The Effect of Nanoclay, PP and PP-g-MA Type on Properties of PP/clay Nanocomposite: A Way to Investigate the Dyeability Mechanism

M. M. Salehi[1], M. Ataeefard[2], S. Moradian[*3]

[1.] Polymer and Science Technology Division, Research Institute of Petroleum Industry, P.O. Box: 1599653111, Tehran, Iran.

[2.] Department of Printing Science and Technology, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran.

[3.] [a)] Center of Excellence for Color Science and Technology, Institute for Color Science and Technology; [b)] Faculty of Polymer and Color Engineering, Amirkabir University of Technology, P.O. Box: 15875, Tehran, Iran.

ABSTRACT

Polypropylenes loaded with different alkyl ammonium-modified montmorillonite are prepared to utilize a melt-mixing technique in various ways. Two types of polypropylene and compatibilizer are incorporated to improve the dispersion of various types of nanoclay and the dyeing behavior of the nanocomposites with various disperses, acid and basic dyes were studied. For the first time, the aim of this study was to investigate the effect of operational and material parameters in dyeing behavior and color buildup of producing nanocomposite due to better understanding of the dyeability mechanism of PP/nanoclay composite. The extent of exfoliation and dispersion of the nanoclay in PP was analyzed by XRD and TEM analytical techniques and the dyeability was studied through color build up and spectrophotometric measurement. The results showed that the mixing condition had no significant effect on dyeability. The lower the molecular weight of polypropylenes and compatibilizer caused the better the dyeability. The most intercalated nanocomposite also showed better dyeability and within various types of dye, disperses dye showed better dyeability. All things considered, it is appeared that between the two mechanisms suggested for dyeing improvement in the PP/nanoclay composite, the dominant mechanism is creating the path. *Prog. Color Colorants Coat. 10 (2017), 73-84© Institute for Color Science and Technology.*

1. Introduction

Polypropylene (PP) is one of the most widely used non-polar polyolefins, which exhibits balanced stiffness and processability [1]. PP has several advantages over other polymers, including low cost, high flexibility and abrasion resistance, as well as light weight [2]. PP is used in many industrial fields and is particularly promising in the textile industry [3]. For

*Corresponding author: moradian@aut.ac.ir

this kind of applications, the main disadvantage of PP is its lack of dyeability [4]. The dyeing behavior depends on its both physical and chemical structures. Regarding the chemical structure, dyeability is governed firstly by the presence of polar groups which interact with water molecules and allow swelling and, secondly, by functional groups which attract dye molecules. As for the physical structure, the fiber must be accessible to water, dyes, and other reagents [5]. It must possess a certain permeability to particularly permit the dye particles to penetrate into the character matrix [6]. The structural modification of PP by chemical reactions and graft copolymerization yield dyeable PP. Another method of achieving dyeable PP is blending it with other polymers [2]. It has been described that the PP matrix can also be dyed by the incorporation of nanoclays [3].

Nano-size particulates filled polymers (nanocomposites) are of great interest due to their lower density, excellent performances and attractive prospect, compared to conventionally filled polymers [7-10]. Montmorillonite is a clay mineral that is regarded as the most widely used filler for preparing nanocomposites [10]. As PP is too non-polar to interact with the modified layers correctly, a compatibilizer can be used to improve clay dispersion in PP and to facilitate subsequent exfoliation of the clay platelets by PP. Several studies report the use of maleic anhydride grafted PP (PP-g-MA) as compatibilizer [11].

Nanocomposite properties can be directly affected by the intercalation/ exfoliation levels in nano-composite morphology, which depend on the raw material and processing characteristics such as clay type and content, compatibilizer content and matrix viscosities [12, 13]. Therefore, in order to achieve the superior properties as the guidance of the material design and formulation, it is crucial to investigate the material parameters effectively. In previous studies, the authors studied the effect of nanoclay on the surface [14] and bulk [15] properties of PP/nanoclay composite. Besides the dyeability of those composites [4] and related fiber [16] associated to kinetic and thermodynamic of dyeing [6] are investigated. It was shown that all PP/clay nanocomposites exhibited better dye uptake comparing to pure PP. The dyed nanocomposites exhibited excellent wash fastnesses and satisfactory light fastnesses. In addition, the results indicate that the tensile modulus as well as the storage modulus of PP/clay nanocomposite was substantially higher over their pristine counterpart. Nevertheless, such nanocomposites showed decreased elongation at break compared with pure PP.

