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Production of POSS nanoparticle containing polypropylene fibres dyeable with acid and basic dyes

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Acid and basic dyeable polypropylene (PP) fibres have been produced with the inclusion of polyhedral oligomeric silsesquioxane (POSS) nanoparticles via melt spinning technique. Octa ammonium POSS (OA-POSS) and tris sulfonic acid ethyl POSS (SA-POSS) have been used for the modification of PP fibre. The tensile, thermal and morphological properties of the fibre samples are characterized by tensile testing, differential scanning calorimeter and scanning electron microscopy respectively. The effects of dye concentration, dyeing temperature and time are investigated on the dyeability properties of the fibre samples. The wash fastness of fibre samples is also studied. It is observed that the addition of OA-POSS and SA-POSS increases the dyeability of PP fibre with appreciable mechanical properties. Both POSS nanoparticles increase the dyeability of PP fibre by increasing ion-ion interaction.

Keywords: Acid dyes, Basic dyes, Fibre, Nanoparticles, Melt spinning, Polyhedral oligomeric silsesquioxane, Polypropylene

1 Introduction

Polypropylene (PP) fibre is widely used with or without other textile fibres in upholstery fabrics, carpet industry and other industrial sectors. The inherent properties including non polar character, high crystallinity and high stereo-regularity of PP fibre hinder dyeability with conventional dyeing techniques. Accordingly, PP is dyed commercially during melt spinning with the inclusion of organic and inorganic pigments. The mass coloration of PP fibres during spinning limits the wider application and the number of available shades[1,2].

Different physical or chemical modifications have been applied to increase the dyeability of PP fibres especially with disperse dyes[3]. Both modifications depend on the basis of introducing dye receptor sites and/or enhancing molecular diffusion into the PP fibre. Physical modification can be achieved basically with the inclusion of additives such as polyamide-6[4,5] hyper branched polymers[6,7] and nano clay during melt spinning[8-13]. Although no study has been conducted on the efforts made to increase the dyeabilty of PP fibre with cationic dyes, limited number of studies have been done to increase the dyeability of PP fibres by anionic dyes with the inclusion of nano clay, amine modifiers (polyamide 6, polyether amine), styrene amine resin[10,13,14], etc. The basic logic used in these studies is to introduce basic dye sites which interact with anionic dyes in the PP fibre.

Polyhedral oligomeric silsesquioxanes (POSS) bearing different functional groups on their outer surface have been used for different purposes in polymer and textile industries[15,16]. In previous studies, the mechanical and the flame retardant properties of textile fibres were improved with the addition of POSS nanoparticles during melt spinning[17,18].

The aim of this study is to produce acid and basic dyeable polypropylene (PP) fibres using POSS nanoparticles. In this study, two different POSS nanoparticles, octa ammonium POSS (OA-POSS) and tris sulfonic acid ethyl POSS (SA-POSS), have been used to increase the dyeability of PP fibre with acid and basic dyes respectively. The effect of parameters such as dyeing temperature, dyeing time and dye concentration on dyeing behaviour of PP fibre are also examined.

2 Materials and Methods

2.1 Materials

Polypropylene (Petoplen EH-251) with a melt flow index (MFI, 2.16 kg, 230 °C) of 20-28 g/10 min was obtained from PETKIM A.Ş in Turkey. OA-POSS and SA-POSS were purchased from Hybrid Plastics Inc. (Hattiesburg, the USA). OA-POSS and SA-POSS are found in the form of white powder and viscous liquid respectively (Fig. 1). Acid Red 357 was purchased from SUM-PA (Istanbul, Turkey). Basic

