Research Article

Disperse and Acid Dyeable Polypropylene Polyblend Fibers

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Abstract

The role of nanoclay (NC) in influencing the structural properties of polypropylene (PP) and polytrimethylene terapthalate (PTT) polyblend fibers formed in presence of maleic anhydride grafted polypropylene (MAPP) has been investigated. The structural changes in thermal properties, tensile properties and dyeability for varying concentration of NC i.e. 0.25%, 0.5%, 0.75% & 1% were studied. The thermal properties were evaluated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The dyeability of polyblend fibers with respect to disperse dye and acid dye was studied along with evaluation of its fastness properties. NC addition in small loadings (< 1%) enhanced the thermal stability and tenacity upto 9.7%. The poly blend fibers showed excellent disperse dyeability exhibiting good fastness properties. The quaternary salts present in NC also induced acid dyeability to the polyblend fibers.

Keywords: Polypropylene, Nanoclay, Dyeability, Polytrimethylene terapthalate.

1. Introduction

Polymer melt blending is one of the commonly used techniques to modify properties of polymers and produce new materials with enhanced or induced properties. Polypropylene (PP) fibers which are very difficult to dye due to its inert and compact structure have been made dyeable using melt blending technique (Dayioglu, 1992), (Son, *et al.* 1999), (Mani, *et al.* 2003), (Fan, *et al.* 2003), (Gupta, *et al.* 2011). In our earlier work, we have made PP disperse dyeable by blending it with different types of polyester (Teli and Desai, 2013) (Teli, *et al.* 2004) and observed that the polyblend fibers formed showed excellent disperse dyeability.

However, the major challenge in these PP polyblend fibers is poor mechanical properties and thermal stability arising due to its immiscible nature. Studies have been carried out to improve the compatibilities between immiscible blends by using different types of compatibilizer (Dean, *et al.* 2004), (Xue, *et al.* 2007). Recently, nanoclays (NC) have been explored as a compatibilizer for immiscible polymer blends such as PP/nylon, PP/polystyrene and PP/polyester (Chow, *et al.* 2004), (Tang, *et al.* 2004), (Feng, *et al.* 2004), (Ray, *et al.* 2004). The presence of NC in very small percentage helps in improving/increasing the mechanical properties, heat resistance, surface properties, reduced gas permeability, improved solvent resistance, enhanced ionic conductivity, and dyeability of PP matrix (Ataeefard and Moradian, 2011), (Toshniwal, *et al.* 2007), (Yano, *et al.* 1993), (Ataeefard and Moradian, 2011), (Deshmanea, *et al.* 2007), (Wang, *et al.* 2006), (Fan, *et al.* 2004). Presence of NC in the PP fiber matrix has lead to formation of acid dyeable fibers. The acid dye particles adhere to the fiber, primarily due to the ionic attraction between NC particles and the charged chemical group sites in the dye structure (Mani, *et al.* 2005).

Enhancement or induction of the properties is dependent upon the dispersion of NC in fiber matrix and are observed in three forms. First is phase separated structure formed due to their immiscible nature resulting in reduced mechanical properties. Second is intercalated structure, wherein polymeric chains get penetrated into interlayer of clays. Third type is exfoliated structure formation, wherein the layers of nanoclay are dispersed uniformly in polymer matrix (Giannelis, *et al.* 1999) and this form shows better results because of its large aspect ratio providing high interfacial area causing strong interaction between polymer chains and clay nanolayers (Kusmono and Ishak, 2013).

PP is not capable of intercalating or exfoliating between the clay layers as it is not polar enough to interact with clays layers (Xu, *et al.* 2003), (Walter, *et al.* 1999). However, a compatibilizer could be used to improve clay dispersion within PP and facilitate subsequent exfoliation of the clay platelets. Many researchers have reported that PP/NC nanocomposites formed with the addition of maleic anhydride grafted polypropylene (MAPP), prepared by intensive shear mixing or twin screw extrusion, have been very

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effective in producing exfoliated structure (Ataeefard and Moradian[1], 2011), (Mani, *et al.* 2005), **(**Vaia, and Giannelis,1997).