In continuation of the authors' previous works, the aim of the current study is to investigate, for the first time, the effect of PP and PP-g-MA molecular weight, nanoclay, dyestuffs types and the mixing parameter on dyeing behavior and color buildup of PP nanocomposite due to better understanding about the dyeability mechanism of PP/clay nanocomposite. Thus, the result of two major classes of factors will be considered in dyeing behavior with various dyes, namely, processing parameters (three methods of mixing) as comfortably as the raw material grades and contents (nanoclay, PP and PP-g-MA type and capacity). In this regard, four different cases are considered and discussed:
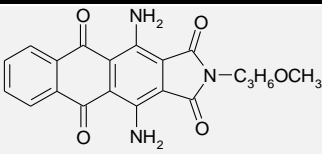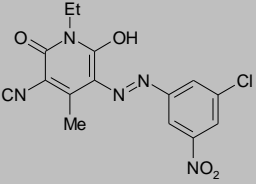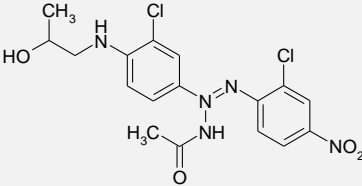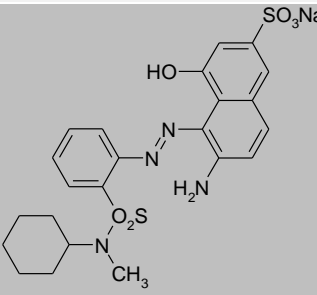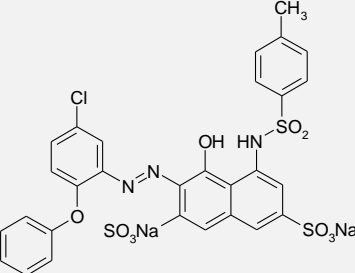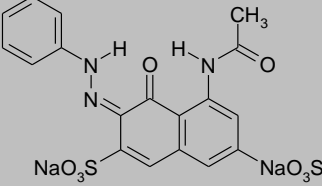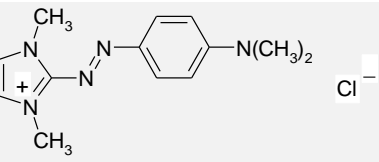
(i)   Investigating the effect of mixing parameters
(ii) Investigating the effect of molecular weight of PP and PP-g-MA
(iii) Investigating the effect of nanoclay types
(iv) Investigating the effect of dyes

2. Experimental

2.1. Materials

Closite 15A, Closite 20A, and Closite 30B organically modified montmorillonite nanoclay supplied by Southern Clay Products (USA) were used as received to prepare a series of three component PP/PP-g-MA/nanoclay hybrids. Polypropylene (PP grade V30S, HP500H) was supplied from Arak Petrochemical Company (Iran). Maleic anhydride grafted Polypropylene, PP-g-MA (Fusabond P MD353D, ADPOLY [CM-1120]), was supplied from DuPont (USA) and Honam petrochemical Company (Korea). Seventh disperse, acidic and basic dyestuffs were supplied from CIBA Company (Switzerland, Iran – Branch). The specification of raw materials is shown in Table 1.

Table 1: Generic and commercial names of three disperse dyestuffs.