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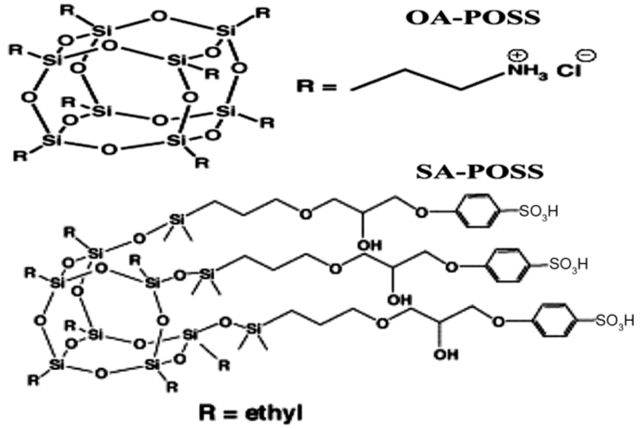

Fig. 1─Chemical structures of POSS nanoparticles

Red 14 was purchased from Alfa Kimya (Istanbul, Turkey). Analytical grade acetic acid was purchased from Sigma Aldrich.

2.2 Preparation of Monofilament PP Fibres

Polypropylene was dried at 80 ºC for 8 h before the fibre spinning process. The mixing of PP with POSS nanoparticles (1 wt %) was done in a twin screw microextruder (15 mL microcompounder®, DSM Xplore) coupled with winding a unit (DSM Xplore) at 100 rpm and 230 °C. After mixing was complete, the twin screw extruder was brought to force controlled mode, which ensures a uniform polymer melt flow. The diameter of the die was 0.25 mm. The spinning speed was 200 m/min. After the spinning process, as-spun monofilaments were obtained with varying diameters of 55-60 µm for PP fibre. No additional cooling was applied to the extrudate except for the ambient conditions (25 °C). The as-spun fibres were drawn at 130 °C with a draw ratio of 4.

2.3 Dyeing Procedure

All dyeing processes were carried out according to the exhaustion technique in a laboratory type dyeing machine (Termal, Turkey) at a liquor ratio of 1:20 at *p*H 5.5. Samples were washed with Sandoclean PC at a concentration of 0.5 g/L and temperature of 80 °C for 10 min and then rinsed at 70 °C for 10 min. The general representation of the dyeing procedure is shown in Fig. 2.

To optimize dyeing conditions, pristine PP and modified PP fibre samples were dyed at a constant dye concentration (3 % owf) with varying dyeing temperature (20-120 °C) and time (10-60 min). The other parameter, namely dye concentration (1, 3 and 5 % owf) was examined at optimized dyeing temperature and time.

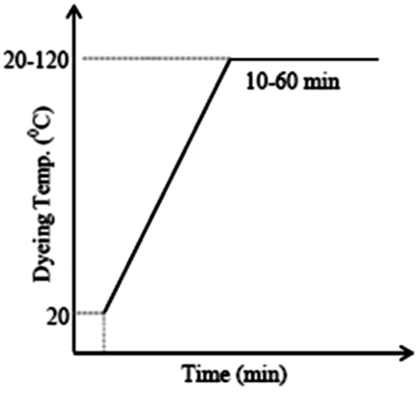

Fig.2─General dyeing procedure

2.4 Characterization Methods

The measurement of the tensile properties of the monofilaments was carried out following the standard ASTM D 3822 on Shimadzu AG-X tensile testing machine with a load cell of 10 N. Differential scanning calorimeter (DSC) analyses were carried out on Perkin Elmer Diamond at a heating rate of 10 ºC/min up to 200 °C under a nitrogen flow of 50mL/min.

The surface morphology of the fibre samples was examined with scanning electron microscopy (SEM) (LEO 440 computer controlled digital, 20 kV). All specimens were sputter-coated with Au/Pd before examination.