In our previous work, 5% addition of polytrimethylene terapthalate (PTT) in PP polyblend fibers showed excellent disperse dyeability (Teli and Desai, 2013). Subsequent study on effect of MAPP compatiblizer in enhancing the compatibility of polyblend fibers showed that the best results were observed for 3% MAPP addition. In the present work, the combined effect of NC and MAPP as compatibilizer for PP/PTT blend is being investigated to enhance the thermal stability, tensile properties and dyeability of the polyblend fibers. The compositions of different polyblend fibers studied for predicting the influences of NC are given in Table 1. The polyblend fibers have been evaluated for structural changes and its effect on dyeability.

Table 1 Polyblend fibers denotation and their compositions

Sr. No.	Denotations (PP:PTT:MAPP:NC)	Composition (% by weight)			
		PP	PTT	MAPP	NC
1	95:5:3:0	95	5	3	0
2	95:5:3:0.25	95	5	3	0.25
3	95:5:3:0.50	95	5	3	0.50
4	95:5:3:0.75	95	5	3	0.75
5	95:5:3:1	95	5	3	1.00

2. Materials and methods

2.1 Materials

PP (Repol H350FG) chips, having MFI 35 were supplied by Reliance Industries Ltd, India. PTT having 0.93 IV were supplied by Futura Polymers, India. MAPP with 0.4 % maleic anhydride content, was procured from Pluss Polymer, India. Ogano-nanoclay (Closite 15A) was given by Southern Clay Products, USA. Disperse (Dianix Blue ER) and Acid dye (Telon Red FRL) were supplied by Dystar India Pvt. Ltd., Mumbai, India.

2.2 Fiber spinning

PP, PTT, MAPP and NC were pre dried in vacuum oven and melt blended at pre determined concentration in twin-screw extruder (APV Baker, UK). This process ensures better mixing and dispersion of NC. The melt blended compounded chips were then melt spun into fibers in melt spinning machine (Fair Deal Associates, India). The temperatures of the extruder zones were kept 15-20 ^{0}C above the melting temperature of polyblend fibers. The extruded filaments from spinneret were quenched and subsequently drawn at an optimized draw ratio using two-stage drawing process.

2.3 Dyeing of fibers

The disperse and acid dyeing of the pre-scoured polyblend fibers was carried out in a high temperature/high pressure beaker dyeing machine using a standard method of the dyeing of synthetic fibers (Burkinshaw, 1995). The dyed samples were then subjected to reduction clearing treatment to remove unfixed dye, followed by neutralization, washing and drying.

2.4 Characterization of fibers

The thermal properties and crystallization behavior were studied using differential scanning calorimetry (Shimadzu, Japan). The thermal stability of the samples was studied by carrying out thermogravimetric analysis using DTG-60H thermogravimetric analyzer (Shimadzu, Japan). X-ray diffraction analysis was performed using powder technique on a XRD-6100 (Shimadzu, Japan). Crystalline orientation factor (f_c) and amorphous orientation factor (f_a) was calculated by Wilchinsky's method (Wilchinsky, 1959) and Stein-Norris method (Stein and Norris, 1956) respectively. The birefringence of fiber was calculated by retardation method using polarizing microscope fitted with Bereck compensator (Happey, 1978). Tensile testing of filaments was carried out on Tinius Olsen tensile testing machine. The gauge length was 100 mm and strain rate was kept at 50 mm/min.

The dyed samples were evaluated for color depth by computer color-matching system in terms of Kubelka Munk function (K/S), using Spectra Flash SF 300 (Datacolor International, USA) (Ingamells, 1993).

Table 2 DSC analysis of polyblend fibers

Sample	Onset temp (^{0}C)		Endset temp (^{0}C)		Peak temp (^{0}C)		Heat of melting (J/g)		Crystallinity (%)
	(PP)	(PTT)	(PP)	(PTT)	(PP)	(PTT)	(PP)	(PTT)	
95:5:3:0	155.42	219.7	170.92	230.18	166.97	226.06	107.96	3.05	54.25
95:5:3:0.25	154.73	221.94	171.2	233.46	167.13	227.73	108.35	3.74	54.91
95:5:3:0.50	155.18	222.53	171.39	233.87	167.59	228.04	110.21	3.92	55.94
95:5:3:0.75	155.46	223.15	171.63	234.05	167.74	228.41	110.64	4.28	56.39
95:5:3:1	155.84	223.56	171.78	234.32	167.82	228.73	110.85	4.32	56.52

Kubelka Munk function (K/S) is derived using following equation:

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

where, R is reflectance at complete opacity, K is the absorption coefficient and S is scattering coefficient. Color fastness to washing was evaluated as per ISO 105-C10:2006 B and Color fastness to light was evaluated as per BS 1006 test method.

