Investigation of Tensile Properties and Dyeing Behavior of Various Polypropylene/Amine Modifier Blends

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ABSTRACT: Polypropylene is utilized in manifold applications due to its unique properties. However, its use has been limited in the textile industry because conventional dyestuffs have no affinity for this polymer. Amine modifiers, generally improve the dye-ability of polypropylene. Polyamide 6 (PA6) is a traditional amine modifier which improves the dyeing ability of polypropylene with disperse dyes. In this investigation, polyetheramine (PEA) is introduced as a novel amine modifier which improves the dye-ability of polypropylene with disperse and acid dye-stuffs. To this end, the dyeing behavior as well as possible impairments of tensile properties of PEA modified polypropylene were studied and compared to PA6 modified polypropylene. As with the PA6 containing blends, the ten-

INTRODUCTION

Because of suitable properties such as high tensile strength, high chemical resistance, low density and low cost, polypropylene (PP) is utilized in manufacturing many products such as packaging films and fibers. However its use has been limited in the textile industry because conventional dyes lack affinity for this polymer.¹ Principally, the ability to be dyed (dyeability) is controlled not only by thermodynamic factors such as affinity but also by kinetic factors such as crystallinity which controls the diffusion of dyes into and within the polymer matrix.² A nonpolar, aliphatic structure as well as possessing high crystallinity makes pp to have insufficient chemical affinity for conventional dyes. Therefore, polypropylene is undyeable due to the absence of ionic or polar groups within its polymer chain, so that the retention of dye molecules is only possible by weak non polar physical forces. Additionally, PP's high degree of crystallinity encounters poor accessibility and prevents the diffusion of dyes into the polymer matrix.³

To improve the dye-ability of polypropylene, both physical and chemical modification methods have sile properties of the incompatible PP/PEA blends decreased due to weak interfacial adhesions between the components of the blends. However, the incorporation of a compatibilizer into such blends led to better dispersions of modifiers in the matrix as well as formation of amide or imide linkages which in turn reincreased the tensile properties almost to their initial values. Both PEA and PA6 modifiers improved the disperse dye uptake of the blends. However, Only Jeffamine ED-2003 (i.e., PEA) was capable of enhance the acid dye uptake of modified polypropylene. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2162–2171, 2012

Key words: polypropylene; polyetheramine; maleic anhydride polypropylene; disperse dyestuffs; acid dyestuffs

been reported in the literature. The former could be performed simply by mixing a host polymer with polymeric additives, metal compounds, low molecular weight materials and even organic or inorganic nano-materials in a batch mixer or an extruder.^{4–7} On the other hand, chemical modifications are carried out by placing various dye receptor sites in the polymeric chains via block or graft copolymerization.⁴ Because of technical feasibility and economical viability, physical modification methods have been used more extensively than the chemical modification techniques.

Among the modifiers, amine modifiers could, theoretically improve disperse as well as acid dyeing behaviors of polypropylene. Polyamide 6 (PA6) is a conventional amine modifier which could improve dye-ability of polypropylene with disperse dyes. Kotek et al.² have studied dyeing behavior of an alloy fiber of polypropylene and polyamide 6 produced by melt spinning with three disperse dyes. Seves et al.⁸ have studied dyeing characteristics of a PP/PA6 blend fiber. They showed that the fiber was easily dyeable with disperse dyes and wash and dry cleaning fastnesses of the blend fiber were quite satisfactory.

According to the literature, polyamide 6 is only capable of improving dyeing of polypropylene with disperse dyes. Two important factors, namely the basicity of the amine's nitrogen and the required

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	1			
Amine modifiers	Density (g/cm ³)	Relative viscosity	Melting point (°C)	Amine content (meq/kg)
Jeffamine ED-2003 Akulon F130 TFC 234	1.068 1.13 1.12–1.15	134 ^a 3.04 ^b (medium viscosity) 2.34 ^b (low viscosity)	43 220 220	$\begin{array}{c} \sim 1000 \\ 38 \\ 50 \end{array}$

TABLE I Properties of Three Amine Modifiers

^a cSt @ 50°C.

