocomposite fibers and the organoclay retards the crack propagation in the fibers.

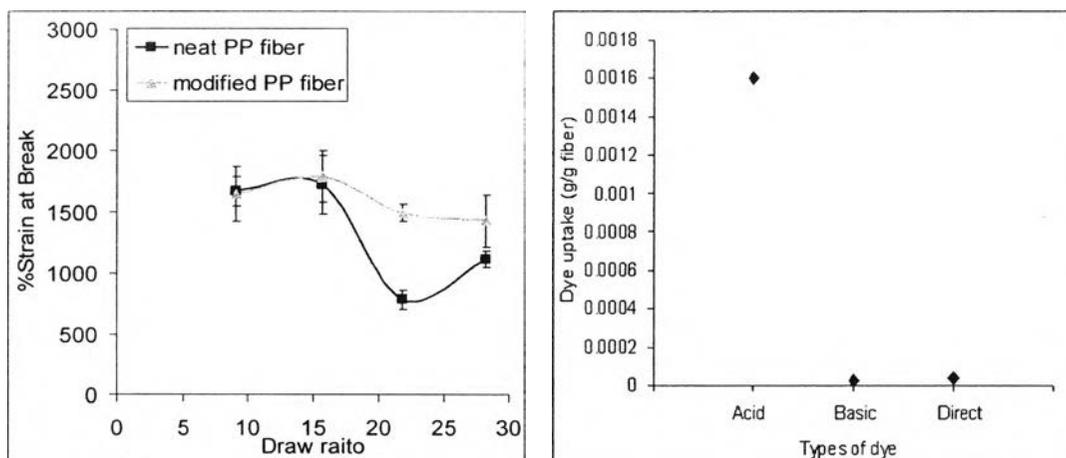


Figure 7.5 %Strain at break of materials. **Figure 7.6** Dye uptake of fiber.

7.3.4 Dye-ability

By introducing organoclay into the PP fiber, the dye absorption ability of the PP fiber becomes higher than the neat PP fiber (shown in Figure 7.6). The introduction of a functional group in the organoclay to the PP fiber allows the PP fiber to react with the acid dye site. In addition to that, the organoclay has very strong sorption ability due to its high surface areas, and its hydrophobic and ionic interactions with dyes. Among the acid, basic and direct dyes, the dye uptake value

of acid dye is the highest. Due to the positive charge characteristic in organoclay, there is more attractive force between the organoclay and acid dye (4). In contrast, the basic dye has the lowest dye uptake value; the dye is not attached to the fiber because it has the same charge as the organoclay, and so introduces the repulsion force. For direct dye, the dye uptake is very low because the direct dye adsorption occurring by H-bonding is small for these fibers.

The effect of draw ratio on organo-modified clay PP nanocomposite fibers is shown in Figure 7.7. It shows that the minimum dye uptake at a 15.7 draw ratio corresponded to the highest crystallinity. As mentioned before, increasing the draw ratio causes PP to be more crystallized because the dye dispersion in the crystalline structure is not as good as in the amorphous (7). For the organoclay-modified PP nanocomposite, by increasing the draw ratio, the dye adsorption is greater than the neat PP. Increasing the draw ratio has no effect on the cross section area of the fiber from a 9.1 to 15.7 draw ratio, but with further increasing the draw ratio a change in fiber cross section area is clear. The drawn fiber has a low cross section area with increasing draw ratio starting from the 21.7 draw ratio. This result suggests that a 15.7 draw ratio is the effective draw ratio to allow uniaxial drawing, thus causing increased melting temperature and crystallinity, which contribute to high mechanical properties and low dye uptake. The thinner cross section of fibers with increasing draw ratio makes more organoclay exposed to dye and also perturbs crystallization, so dye absorption increases.

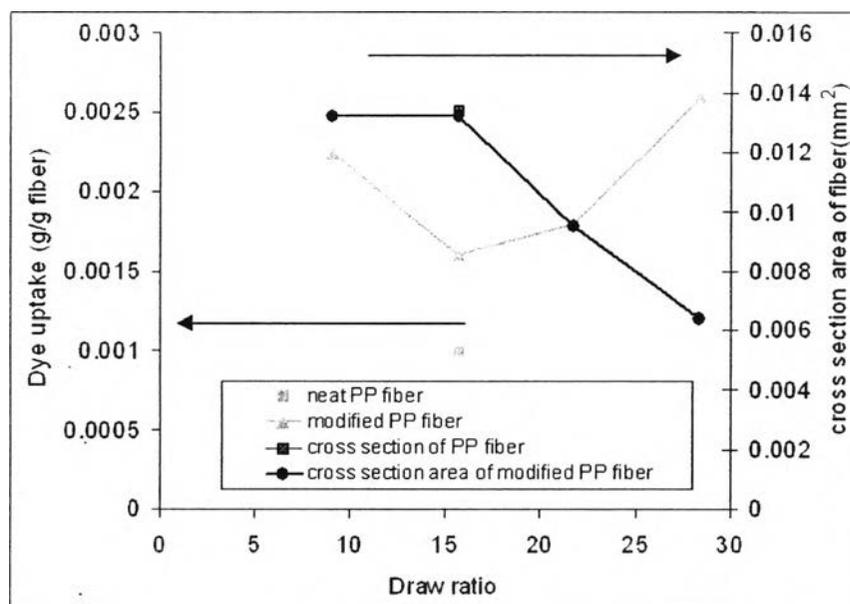


Figure 7.7 Dye uptake of acid dye PP and modified PP fibers.

7.5 Conclusions

The effect of draw ratio (9.1–28.3) on the thermal properties, mechanical properties and dye-ability of neat PP fibers and organo-modified PP nanocomposite fibers was studied. The addition of sodium ionomer into the organo-modified clay nanocomposite PP improved the dispersion and distribution of the organo-modified clay in the PP matrix. Additionally, by adding the organo-modified clay into the PP matrix, organo-modified clay does not affect the structure of the PP. Moreover the change in the draw ratio caused the improvement of crystallinity, the melting and the decomposition temperatures, and the mechanical properties and dye-ability of the fibers. However, increasing the draw ratio brought about lower strain at break. By introducing organo-modified clay into the PP fibers, it is clear that all properties were improved, except the crystallinity, which was decreased. Among the three dye types, the acid dyes showed the highest adsorption on neat PP and organo-modified PP nanocomposite fibers. At a draw ratio of 15.3, the organo-modified PP nanocomposite fibers had the lowest dye-ability due to highest level of crystallinity. The highest dye-ability was found at the draw ratio of 28.3 because, at this level, the cross section appears to be the thinnest. The thinner cross section of fibers allows

greater chance for the organoclay to be exposed to the dye and, hence, greater dye absorption was observed.

7.6. Acknowledgments

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7.7. References

1. Shah, C.D.; Jain, D.K. *Text Res Journal* **1983**, 53, 583
2. Dayiohlu, H. *J. Appl Polym Sci* **1992**, 46, 1539
3. Mizutani, Y.; Nago, S.; Kawamura, H. *J. Appl Polym Sci* **1997**, 63, 133
4. Qinguo, F.; Samuel, C. *NTC annual report* Nov **2004**
5. Ali, R.T.B.; Shoushtari, A.M.; Malek, R.M.A.; Abdous, M. *Dyes and pigments*. **2004**, 63, 95-100.
6. Liu, L.; Lim, H.T.; Anh, K.H.; Lee, S. *J. Applied Polym Sci* **2007**, 104, 4024
7. Yu, C.; Zhu, M.; Shong X.; Chen, Y. *J. Applied Polym Sci* **2001**, 82, 3172