3. Results and discussion

3.1 Thermal analysis

Results of DSC analysis given in Table 2 indicate that NC has a significant influence in altering the crystallinity of fibers. The polyblend fibers showed two distinct melting points representing PP and PTT, respectively. Addition of NC, led to formation of dominant PP and PTT melting peak and slight shifting to higher temperature, thus showcasing its positive influence in formation of crystalline structure. NC has acts as a nucleating agent which favours the formation of PTT crystalline structure and with a gradual increase in the NC content, the crystallinity of the fibers increases as observed here. Thus overall increase in crystallinity of the polyblend fibers thus could be attributed to the nucleating effect of nanoclays (Pozsgay, *et al.* 2005) (Maiti, *et al.* 2002) (Xu, *et al.* 2003).
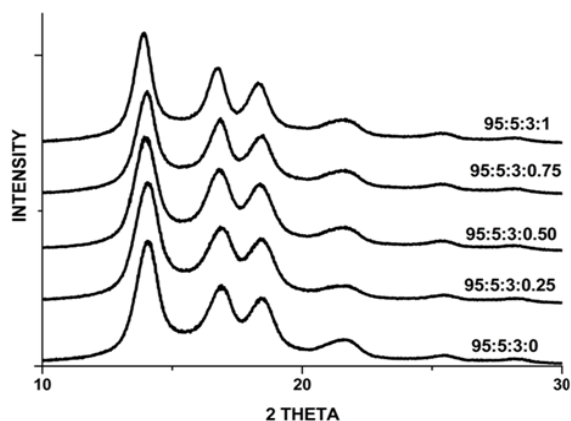

Fig. 1 X-ray diffractogram of polyblend fibers

3.2 X-ray analysis

The x-ray diffractograms of polyblend fibers as seen from Fig. 1 exhibit the effects of NC on fiber structural properties. The presence of NC has slightly improved overall crystallinity, crystalline orientation factor (fc) and amorphous orientation factor (fa) as seen from Table 3. Maximum increase in fa was observed for 0.75% addition, which distinctly enhances the tensile properties of fibers (Kunugi, *et al.* 1983). Thus addition of NC has positive influence on fiber properties.

Table 3 X-ray crystallinity and orientation of polyblend fibers

Fibers (PP:PTT: MAPP:NC)	Crystallinity (%)	Orientation	
		Crystalline (fc)	Amorphous (fa)
95:5:3:0	54.69	0.92	0.63
95:5:3:0.25	54.86	0.92	0.62
95:5:3:0.50	55.05	0.93	0.64
95:5:3:0.75	55.37	0.93	0.66
95:5:3:1	55.23	0.93	0.65

3.3 Thermal stability

The effect of the NC on the thermal stability of the polyblend fibers was studied by means of thermogravimetric experiments. The TGA curves as seen in Fig. 2 showed that the presence of NC has shifted the thermal decomposition of fibers to higher temperature thus increasing the thermal stability of the fibers. This increase can be attributed to increased crystallinity which is evident from the DSC study of the blend fibers and NC inherently acting as a heat barrier. Thus a positive influence of NC in enhancing the thermal stability of polyblend fibers, has been quite evident.
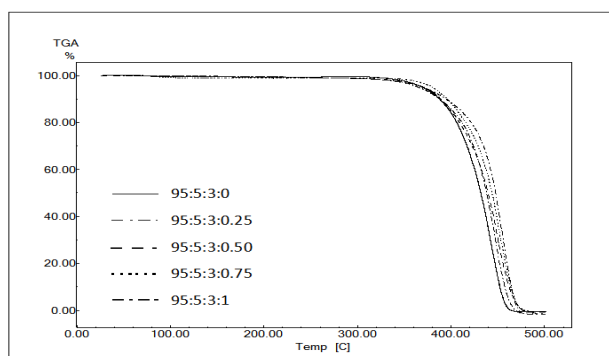