^b Relative viscosity in formic acid.

amount of such amine nitrogen should be considered for improving acid dye-ability of polypropylene. The more basic the nitrogen, the lesser would be the required amount of the amine modifier in the PP matrix.⁹ Akrman et al.^{9–12} have synthesized two amine polymeric additives with molecular mass of 4500 and 4300 (g/mol) and basic nitrogen content of 3.7 and 4.9%, so that after blending with polypropylene improved dye-ability with acid dyes could be encountered. They have evaluated kinetic and thermodynamic parameters of the dyeing system, ionic exchange mechanism of dyeing and effect of drawing on dye-ability of the modified polypropylene fibers. Therefore, it could be concluded that dyeing polypropylene with acid dyes will be more feasible and efficient if amine modifiers of low molecular weight and high basic nitrogen content were incorporated into the PP matrix instead of the high molecular weight counterparts which possessed low basic nitrogen content exemplified by polyamide 6.

In this research therefore, polyetheramine (PEA) is introduced as a novel high amine content, low molecular weight amine modifier which would be capable of improving the acid dye-ability of polypropylene. It is important to note that enhanced dye-ability of polypropylene should not adversely impair its mechanical properties. Therefore, it is necessary to evaluate mechanical properties of polypropylene during any process in which enhanced dye-ability is sought after.

For this reason, in the present investigation, dyeing behavior and tensile properties of PEA modified polypropylene were simultaneously studied and compared with the corresponding PA6 modified blends. In addition to measuring tensile properties (represented by the tensile strength and the elongation at break) and dye uptake (represented by the Kubelka-Munk's *K/S* ratio), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) were also used to analyze the morphology of the resultant blends.

EXPERIMENTAL

Materials

An isotactic polypropylene (fiber grade), known as Moplen V30S with a melt flow index (MFI) of 18 g/

10 min and density of 0.92 (g/cm³) was supplied by the Iranian Arak petrochemical company. A polyetheramine, known as Jeffamine® ED-2003, was obtained from the Huntsman company. It is a waxy solid at room temperature with an approximate molecular weight of 2000 (g/mol). Two fiber grades of polyamide 6, known as Akulon F130 (industrial grade) and TFC 234 (textile grade) were obtained from the DSM company and the Tehran Fiber company, respectively. Table I depicts some properties of the utilized amine modifiers.

A maleic anhydride grafted polypropylene (MAH-PP), namely, Fusabond® P MD353D acting as a compatibilizer was supplied by the Dupont company. This material had a melting temperature of 136°C and a MFI of 450 g/10 min (190°C/2.16 kg). The grafting level of this maleic anhydride was reported to be very high.

In this work, C.I. Disperse Yellow 3 (Cibacet Yellow 2GC) and C.I. Acid Yellow 110 (Polar Yellow 5GN) were supplied by the Ciba company. The disclosed structure of the disperse dye is shown in Figure 1.

Sample preparation

On the basis of the authors' previous research, three compatible blends (coded as CPP samples) and three incompatible blends (coded as IPP samples) were selected. Additionally, two neat PP samples, namely nPP 190 and nPP 240 were made to experience the same thermal history of the mixing process for PP/ PEA and PP/PA6 blends, respectively. Table II illustrates the proportions of components in each coded sample.

To remove residual moisture, Akulon F130, TFC 234, and Fusabond® P MD353D were dried at 80°C



Figure 1 Structure of disperse yellow 3.