The color strength (*K*/*S*) values of the samples were measured using a spectrophotometer (Minolta 3600d, Japan) coupled to a PC under D65 illuminant/10° observer with a specular component included. The reflectance measurements expressed as *K*/*S* value were determined by the Kubelka-Munk equation. The transmittance measurement of the dyebath was determined by using UV- spectroscopy T 70 (PG Instruments Ltd., England) spectrophotometer at maximum absorption peak occurring at 510 nm and 520 nm for acid dye and basic dye respectively. The correlation coefficient (R^2) of calibration curves for acid and basic dyes were 0.9816 and 0.974344 respectively. The dye uptake was calculated as follows:

$$\text{Dye Uptake} = [C_0 - C)/C_0] \times 100$$

where C_0 and C (mg/L) are the concentrations of the dye in the solution before and after the adsorption respectively.

Differential scanning calorimetric analyses were carried out on Perkin Elmer Diamond at a heating rate of 10 °C/min up to 200°C under nitrogen a flow of

50 mL/min. DSC analyses were performed on the PP and modified PP fibre samples in order to determine the melting point (T_m) and Xc values. The Xc values of the fibre samples can be determined from the following equation:

$$Xc\ (\%) = [\Delta Hc / (1-\Phi) \times \Delta H^{o}m] \times 100.$$

where ΔHc is the measured enthalpy of crystallization; ΔH^{o}m, the enthalpy of 100 % crystalline PP (209 Jg^{-1}); and Φ , the weight fraction of POSS nanoparticle in the fibre.

The wash fastness of the fibre samples was tested using the method given in ISO 105 C06 B1S19.

3 Results and Discussion

3.1 Morphological Analysis

The SEM images of pristine PP fibre and POSS modified PP fibre samples at a magnification of ×2500 are shown in Fig. 3. The pristine PP has a smooth surface and the inclusion of SA-POSS, which in the viscous liquid form does not deteriorate the surface smoothness. OA-POSS containing fibre sample contains agglomerations protruding through its surface. These protuberances deteriorate the surface smoothness.

3.2 Tensile Properties

Tensile tests on the monofilament fibre samples have been done to investigate the effect of POSS nanoparticles on the mechanical properties of the fibres. Stress at break values (σ) and elongation at break values (ε) are listed in Table 1. The incorporation of OA-POSS nanoparticle causes reduction in both σ and ε values due to the formation of agglomerates (Fig. 3). It is thought that the physical form of SA-POSS at mixing temperature (viscous liquid) hinders the formation of agglomerates and favors the dispersion in PP matrix. Hence, addition of SA-POSS does not deteriorate the mechanical properties of PP fibre.

3.3 DSC Analysis

One of the parameters that affects the dyeability of synthetic fibres is the % crystallinity (Xc). It is known that the dye molecules diffuse into the amorphous region of synthetic fibres[7,20]. The higher crystallinity of the fibres causes the lower dyeability of synthetic fibre[1]. Accordingly, DSC analyses are performed on PP and POSS modified fibre samples in order to determine the melting point (T_m) and Xc values. The DSC data of the fibre samples are listed in Table 1. The addition of OA-POSS slightly reduces T_m and Xc of PP fibre. As stated before OA-POSS tends to form