Wavelength of maximum absorption (nm)	Activation energy	Chemical structure	Chemical structure	Generic name	Commercial name
660	Medium		Anthraquinone	C.I Disperse blue 60	Terasil blue BG
460	Medium		Pyridine	C.I Disperse yellow 211	Terasil yellow 4G
520	Medium		Mono azo	C.I Disperse red 324	Terasil red R
530	Super-milling		Mono azo	C.I. Acid red 361	Tectilon red 2B
530	milling		Mono azo	C.I. Acid red 249	Polar brilliant red B
530	leveling		Mono azo	C.I. Acid red 1	Erio floxine 2GN
530	basic		azo	C.I. basic Red 51	Maxilon red M-RL

2.2. Sample Preparation

The approach for making polymer layered silicate nanocomposites was polymer melt-direct intercalation that was performed by using a conventional Brabender PL2000 plasticorder melt mixer (Germany). The variable parameters of such a mixer were set at a screw speed of 60 rpm at 180°C for 15 min. Nanocomposite films of 300 µm thickness were subsequently prepared by a Carver laboratory press (Germany) at pressure of 100 bar at 190°C. Nanoclay concentration of 3% by weight of PP was used and the ratio of nanoclay: PP-g-MA was 1:1 and 1:3.

Four different cases are considered:

(i) the effect of mixing parameters (NC1-1-to NC1-3, section 3.2.1)
(ii) the effect of molecular weight of PP and PP-g-MA (NC2-1-to NC2-8, section 3.2.2)
(iii) the effect of nanoclay types NC3-1-to NC3-3, section 3.2.3).

2.3. Dyeing

The resultant PP nanocomposites dyed to depths of shade of 1 % on the weight of the prepared films. Moreover, for comparison purposes, pure PP was dyed with the same dyestuffs at the same concentrations by using the same dyeing procedure. The commercial dyes were used without any purification and are listed in Table 2. The dyeing procedure for disperse dyes was a semi-conventional technique used for dyeing polyester at 100 $^{\circ}$C without any carriers, the liquor to goods ratio was 100:1. A pH of 5.5 was reached in each dye bath by adding 3% owf (over weight of fabric) of acetic acid supplied by Merck company (Germany). 1 gL^{-1} of the dispersing agent Invalon HTB, supplied by Ciba company (Switzerland), Iran –Branch was also added to each dye bath. Dyeing was performed by raising the initial temperature (40 $^{\circ}$C) to a final temperature (100 $^{\circ}$C) at a rate of 2 $^{\circ}$Cmin^{-1}, and holding at 100 $^{\circ}$C for 60 min.

A subsequent reduction clear procedure was performed on each sample after dyeing. This comprised of treating each sample in a solution of 2 gL^{-1} sodium hydroxide supplied by Ciba Company (Switzerland) Iran–Branch and 3 gL^{-1} sodium hydrosulfite also supplied by the same company carried out at 70 $^{\circ}$C for 20 min. Afterwards, the samples were rinsed in cold water. The dyeing conditions with acidic and basic dyes are shown in Table 2.

2.4. Sample Characterization

Wide-angle X-ray diffraction was conducted at ambient temperature on a Rigaku rotating-anode diffractometer with Cu radiation at a wavelength of 1.54 A$^{\circ}$ supplied by Philips, X'Pert (Netherlands). The accelerating voltage was 40 KV. The montmorillonite clay particles i.e. Closite 15A were measured in powder form and the nanocomposites were studied in the form of opaque films. The extents of intercalation and exfoliation of the clay were monitored by Transmission Electron Microscopy (TEM), Philips CM 120 (Netherlands). The preparation of samples for TEM was carried out by the IBB laboratory of Tehran University (Iran). Samples were scanned by TEM at an accelerating voltage of 100 KV.

Reflectance values of all dyed nanocomposites and their respective controls were obtained by using a Macbeth Color Eye 7000A spectrophotometer (Gretag Macbeth company, USA). The samples were all mounted on the same white background and the specular- in mode was selected for all measurements. All measurements were carried out on five different positions of each sample and the average value was reported. The K/S values of all samples were calculated by using the Kubelka-Munk one constant theory [17].

Table 2: The dyeing condition with acidic and basic dyes.