Proportions of the Components in Each Sample										
	Propo	rtions of th	ne components							
		Amine modifier								
PP	MAH-PP	PEA	Akulon F130	TFC 234	Mixing process condition					
1	0	0	0	0	Without thermal history of mixing process					
1	0	0	0	0	Similar to PP/PEA blends					
1	0	0	0	0	Similar to PP/PA6 blends					
0.85	0	0.15	0	0	Related to PP/PEA blends					
0.85	0	0	0.15	0	Related to PP/PA6 blends					
0.85	0	0	0	0.15	Related to PP/PA6 blends					
0.7	0.15	0.15	0	0	Related to PP/PEA blends					
0.7	0.15	0	0.15	0	Related to PP/PA6 blends					
0.7	0.15	0	0	0.15	Related to PP/PA6 blends					
	PP 1 1 0.85 0.85 0.85 0.7 0.7 0.7 0.7	Propo Propo PP MAH-PP 1 0 1 0 1 0 0.85 0 0.85 0 0.85 0 0.7 0.15 0.7 0.15 0.7 0.15	Proportions Proportions of th PP MAH-PP PEA 1 0 0 1 0 0 1 0 0 1 0 0 1 0 0 0.85 0 0.15 0.85 0 0 0.7 0.15 0.15 0.7 0.15 0 0.7 0.15 0	Proportions of the Components Proportions of the components Amine modifier PP MAH-PP PEA Akulon F130 1 0 0 0 1 0 0 0 1 0 0 0 1 0 0 0 1 0 0 0 0.85 0 0.15 0 0.85 0 0 0 0.7 0.15 0.15 0 0.7 0.15 0 0.15 0.7 0.15 0 0.15 0.7 0.15 0 0	Proportions of the Components in Each S Proportions of the components Amine modifier PP MAH-PP PEA Akulon F130 TFC 234 1 0 0 0 0 1 0 0 0 0 1 0 0 0 0 1 0 0 0 0 0.85 0 0.15 0 0 0.85 0 0 0.15 0 0.7 0.15 0.15 0 0 0.7 0.15 0 0.15 0 0.7 0.15 0 0.15 0 0.7 0.15 0 0.15 0					

TABLE II Proportions of the Components in Each Sample

for 16 h. Jeffamine ED-2003 was used as received. For preparing PP/PEA blends, PP V30S and Fusabond® P MD353D were melt blended together in the mixer at 190°C and 60 rpm for 3 min. Then Jeffamine ED-2003 was added and the operation continued for one further minute after the mixer torque became constant. The total blend time was approximately 15 min for each sample.

To prepare PP/PA6 blends, PP V30S and Fusabond® P MD353D were melt blended in a batch mixer brabender® plasticorder® W50 at 190°C and 60 rpm for 1 min. Then temperature of the batch mixer was automatically raised from 190 to 240°C during 2 min. When the temperature was fixed at 240°C, polyamide 6 was added to the mixer. The mixing operation was continued for one further minute after the mixer torque became constant. The total blend time was about 8 min for each sample.

Also, two neat PP samples, namely nPP 190 and nPP 240 also experienced the same thermal history of the corresponding mixing process.

After blending, the samples were dried at 80°C for 16 h to remove any possible absorbed moisture. Immediately after, the samples were molded by a compression molding machine, namely, the Dr Collin PCS II P 400P® working at 1.5 MPa and 190°C to prepare films of 150 μ m thicknesses ready for tensile measurements and dyeing with disperse or acid dyes. Additionally, samples of 2000 μ m thickness were also prepared under the same condition for morphological evaluation by scanning electron microscopy (SEM).

Dyeing

The prepared film samples for disperse dyeing had dimensions: $3 \text{ cm} \times 3 \text{ cm} \times 150 \mu\text{m}$. The dye concentration in the dyebath was 3% w/w (weight of dye per weight of film) and the liquor to goods ratio was 100 : 1. pH of the dyebath was adjusted by acetic acid to be 5 to 5.5. 0.5% w/w of the dispersant

Eriopon OL was used to improve the dispersion of dye particles in the bath. Each sample was added to the prepared dyebath at room temperature. The temperature was then raised to the boil at a rate of 2°C/min and the dyeing process was continued for a further 60 min at the boil. To remove excess dye precipitated on the surface of dyed film, a reduction clear process was performed after the dyeing process. The reduction clear bath had 2 mg/cm³ of sodium hydroxide, 3 mg/cm³ of sodium hydrosulfite and 2 mg/cm³ of detergent with a liquor to goods ratio of 100 : 1. The process was performed at 70°C for 20 min.