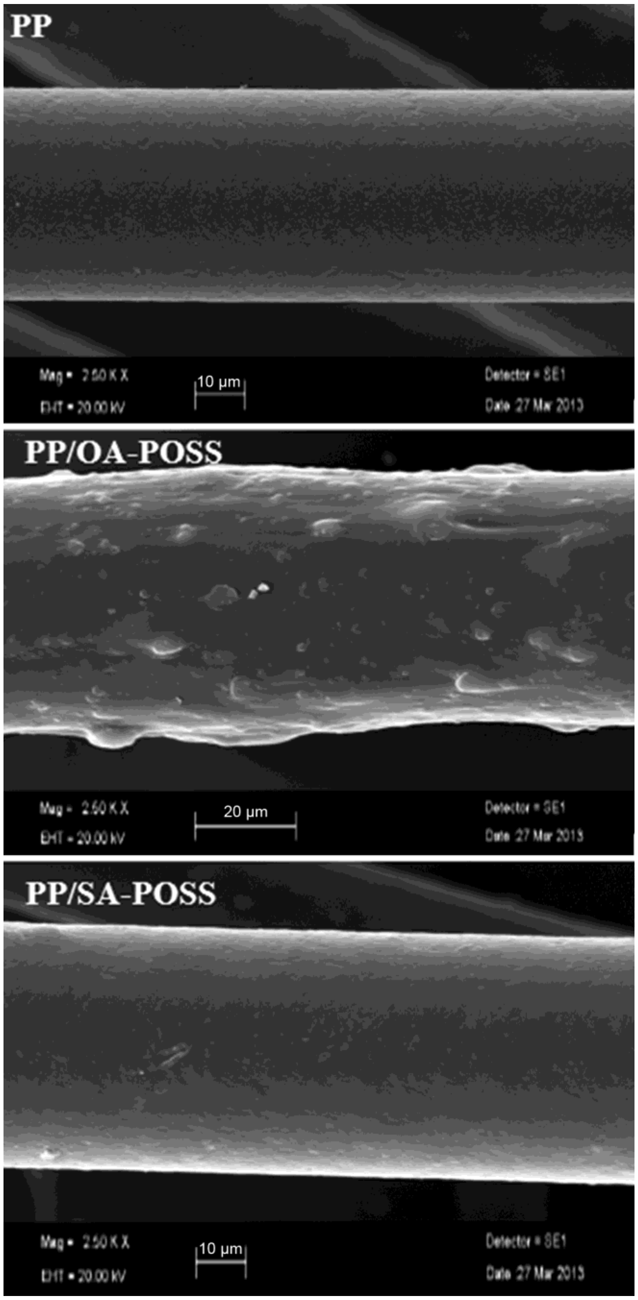

Fig. 3—SEM images of fibre samples at a magnification of ×2500

Table 1—Tensile and DSC data of fibre samples

Sample	σ, MPa	E, %	T_m, °C	Xc, %
PP	33.1±1.7	85±21	163.0	39.6
PP/OA-POSS	27.3±1.1	62±17	161.5	36.8
PP/SA-POSS	31.2±1.2	74±15	163.1	38.7

σ—stress at break, ε—% strain at break , T_m—melting point, Xc—% crystallinity.

agglomerates and these agglomerates may interfere the crystallization and reduce the T_m and Xc values. With the addition of SA-POSS, the T_m and Xc values do not change significantly with respect to the pristine PP fibre.

3.4 Optimization of Dyeing Temperature

In order to determine the effect of dyeing temperature on the *K*/*S* values of fibre samples, pristine PP and POSS containing fibre samples have been dyed at varying temperature between 20 and 120 °C with the increment of 20 °C at a constant dye concentration (3 % owf) and dyeing time (40 min). The *K*/*S* values versus temperature graphs of the dyed samples are shown in Fig. 4. The *K*/*S* value of pristine PP fibre does not change significantly with increasing dyeing temperature due to the lack of active dye sites for acid and basic dyes. As the dyeing temperature increases, the *K*/*S* values of both modified fibre samples increase up to a certain dyeing temperature due to the fibre swelling which promotes dye migration in fibre structure.

The *K*/*S* values of the OA-POSS containing fibre samples increase up to 80 ^{o}C and reduce with further increment in dyeing temperature due to the migration of OA-POSS nanoparticles into the dyebath. As the temperature increases, the amorphous regions of the PP fibre become loose and the migration of the OA-POSS nanoparticle to the dye bath increases. In order to show the migration of the OA-POSS nanoparticle, the OA-POSS containing fibre sample is steeped in hot water (80 °C) for 24 h. The SEM images of the OA-POSS containing fibre sample at a magnification of ×1000 before and after treatment are shown in Fig. 5. The surface of the OA-POSS containing fibre has many more protrusions and much rougher appearance after treatment.