Basic		Acid super milling		Acid leveling		Acid milling	
1%	dye	1%	dye	1%	dye	1%	dye
2%	acetic acid	–	–	4%	acetic acid	4%	sulfuric acid
–	–	3%	Ammonium sulfate	10%	Sodium sulfate	10%	Sodium sulfate
100:1	L:G	100:1	L:G	100:1	L:G	100:1	L:G

The Kubelka-Munk K/S values were calculated by equation 1:

$$K_\lambda/S_\lambda = (1-R_\lambda)^2 / (2\times R_\lambda) \qquad (1)$$

where K_λ is, the absorption coefficient, S_λ is the scattering coefficient, and R_λ is the measured reflectance values at 10 nm intervals throughout the visible spectrum namely (360-750 nm). The corresponding K/S values at wavelength of maximum absorption (Table 2) are indicative of color yield up of the chosen dyes on dyed PP nanocomposites.

3. Results and Discussion

3.1. Microstructure Characterization

3.1.1. X-ray Diffraction Analysis

XRD can be used to estimate the degree of dispersion of nanoclays within the PP matrix through obtaining the distance between individual platelets of nanoclay. A shift to lower angles of detecting diffraction peak suggests an increase in the interlayer spacing or gallery of the nanoclay, which is referred to as intercalation [18]. Disappearance of the nanoclays interlayer diffraction peak indicates possible exfoliation of the nanoclay platelets and the broadening of the peak is considered to be the result of partial exfoliation. The degree of dispersion was measured by calculating the d-spacing from Bragg's law and is depicted in Table 3.

Table 3: XRD parameters for various PP nanocomposites.

Parameters	Sample	Peak 1 2θ (°), d-spacing (A°)	Peak 2 2θ (°), d-spacing (A°)
Effect of Mixing Parameter*	Cloisite 15A	2.80, 31.5	6.89, 12.8
	NC1-1	2.28, 38.7	4.52, 19.5
	NC1-2	2.27, 38.9	4.48, 19.7
	NC1-3	2.28, 38.7	4.48, 19.7
Effect of Molecular Weight of PP and PP-g-MA*	Cloisite 15A	2.80, 31.5	6.89, 12.8
	NC2-1	4.16, 21.2	6.25, 14.1
	NC2-2	4.20, 21.0	6.34, 13.9
	NC2-3	2.30, 38.3	4.50, 19.6
	NC2-4	2.27, 38.9	4.45, 19.8
	NC2-5	4.10, 21.5	6.30, 14.0
	NC2-6	4.03, 21.9	6.21, 14.2
	NC2-7	3.92, 22.5	6.25, 14.1
	NC2-8	3.83, 23.0	6.12, 14.4
Effect of Nanoclay Types*	Cloisite 15A	2.80, 31.5	6.89, 12.8
	NC3-1	2.28, 38.7	4.48, 19.7
	Cloisite 20A	3.80, 23.5	7.30, 12.1
	NC3-2	2.61, 34.2	4.53, 19.5
	Cloisite 30B	4.77, 18.5	-
	NC3-3	3.79, 23.3	6.17, 14.3

*preparation conditions are explained in section 3.2.1 to 3.2.3

The increased d-spacing in the resultant nanocomposites might be attributed to the presence of PP and /or PP-g-MA molecules within the nanoclay particles. Therefore, it is highly probable that during the formation of nanocomposites, PP and /or PP-g-MA molecules enter the galleries of the clay particles. Results show that intercalation has occurred in all nanocomposites because all 2θ values are lower than the nanoclay itself.

For Cloisite 15A, the interlayer spacing is calculated as d = 31.5 A° since the characteristic diffraction peak is at 2.80°. As for Cloisite 20A, d is equal to 23.5 A° at 2θ = 3.80°. The interlayer spacing of Cloisite 30B is calculated as 18.5 A°. XRD diffractograms of Cloisite 15A and 20A organoclays show two diffraction peaks. The second peak can result from a second silicate layer if 2θ is about two times of the value of the first characteristic peak of the clay. However, as observed here, this is not the case. The second peak corresponds to 12.8 A° and 12.1 A°, which is the d-spacing of unmodified Na^+ montmorillonite according to Shouthern Clay. Thus, it corresponds to the clay which is not modified by the quaternary ammonium salt. As it can be seen in Table 4, there is no significant difference between the NC1-1, NC1-2 and NC1-3 nanocomposites. The characteristic diffraction peak of Cloisite 15A shifts to lower angle for these nanocomposites. Exfoliated structures cannot be achieved by changing the mixing order of PP, PP-g-MA and nanoclay in these nanocomposites.