Fig. 2 Thermogravimetric analysis of polyblend fibers

3.4 Tensile properties

Results in Table 4 indicate that presence of NC has improved the tensile properties of polyblend fibers. With the increase in NC content, the tenacity of the fibers increased gradually. This improvement could be attributed to reinforcement of the fiber matrix due to NC, more crystalline fiber structure formation and presence of rigid NC exfoliated structure which ensures

Table 4 The effect of NC content on tensile properties of polyblend fibers

Sample	Tenacity (gf/d)	Peak elongation (%)	Strength gain (%)
95:5:3:0	4.84	14.81	--
95:5:3:0.25	4.96	14.58	2.48
95:5:3:0.50	5.07	14.43	4.75
95:5:3:0.75	5.22	14.26	7.85
95:5:3:1	5.31	14.08	9.71

Table 6 Light and washing fastness properties of disperse and acid dyed polyblend fibers (shade 3%)

Sample	Light Fastness		Washing Fastness	
	Dianix Blue ER	Telon Red FRL	Dianix Blue ER	Telon Red FRL
95:5:3:0	5	2	4	2
95:5:3:0.25	5	3	4	2
95:5:3:0.50	5	3	4	2
95:5:3:0.75	5	4	4	3
95:5:3:1	5	4	4	3

better interactions between the polar groups i.e. maleic anhydride and terminal hydroxyl groups of PTT. Thus the presence of NC plays a significant role as compatiblizer leading to improvement in its mechanical properties.

3.5 Dyeability

The results relating to disperse dyeability and acid dyeability of the polyblend fibers for 3% shade are given in Table 5. Addition of NC leads to increase in K/S values of disperse dyeing. This increase can be attributed to the fact that NC act as sorbents for dyes. Disperse dyes penetrate in to the layers of clay particles and remain in the voids between these layers of clay. According to Fan et. al. (Fan, *et al.* 2003), (Fan, *et al.* 2004) NC have very strong sorption ability due to its high surface area, strong van der Waals forces and ionic interactions with dyes (Mani, *et al.* 2003). While diffusion plays a very important role in enhancing the disperse dyeability, affinity plays a very important role in acid dyeability. The quaternary ammonium salts present in NC act as effective dye sites for acid dyes, as a result, acid dyeability is induced into the polyblend fibers. However the acid dyeing obtained was of very light shade and with the increase in NC content, the acid dyeability increased. However after 0.75% NC add-on, there is only a marginal increase in K/S values. Thus presence of NC increased slightly the disperse dyeability and imparted acid dyeability to polyblend fibers.

Table 5 K/S values of disperse dyed and acid dyed polyblend fibers (shade 3%)

Sample	Disperse dyeability Dianix blue ER		Acid dyeability Telon red FRL	
	K/S	Color strength gain (%)	K/S	Color strength gain (%)
95:5:3:0	28.8262	100	0.6665	100
95:5:3:0.25	29.2674	101.53	0.748	112.23
95:5:3:0.50	29.9368	103.85	1.2158	182.42
95:5:3:0.75	30.4832	105.75	1.5018	225.33
95:5:3:1	30.7086	106.53	1.5077	226.21

3.6 Fastness properties

The fastness properties of the dyed fibers given in Table 6, show that the deep shades obtained by disperse dyeability of modified fibers also gave very good color fastness to washing i.e. grade 4 and light fastness maximum rating of 5 i.e. good. It can be seen from the results that both light fastness and wash fastness of fibers were of quite acceptable degree.

Conclusions

NC has a significant influence on the structure formation of polyblend fiber. The very presence of NC leads to formation of fiber structure with improved thermal stability and tensile properties. The disperse dyeings of polyblend fiber were of deep shades with very good wash and light fastness properties, whereas acid dyeings were of lighter shades. Thus, NC in very low concentration is very effective in altering the structure for enhancing the serviceability of polyblend fibers.

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