The *K*/*S* value increases with increasing dyeing temperature for SA-POSS containing PP fibre samples up to 100 °C and remains almost the same with the further increment of temperature to 120 °C. In contrast to the OA- POSS containing fibre sample, no reduction in *K*/*S* value is observed in the SA-POSS containing PP fibre throughout the whole dyeing temperatures due to the water insoluble character of SA-POSS. Accordingly, the optimum dyeing

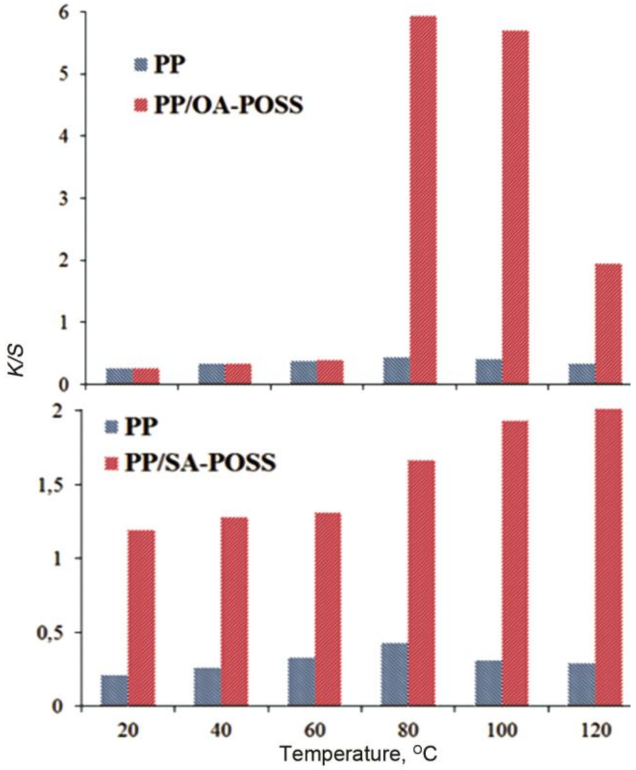

Fig. 4─Effect of dyeing temperature on *K*/*S* values

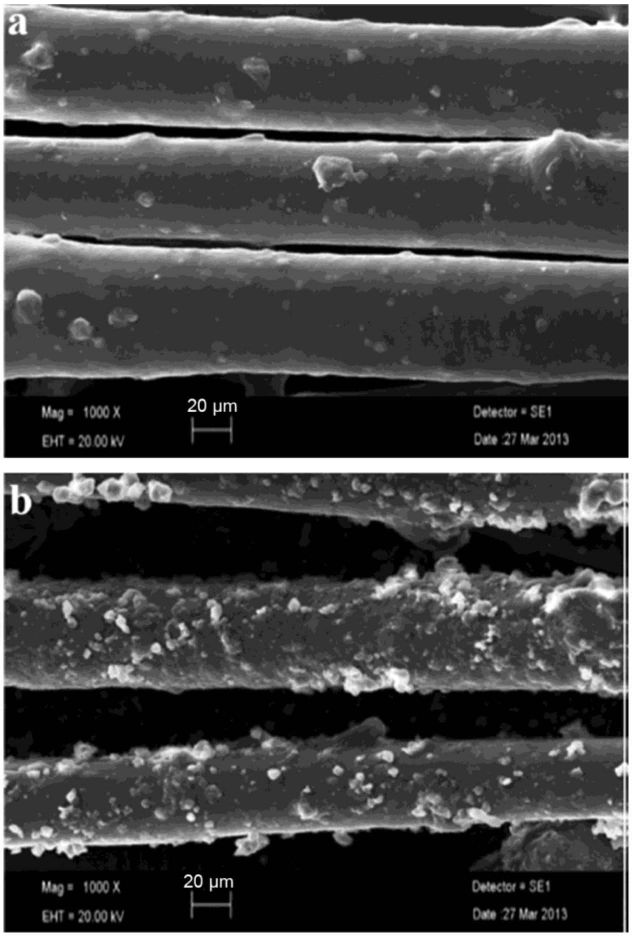

Fig. 5─SEM images of OA-POSS containing fibre sample before (a) and after (b) treatment temperatures are found to be 80 °C and 100 °C for acid dye and basic dye respectively.