The nanocomposites NC2-3 and NC2-4 show the maximum increase in the interlayer spacing with respect to other NC2 nanocomposites. In these samples, the PP-g-MA has lower viscosity (higher MFI) than PP. Thus, it is thought that the PP-g-MA chains may diffuse into the interlayer spacing more easily than PP chains. Once, the d-spacing of the clay increases due to this diffusion, the PP chains may then enter between the silicate layers, especially in the ease of nonpolar clays such as Cloisite 15A.

According to Table 4, the nanocomposites containing Cloisite 15A (NC3-1) shows the maximum increase in the interlayer spacing with respect to Cloisite 20A and 30B (CN3-2 and CN3-3). This may be attributed to the more affinity between the PP and Cloisite 15A. PP and Cloisite 15A are both nonpolar, apparently PP molecules can enter between the silicate layers in this process. This affinity is lesser between PP and Cloisite 20A and 30B.

3.1.2. TEM

Transmission Electron Microscopy (TEM) is a commonly used technique for measuring clay dispersions. Figure 1 shows TEM micrographs of nanocomposites. For the PP /PP-g-MA/ Cloisite15A composites, a uniform dispersion of the clay particles in the polymer matrix was observed. It was shown that exfoliation not only depends on maximization of favorable interactions between the polymer matrix and the organically modified silicate such as Lewis-acid/base interactions or hydrogen bonding, but also on minimization of unfavorable interactions such as poor physical interactions between the polymer matrix and the alkyl chains of the organic modifier present on the silicate. This explains the need to utilize functionalized polymer with polar groups, such as PP-g-MA, to favor intercalation and exfoliation. It has been well established that an intercalated/exfoliated structure is usually formed in a PP-nanoclay system by using PP-g-MA as a compatibilizer. However, the formation of a clay network depends on connecting clay layers and tactoids [19].

In the TEM images, some aggregations of nanoclay tactoids are also detectable which indicates that the degree of intercalation in such PP/nanoclay nanocomposites (synthesized via melt compounding) is lower than that of polar polymer/ nanoclay systems in which well-defined exfoliations of clay were frequently confirmed by XRD and TEM. The lower degree of exfoliation can be ascribed to the fact that chemical miscibility and interaction between PP chains and nanoclay particles are still weak compared to polar polymer-based nanocomposites even when a compatibilizer is incorporated [20].

3.2. Dyeability

The dyeing behavior of a substrate depends on its physical and chemical structure. Regarding chemical structure, dyeability is governed firstly by the presence of polar groups which interact with water molecules and allow the substrate swelling and, secondly, by functional groups which attract dye molecules. Physical structure, enable the substrate to be accessible to water, dyestuffs and other reagents. Physically, the substrate must have the certain permeability to various reagents particularly. It must permit dyestuffs molecules to diffuse into the substrate's matrix. In PP nanocomposites, the accessibility can be improved by the introduction of particulates into its matrix [21].
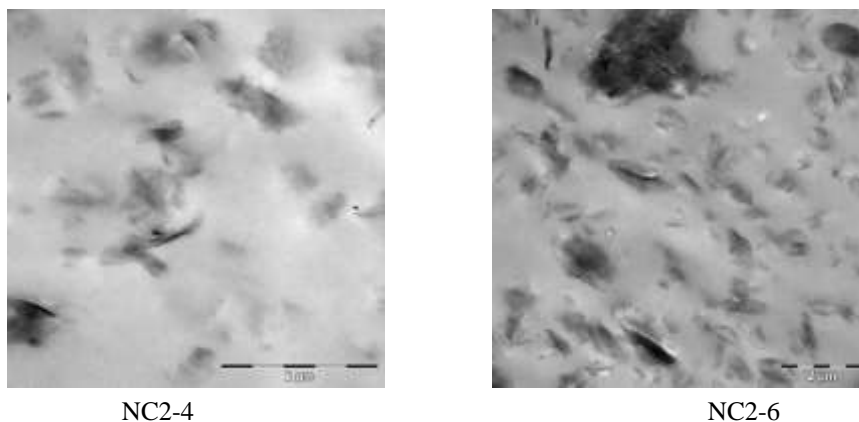
NC2-4   NC2-6