Film dimensions, acid dye concentration and liquor to goods ratio for the acid dyeing process were exactly like those for the disperse dyeing process. However the initial pH of the dyebath was adjusted to 4.5 by acetic acid. Totally, 1 mg/cm³ of Ammonium sulfate was also used for final pH adjustments at the boil. The dyebath temperature was raised to the boil at a rate of 2°C/min and the dyeing process continued for a further 60 min at the boil. Figure 2 shows the temperature profile of the dyeing process.

Tensile measurement

In accordance to the ASTM D882 standard test method for measuring the tensile properties of polymeric films, the samples were cut to the required dimensions having thicknesses of 150 μ m. Tensile



Figure 2 Temperature profile of the dyeing process.



Figure 3 Tensile properties of blank PP, nPP 190, and nPP 240 samples.

testing was carried out on a Gotech® universal testing machine AL-700 LA5 after conditioning the test samples at 23 \pm 2°C and 50 \pm 5% relative humidity for 24 h. In this investigation, tensile strength and elongation at break are reported.

Spectrophotometry

Reflectance curves $(R_{\infty}(\lambda))$ of the dyed samples were measured on a Gretag Macbeth® spectrophotometer 7000A. These reflectance data were converted to the corresponding Kubelka-Munk ratio $(K/S)_{\lambda}$ of the one constant theory by the use of Eq. (1). The maximum values of K/S at λ_{max} were used as a criterion for dye uptake.

$$(K/S)_{\lambda} = (1 - R_{\infty}(\lambda))^2 / 2R_{\infty}(\lambda) \tag{1}$$

Scanning electron microscopy

To evaluate the morphology of the samples, micrographical images were taken by the aid of a Tescan Vega® scanning electron microscope operating at 20 kV with 2 kx magnifications. For this purpose, the samples were broken under liquid nitrogen and etched by formic acid (96%) for 4 h. SEM images were then taken from the fractured surface of each sample which was coated with gold.

Differential scanning calorimetry

After drying the samples at 80°C for 16 h for removal of any possible absorbed moisture, differential thermal analysis of the samples were carried out using a Mettler-Toledo® DSC 822 instrument. To remove the thermal history induced by previous processes, PP/PEA samples were heated from 25 to 190°C at a scanning rate of 10°C/min (run 1). Also, run 1 was carried out for PP/PA6 samples in the temperature range of 25 to 240°C. The samples were then cooled to 25°C (run 2). Again, PP/PEA and PP/PA6 samples were then reheated from 25 to 190 or 240°C, respectively, at the same scanning rate (run 3). In this paper, run 3 thermographs are reported.

RESULTS AND DISCUSSION

Tensile properties

Before evaluating tensile properties of the blends, it is necessary to consider the effect of thermal history of the mixing process on tensile properties of the PP matrix. Figure 3 shows that tensile strength has decreased from 29.5 MPa for neat PP sample to 24.8 and 19.7 MPa for nPP 190 and nPP 240 samples and also elongation at break has decreased from 7% for blank PP to 3.4 and 2.5% for nPP 190 and nPP 240 samples, respectively.

The declined tensile properties of the neat PP samples are due to thermal degradation of the polymer during the mixing process. In other words, the high temperature as well as the applied shear stress during the mixing process leads to polymer chain scission which in turn lowers the tensile properties of the polymer. The higher the temperature, the more extensive will be the chain scission. Therefore, the tensile properties for nPP 240 are less than those of nPP 190. The tensile properties and the dyeing behavior of PP/PEA and PP/PA6 blends were compared with the corresponding nPP 190 or nPP 240 samples, respectively.

As Figure 4 shows tensile strength of an incompatible PP/PEA blend has decreased from 24.8 MPa for nPP 190 to 15.3 MPa for IPP1. However, the tensile strength reincreased to 19.4 MPa for the compatible PP/PEA blend (i.e., CPP1 sample). Principally, significant difference in the polarity of the discrete phase i.e., PEA and that of the PP matrix causes these two phases to be immiscible. In such a case, not only the discrete phase tends to form coarser particulates but also the interfacial adhesion between the two phases becomes weaker so that the interface can not withstand the applied stress.¹³ Also the high surface tension of the amine modifier causes unsuitable wetting of its particles by the PP matrix to



Figure 4 Tensile strength of compatible and incompatible blends.