3.5 Effect of Dyeing Time on Dye Uptake

The dye uptake values of the related fibre samples are calculated from the calibration curve and are given in Fig. 6. Acid dyes bearing one or more sulfonate groups are water soluble and behave with an anionic character in the dye bath. It is known that the substantivity of acid dyes towards the textile fibres arises primarily from ion –ion attractions[1]. In order to favor the ion-ion interaction between acid dye and PP fibre, a cationic group bearing POSS nanoparticle (OA-POSS) containing PP fibre is produced. The dye uptake values of the OA-POSS modified fibre samples are higher than those of pristine PP fibre due to the increment of ion-ion interaction between the OA-POSS nanoparticle and the dye molecule.

Basic dyes are also water soluble and have cationic character either localized on one atom or delocalized over the entire dye molecule[1]. An anionic group bearing POSS nanoparticle (SA-POSS) containing PP fibre is produced to favor the ion-ion interaction between basic dye and PP fibre. Although both modified fibres contain same amount of the POSS nanoparticle by mass, the dye uptake value of the OA-POSS containing fibre is higher than that of the SA-POSS containing one. The difference in the dye up take values of both modified fibres may arise from the number of active dye sites. When the molecular weights of POSS nanoparticles are considered, the number of the OA-POSS (1173 g/moL) molecules is higher than that of the SA-POSS (1634 g/moL) molecules. In addition, the number of available dyes sites per OA-POSS molecule is higher than that of SA-POSS molecule (Fig. 1). The dye uptake value sharply increases up to 30 min and a negligible increase is observed from 30 min to 60 min for both modified PP fibres. Accordingly, the optimum dyeing time is taken as 30 min for further studies.

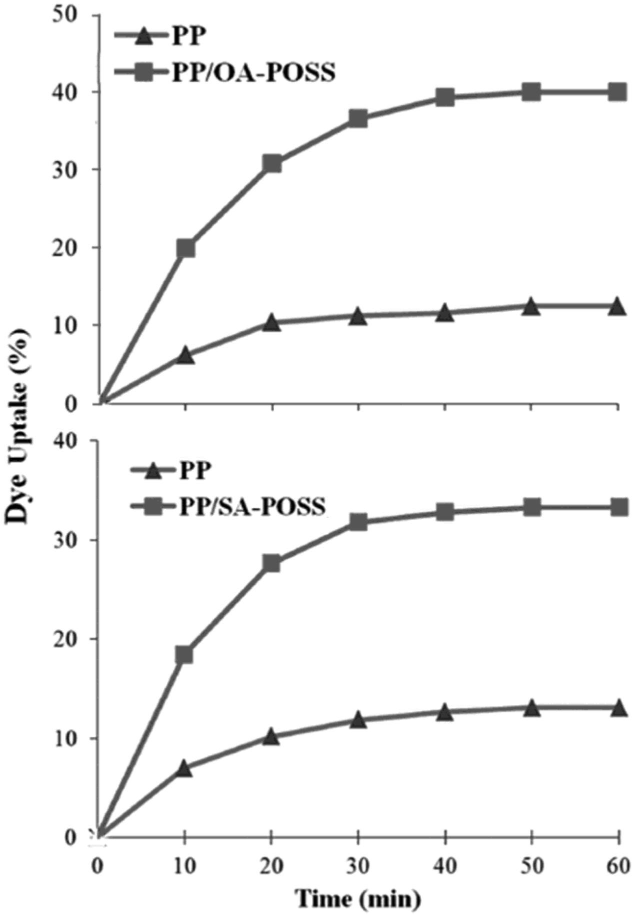

Fig. 6—Effect of dyeing time on dye uptake values of selected fibre samples

3.6 Effect of Dye Concentration on *K*/*S* Values

The effect of dye concentration on the *K*/*S* values is shown in Fig. 7. The *K*/*S* value of pristine PP fibre