Figure 1: TEM micrographs of PP ⁄ PP-g-MA ⁄ Cloisite 15A nanocomposites.

Table 4: Color yields (K/S) of nanocomposites prepared in different ways and dyed with various disperse dyes.

Name	NC1-1	NC1-2	NC1-3
Preparation	mixing all component together	preparing master batch of nanoclay and PP-g-MA and then add PP	first mixing PP and PP-g-MA and then add nanoclay
Yellow	7.54	7.65	7.70
Red	5.37	5.52	5.81
Blue	1.38	1.15	1.01

Three different possibilities could enhance dyeability of PP nanocomposites:

1. Provision of sites within bulk of nanocomposites capable of chemical and/or physical linkage to particular dyestuffs. Therefore, nanoclays should carry or be able to develop charged or other functional groups capable of interacting with certain dyestuffs.

2- Pores and cracks may develop on the surface and or the bulk of a nanocomposite during processing. Such submicroscopic voids may allow diffusion of dyestuffs into the nanocomposite.

3- Dye diffusion may occur through a wicking process [22-24].

All the mentioned possibilities could synergistically be combined to enhance dyeing of PP nanocomposites. The greater the compatibility of clay particles within the PP matrix, the greater is the dispersion uniformity of nanoclays within such a matrix and consequently the better will be the dyeing properties of the resultant nanocomposite. Secondary forces such as Van der Waals forces may be active between disperse dye molecules and clay particles, as well as between disperse dye molecules and modified PP matrix [4]. Nanoclay had very strong sorption ability due to its high surface area and strong Van der Waals forces, as well as hydrophobic and ionic interactions with dyes. The Van der Waals forces and hydrophobic interactions were the two major forces for dye sorption onto clay and is the reason why dye sorption is better with disperse dyes comparing to acidic dyes [23].

3.2.1. Effect of mixing parameter

In this step, in order to evaluate the best way for preparing nanocomposite, three methods were suggested (Table 4). Nanocomposites were prepared by melt mixing with three methods in an internal mixer (i) mixing all components together, (ii) preparing master batch of nanoclay and PP-g-MA and then add PP, and (iii) initial mixing of PP and PP-g-MA and then adding the nanoclay. Nanoclay concentrations of 3% by weight of PP were used and the ratio of nanoclay: PP-g-MA was 1:1.

The outcomes exhibit that the preparation methods do not cause a substantial effect on dying properties

and color yield up. Therefore, the third way for preparing nanocomposite was chosen because less time and material are used in this method.

3.2.2. Effect of PP and PP-g-MA molecular weight

As it was pointed out in the literature [25], the molecular weight of the compatibilizer s associated with shear viscosity to generate enough stress to break up the stacked silicate platelets, compatibilizer diffusion, and degree of maleic anhydride on the compatibilizers are vital to facilitate the formation of exfoliated nanocomposites in a melt mixing technique. Moreover, the effect of the MA content on the clay dispersion has been studied extensively [26, 27]. However, to the authors' best knowledge; no study on the outcome of selected compatibilizers and polypropylene molecular weight (MFI) on dyeing properties of PP/clay nanocomposites by using a

melting mixing process has been done. Therefore, in order to investigate the effect PP and PP-g-MA molecular weight on dyeing properties of nanocomposite, two types of compatibilizer and PP were chosen to facilitate the nanocomposites with various combinations of PP and PP-g-MA and with several ratios of PP-g-MA (Table 5 and Figure 2).