Figure 5 SEM micrographic images of (a): neat PP; (b): PP/MAH-PP (0.85/0.15); (c): IPP1; (d): CPP1; (e): IPP2; (f): CPP2; (g): IPP3; (h): CPP3.

occur. Therefore, possible defects such as voids are formed around the interfaces which could contribute to the lowering of the tensile strength.^{2,14} On the other hand, the presence of a compatibilizer leads to a significant lowering of the surface tension of the amine modifier which reduces the interfacial tension, hence inducing better wetting and better dispersion of the particulates within the PP matrix to occur.^{15,16} Improvements in dispersion increases the surface area of the amine modifier particulates and this in turn will promote interaction between the amine modifier and the compatibilizer i.e., the reaction between NH₂ and MAH groups, which leads to the formation of amide or imide linkages.^{16–18} Finer



Figure 6 Torque-time plots of the mixing process for neat PP, IPP1, CPP1, and IPP2 samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dispersion of the amine modifier particulates and formation of amide or imide linkages guarantee improvements in the tensile strengths of the compatibilized blends. As is seen in Figures 5(c,d), PEA particulate sizes are greater than 15 microns for IPP1 sample and less than 2 µm for CPP1 sample.

Similarly, immiscibility of polyamide 6 and the PP matrix is the cause for the decreased tensile strength of two incompatible PP/PA6 blends from 19.7 MPa for nPP 240 sample to 17.9 and 18.4 MPa for IPP2 and IPP3, respectively. Again, the presence of the compatibilizer has led to better interfacial adhesion and finer dispersion of the particulates so that the tensile strengths are reincreased to 23.6 and 20.8 MPa for CPP2 and CPP3, respectively. Figures 5(e,g) show that the size of Akulon F130 and TFC 234 particulates in IPP2 and IPP3 samples are both larger than 2 microns within the PP matrix. On the other hand, Figures 5(f,h) illustrate that polyamide 6 particulates become finer with particle sizes of less than 500 nm if 15% of the compatibilizer is incorporated into the PP matrix.

Figure 5 also depicts that within the PP matrix, particle sizes of PEA are always larger than that of PA6 in presence or absence of the compatibilizer. In principle, dispersion of particulates in a media depends on wetting, breaking down of agglomerates in addition to preventing them from re-agglomeration. Immiscibility of PEA and PP results in unsuitable wetting of PEA particulates by the PP matrix. It is clear that melt viscosity of Jeffamine ED-2003 is much lower than that of the PP matrix. For this reason, the melt viscosity of IPP1 sample is lower than that of nPP 190 and IPP2 samples. Lower melt

viscosity of the blend causes less shear stress to be transferred to the PEA particulates via the media. In such a case, the efficiency of the mixing process would be lowered so that the breaking down of PEA particulates within the PP matrix would become considerably more difficult. Figure 6 shows that the torque of the mixing process decreases for IPP1 sample when PEA is added to the blend. Additionally, the low molecular weight of PEA and its immiscibility with the PP matrix, thermodynamically favors the formation of coarser PEA particulates during and after the mixing process. That is why the average particulate size of PEA is larger than 15 μ m for the incompatible IPP1 sample.

It is important to note that the presence of the compatibilizer not only increases the miscibility of PEA and PP phases but also improves the wetting of PEA particulates by the matrix. The better the wetting, the greater the chance for the reaction between



Figure 7 Elongation at break of compatible and incompatible blends.