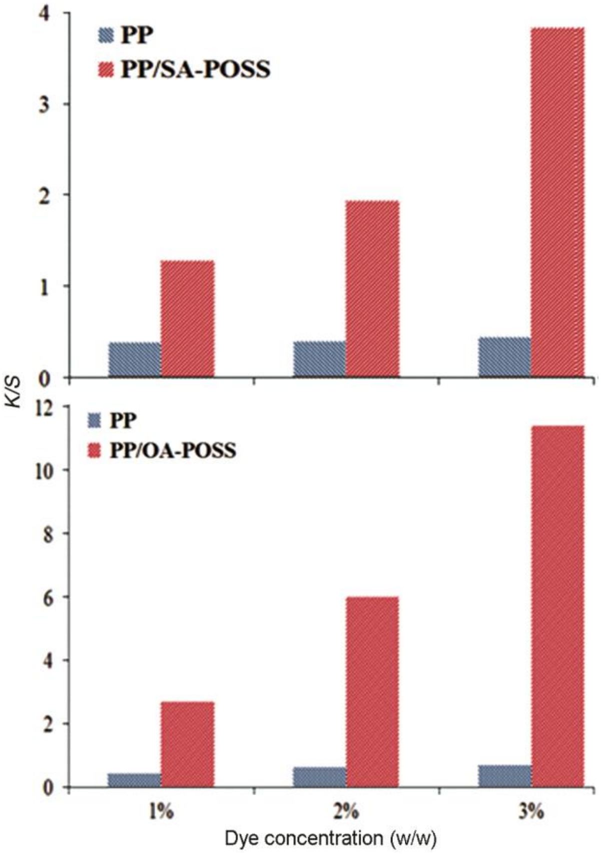

Fig. 7—The effect of dye concentration on *K*/*S* values of fibre samples

Table 2—Wash fastness properties of fibre samples

Sample	Shade	Staining on					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
PP (Acid dye)	4-5	4-5	5	4-5	5	5	4-5
PP/OA-POSS	2-3	3-4	4	2/3	4	4	3
PP (Basic dye)	4-5	4-5	5	4-5	4-5	4-5	5
PP/SA-POSS	3	4	4	4	4	3-4	4

does not change with increasing dye concentration for both dyes. The number of dye molecules interacting with available dye sites in the modified PP fibres increases as the dye concentration increases. Thus, the *K*/*S* values of both modified fibres increase with the increment of dye concentration.

3.7 Fastness Properties

The wash fastness of PP and POSS containing PP fibres are shown in Table 2. The acid and basic dyed pristine PP fibres have better wash fastness than the POSS modified fibres samples due to low dye uptake. The wash fastness in terms of change in shade for both modified PP fibres is moderate due to the water soluble character of both dyes.

4 Conclusion

In this study, it has been aimed to improve the dyeability of PP fibre with acid and basic dyes using anionic and cationic groups bearing POSS nanoparticles. It is observed from SEM images that the SA-POSS uniformly disperses into the PP matrix, whereas the OA-POSS containing fibre sample has agglomerations protruding through its surface. Although the addition of OA-POSS deteriorates the mechanical properties of PP fibre, the inclusion of SA-POSS does not change the mechanical properties of the PP fibre. The melting point (T_m) and % crystallinity (Xc) values of the modified fibre samples are almost close to pristine PP fibre. OA-POSS and SA-POSS nanoparticles are very effective for improving the dyeability of PP fibre with acid and basic dyes at low POSS nanoparticle and dye concentrations. It is believed that this study introduces a new approach to improve the dyeability of PP fibre.

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