Results indicate that the best dyeing result happens in nanocomposite with both lower molecular weights of PP and PP-g-MA. Since using the lower molecular weight of PP and PP-g-MA causes better dispersion of nanoclay in a polymer matrix and prepare more paths for dye penetration. Therefore, PP and PP-g-MA with higher MFI or lower molecular weight prepare nanocomposite with better dyeability. The results also indicate that the ratio of nanoclay and PP-g-MA does not touch on the dyeing properties, therefore, the ratio of 1:1 was chosen.
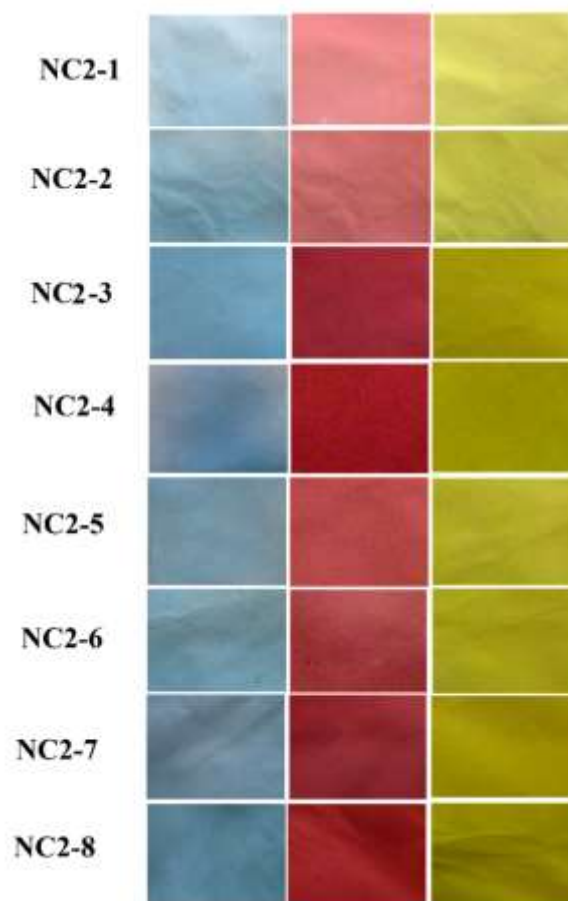
Figure 2: Images of nanocomposites prepared with different PP and PP-g-MA and dyed with various disperse dyes.

Table 5: Color yields (K/S) of nanocomposites prepared with different PP and PP-g-MA and dyed with various disperse dyes.

Name	PP MFI	PP-g-MA MFI	PP-g-MA (%)	Red	Yellow	Blue
NC2-1	18	50	1	2.27	2.73	0.70
NC2-2	18	50	3	2.39	3.22	0.57
NC2-3	18	450	1	5.20	7.81	1.01
NC2-4	18	450	3	6.63	8.66	1.15
NC2-5	1.8	50	1	2.77	3.44	0.74
NC2-6	1.8	50	3	2.61	3.59	0.84
NC2-7	1.8	450	1	3.32	4.93	0.74
NC2-8	1.8	450	3	3.54	5.95	0.81

3.2.3. The effect of nanoclay types

As it was indicated in previous authors' works [4], PP disperse dyeing was improved when clays were incorporated in the nanocomposite. In order to illustrate the mechanisms of dyeing improvement with clay nanoparticles within two proposed mechanisms of creating a path and creating an absorption site, various types of nanoclay and dyes were used to dye PP nanocomposite (Table 6 and Figure 3). The results show that better dispersion of nanoclay (for example, in the case of Closite 15A) causes creating more paths to cross the dye and consequently, the color build up and dyeability increases. In other words, results demonstrate that a direct relationship between the dispersion and the color build up with the increase in exfoliation greater improvement in dyeing can be realized. So, between the two mechanisms suggests for dyeing improvement in PP/clay nanocomposite, it seems that the predominant mechanism is creating the route; however, it is necessary to examine more samples with different dyes.