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Figure 8 $(K/S)_{\lambda}$ curves of disperse dyed samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

NH₂ and MAH groups to form amide or imide linkages would be. Formation of such linkages which has incidently been observed by other researchers^{16–18} increases the viscosity of the blends in the mixing process.¹⁷ In this state, more shear stress is transferred to PEA particulates in CPP1 sample compared with IPP1 sample. Figure 6 clearly illustrates that the torque for CPP1 sample is always larger than that for IPP1 sample during the mixing process. Furthermore, amide or imide linkages would prevent PEA molecules from forming coarser particulates. Therefore, the dispersion of PEA particles within the PP matrix is generally greatly improved in the presence of the compatibilizer.

However, the presence of the present compatibilizer couldn't perfectly compensate for the loss in the tensile strength of PEA containing blends. In other words, although adding 15% of the compatibilizer caused the tensile strength to increase from 15.3 MPa for IPP1 sample to 19.4 MPa for CPP1 but the latter is still smaller than the initial 24.8 MPa for nPP 190 sample. This could be attributed to the low tensile strength of Jeffamine ED-2003 as a consequence of its low molecular weight and waxy nature.

Figure 7 shows that the presence of PEA or PA6 within the PP matrix also caused reductions in the elongation at break from 3.4 and 2.5% for nPP 190 and nPP 240 to 2.1, 2.1, and 2.0% for IPP1, IPP2, and IPP3, respectively. However, the compatibilizer improved elongation at break so that it reincreased again to 5.4, 4.3, and 3.0% for CPP1, CPP2, and CPP3, respectively. This could be explained in terms of the formation of amide or imide linkages which induces interfacial bonding between the amine modifier particles and the PP matrix in the presence of the compatibilizer. The compatibilized blends could withstand tensile deformation at a higher elongation at break because the interfacial adhesion between the amine modifier particles and the PP matrix is sufficiently strong enough to withstand the deformation up to its breaking point.¹⁹



Wavelength (nm)

Figure 9 $(K/S)_{\lambda}$ curves of acid-dyed samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 10 K/S_{max} values for the disperse dyed samples.

Dyeing behavior

The measured reflectance data of the dyed samples were used to calculate the maximum values of K/S (or K/S_{max}). For this purpose, each sample was placed on a white background and then its reflectance data were determined by the spectrophotometer. Then the reflectance data were converted to the corresponding Kubelka-Munk ratio $(K/S)_{\lambda}$ of the one constant theory. Figures 8 and 9 show $(K/S)_{\lambda}$ curves for disperse or acid dyed samples, respectively. K/S_{max} values at 420 nm were used for comparison purposes.

Figure 10 shows that both PEA and PA6 are capable of improving disperse dye uptake of the resultant blends regardless of being compatible or not. The K/S_{max} values increased from 0.9 for neat PP sample to 8.1, 8.5, and 7.2 for IPP1, IPP2, and IPP3 samples and also to 6.4, 11.2, and 11.9 for CPP1, CPP2, and CPP3 samples, respectively. These values

illustrate that the three amine modifiers have increased the disperse dye uptake of blended polypropylene by at least six times.

Principally, the dyeing process comprises of four separate steps namely, diffusion of dye in the bulk solution (dyebath), adsorption at the polymer surface, diffusion into the polymer matrix and finally fixation (immobilization) of the dye by formation of physical and chemical bonds between dye molecules and the polymer. To carry these steps to completion (i.e., dyeing) certain prerequisites are needed such as the presence of polar groups in the polymer chains which are more accessible in the amorphous regions in the blend.

Incorporation of amine modifiers into the PP matrix leads to the creation of two distinct regions within the blend, namely the amine modifier particulates and the interfacial regions in the blends. Both these regions are susceptible to being dyed with disperse dyes. The current theoretical knowledge about diffusion of dyestuff from a solution into a substrate makes it possible to observe that disperse dyes diffuse primarily into the amorphous regions and the interfaces of a blend.³ On the other hand, the presence of polar groups at the interface and interior of the particulates not only increases the affinity between the substrate and disperse dyes but also guarantees better fixation (i.e., retention) of dyes to the blended substrate. For this reason, K/S_{max} values increase from 0.9 for neat PP sample to 8.1, 8.5, and 7.2 for IPP1, IPP2, and IPP3 samples, respectively.

It was mentioned previously that the compatibilizer improves the dispersion of particulates in the



Figure 11 DSC thermographs of nPP 240, IPP1, IPP2, and IPP3 samples.



Figure 12 DSC thermographs of CPP1, CPP2, and CPP3 samples.

media. Better dispersion leads to increased surface area of the discrete phase in the PP matrix, creation of amide or imide linkages between the amine modifier and the compatibilizer and decreased crystallinity of the PP matrix. DSC thermographs of Figures 11 and 12 illustrate that the crystallinity of polypropylene decreases from 49.35, 51.32, and 51.25% for IPP1, IPP2, and IPP3 samples to 48.66, 49.41, and 49.83% for CPP1, CPP2, and CPP3, respectively. Decreased crystallinity of PP as well as development of interfacial regions increases the disperse dye uptake so that K/S_{max} values increase from 8.5 and 7.2 for IPP2 and IPP3 samples to 11.2 and 11.9 for CPP2 and CPP3 samples, respectively. However it seems that the compatibilizer has no significant effect on improving the disperse dye uptake for PEA containing samples.

Acid dyes are anionic water-soluble dyes which migrate from an aqueous dye bath and diffuse into the polymer matrix. Their fixation to the substrate strongly depends on ionic interactions between anionic groups of the dye and cationic dye sites in the polymer chains. For this purpose, basic nitrogen groups are suitable as cationic sites to interact with the anionic groups of acid dyes in an aqueous solution. Akrman et al.¹⁰ have proposed the ion



Figure 13 Ion exchange mechanism of acid dyeing.

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exchange mechanism which is shown in Figure 13 to explain the interaction of an acid dye molecule with a polymeric dye site in an aqueous acetic acid solution.

To obtain higher acid dye uptake, it is necessary that the amine modifier has adequate basic nitrogen groups. Because Jeffamine ED-2003 has a high amine content (i.e., 1000 meq/kg) it must be capable of enhancing the acid dye-ability of polypropylene. Figure 14 shows that the K/S_{max} value has increased from 0.5 for the neat PP sample to 1.9 for the incompatible PEA containing IPP1 sample. Furthermore, the compatibilizer has a significant effect on greatly enhancing the acid dye uptake of PP/PEA blends due to better dispersion of PEA particulates within the PP matrix so that K/S_{max} value increased from 1.9 for IPP1 sample to 5.1 for CPP1 sample.

Because of very low amine content of Akulon F130 and TFC 234 (i.e., 38 and 50 meq/kg, respectively), they could not improve the acid dye uptake of PA6 containing blends in presence or absence of the compatibilizer.



Figure 14 K/S_{max} values of acid dyed samples.

CONCLUSIONS

Because both PEA and PA6 are incompatible with the PP matrix, the tensile strength and the elongation at break of all PP/amine modifier blends decreased in the absence of the compatibilizer. However, the tensile properties of the compatible blends improved due to the formation of amide or imide linkages and suitable interfacial adhesion between the amine modifier and the PP matrix. Although the tensile strength of PP/Jeffamine ED-2003 blend increased to 19.4 MPa in the presence of the compatibilizer but it never reached the initial value of 24.8 MPa of neat PP sample. This is attributable to the low molecular weight and waxy nature of Jeffamine ED-2003.

Because particulates of the amine modifiers as well as the interfacial regions are both susceptible to being dyed with disperse dyes, the amine modifiers increased the disperse dye uptake of the modified PP blends by a factor of at least 6.5 times that of the neat PP sample. Incorporation of the compatibilizer increased the interfacial region as well as decreasing the crystallinity of the modified PP matrix. Both such modifications incrased the disperse dye uptake of compatible blends but to a varying degree of significance.

The acid dye uptake of the PEA containing blends enhanced tremendously due to high amine content of Jeffamine ED-2003, particularly in presence of the compatiblizer. Neither Akulon F130 nor TFC234 were capable of improving the acid dye uptake of the PP/PA6 blends in presence or absence of the compatibilizer due to their low amine contents.

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