3.2.4. The effect of dyes

To illustrate the dyeing mechanism, nanocomposites were dyed with different dyes (acid leveling, acid Super milling, acid milling, and basic dye). Thus, in the case of adsorption sites mechanism, the dyeing behavior and color build up are different with various dyes in the presence of various nanoclays with different sites for dye adsorption. The results (Table 7) show that despite the negative site of all acidic dyes and positively charged nanoclay Closite 15A, 20A color yields up is very low, indicating a lack of affinity of acidic dye for nanoclay. Other researchers also investigated the dyeability of PP /Closite 15A nanocomposite with acidic dye which showed similar results [23]. This phenomenon is also occurred for basic dye and Closite 30B. In other words, low color yields up for all types of nanoclay with various dyes represent the possibility of absence of site adsorption mechanisms for the dyeing.

In order to perform a better investigation on the possible absorption mechanism, nanocomposite with various amounts of Closite 15A was dyed with acid Super milling dye. The results (Table 8) reflect the fact that even in a high percentage of nanoclay, acidic dye uptake and color buildup is very low and the possibility of the site of absorption in the presence of nanoclay is almost eliminated.

Table 6: Color yields up (K/S) of nanocomposites with different types of nanoclay dyed with various disperse dyes.

Name	PP	NC3-1	NC3-2	NC3-3
	-	Closite 15A	Closite 20A	Closite 30B
Blue	0.04	1.01		0.76
Red	0.39	5.20		2.14
Yellow	0.03	7.70		4.87
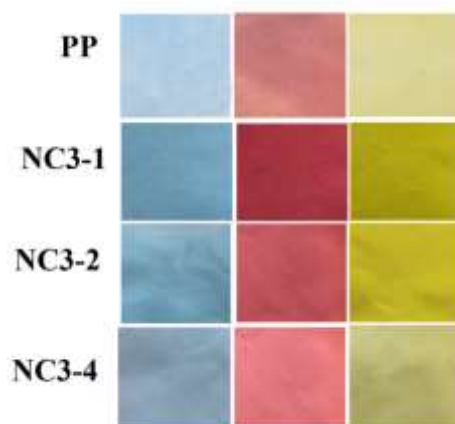
Figure 3: Images of nanocomposites with different types of nanoclay dyed with various disperse dyes.

Table 7: Color yields up (K/S) of nanocomposites with different types of nanoclay dyed with various dyes.

Name	PP	NC4-1	NC4-2	NC4-4
	-	Closite 20A	Closite 30B	Closite 15A
Super milling	0.04	0.07	0.04	0.18
milling	0.03	0.06	0.05	0.08
leveling	0.03	0.03	0.04	0.05
basic	0.04	0.06	0.09	0.07

Table 8: Color yields up (K/S) of nanocomposites with various amounts of Closite 15A dyed with acid super milling dye.

Name	PP	NC4-1	NC4-2	NC4-3	NC4-4	NC4-4
	-	1%	3%	5%	7%	10%
acid super milling	0.04	0.05	0.18	0.11	0.22	0.50

4. Conclusion

An intercalated thermoplastic PP/clay nanocomposite was prepared by using maleic anhydride functionalized PP as a compatibilizer in various ways with low and high molecular weights. Prepared nanocomposites with various types of nanoclay are dyed with various types of dyes to investigate the mechanism of dyeability of PP/Clay nanocomposite. The outcomes demonstrate that the mixing condition has not significant effect on dyeability and lower molecular weight Polypropylenes and compatibilizer caused better durability. The most intercalated nanocomposite prepared with Cloiste 15A also showed better dyeability with all types of dyes. Although higher buildup (K/S ~ 8) was observed with disperse dyes, between the two mechanisms suggests for dyeing improvement in nanocomposite it seems that the dominant mechanism is creating the path.

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How to cite this article:

M. M. Salehi, M. Ataeefard, S. Moradian, The Effect of Nanoclay, PP and PP-g-MA Type on Properties of PP/clay Nanocomposite: A Way to Investigate the Dyeability Mechanism, Prog. Color Colorants Coat., 10 (2017), 73-84.