

## MORPHOLOGICAL, THERMAL, MECHANICAL AND SOLVENT UPTAKE OF CLAY/NYLON 6,6 COMPOSITES

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### ABSTRACT

Clay/nylon 6,6 nanocomposites were prepared via solution casting technique. Kaolin clay was used as filler in polymer matrix. The morphological study presented that clay particles were dispersed and embedded well in nylon 6,6 matrix. The thermal stability of the clay/nylon 6,6 nanocomposites (20-50 °C) were higher than neat nylon 6,6 polymer. The polarized optical microscopy (POM) analyses showed that the spherulites size of clay/nylon 6,6 nanocomposite reduced highly as compare to neat nylon 6,6. The decrease in size of spherulites after loading the clay is might due to nucleation effect of kaolin clay in the nylon 6,6 polymer. The mechanical properties of nanocomposite were decreased as increased kaolin amount. The solvent uptake study presented that the nanocomposite uptake was low as compared to neat nylon 6,6. It was also found that the solvent uptake decreased as increased the amount of kaolin in nylon 6,6.

**Key words:** Clay, Nylon 6,6, spherulites, Composites

### INTRODUCTION

Polymer/clay nanocomposites have attracted great interest at industrial as well as at academic level. This is due the fact that incorporation of a small amount of clay to the polymeric matrix greatly improved materials properties in comparison with neat polymer or conventional composites (like polymer/polymer blend). These remarkable improvements in material properties include higher stiffness, increased strength, increase heat resistance, decreased gas permeability and flammability. Clay filling also increased biodegradability of biodegradable polymers [1-7]. Madakbas et al [8] reported that the Glass-transition temperatures and dielectric conductivity of the clay/ polypyrrole composite was higher than neat polypyrrole. Clay is a natural, fine-grained mineral formed by geological weathering of the surface of the earth. Clay minerals are chemically hydrated aluminosilicates, with two basic structural units, a silica tetrahedron and an alumina octahedron. These minerals are adapted to the field of nanocomposites as a reinforcement material with polymers due to their small particle size and intercalation property [9]. Clay particles having particle size of few nanometer, when properly dispersed in the polymer matrix gives a unique combination of material properties. This high degree dispersion makes polymer/clay nanocomposite suitable for making coatings and films for a variety of industrial applications [10,11].

Nylon 6,6 is a polyamide polymer of hexamine and adipic acid. These polyamide 6,6 (PA 6,6) are use as engineering plastic because of their advance mechanical properties and good processability. The only problem which limits the application of PA 6,6 is flammability and limit thermal stability. Exfoliation of organoclays in nylon 6,6 matrix can improve barrier and flame retardant properties and these nanocomposites have been in use in the automobile industry [12-14].

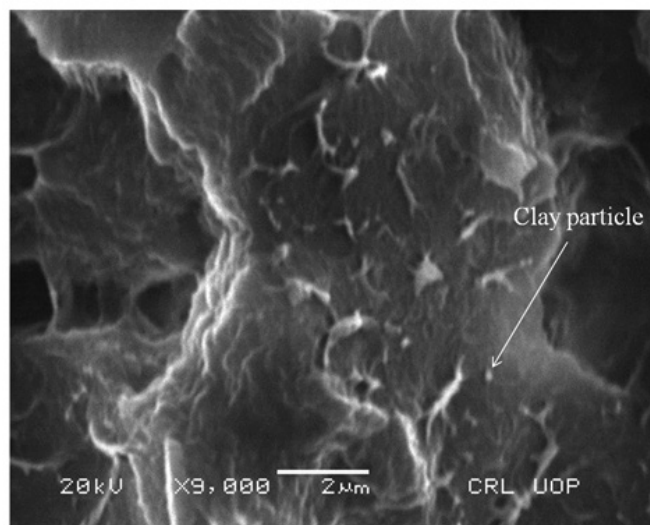
In the present study we used kaolin clay is a reinforcement material for nylon 6,6. Kaolin is named after Kau-Ling, a hill near Jau-chau Fu (China) where it was first mined and thus also called china clay [15]. Kaolin mainly consists of a 1:1 clay mineral kaolinite (85–95%) along with quartz and mica. Molecular formula common to kaolinite group (kaolinite, nacrite, dickite) is  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  [16]. Kaolin clay up to 15 wt% is incorporated to nylon 6,6 via solution casting method and its effect on crystallization, morphology, mechanical and thermal properties on the polymer is studied. After preparation of clay/nylon 6,6 nanocomposites various techniques like scanning electron microscopy (SEM), thermo gravimetric analyzer (TGA), Differential thermal analysis (DTA), Polarized optical microscopy (POM) Instron (for mechanical properties) were used for characterization.

### RESULTS AND DISCUSSION

#### Morphological study of nylon 6,6 and clay/nylon 6,6 nanocomposites

The effect of kaolin clay on the morphology of nylon 6,6 was studied using SEM. Figure 1 show SEM image of 5 wt% clay/nylon 6,6 nanocomposites. The fracture surface (broken in liquid nitrogen) of 5 wt% clay/nylon 6,6 nanocomposite possess some bright spotted regions. These spotted regions represent the presence of clay particles in the polymer matrix. The SEM

micrograph also confirm that clay particles are dispersed in the nylon 6,6 polymer matrix.



**Figure 1:** SEM micrographs of 5 wt% clay/nylon 6,6.

The crystallization pattern of neat nylon 6,6 and 5 wt% clay/nylon 6,6 nanocomposites was studied with POM. Figure 2 (a) and (b) show POM images of neat nylon 6,6 and 3 wt% clay/nylon 6,6 nanocomposites, respectively. The size of spherulites decreases enormously in the case of clay/nylon 6,6 nanocomposite as compare to neat nylon 6,6. The decrease in size of spherulites after loading the clay is due to nucleation effect of kaolin clay in the nylon 6,6 polymer.

#### Thermal properties of nylon 6,6 and clay/nylon 6,6 nanocomposites

The effect of kaolin clay on the degradation temperature and thermal stabilities of the nanocomposites was determined using TGA. Figure 3 show TGA curves for neat polymer, 3 and 15 wt% clay/nylon 6,6 nanocomposites. Figure 3 also show that there is no weight loss in all samples up to 380 °C. The TGA curves start dipping down from 380- 510 °C, showing weight loss in this temperature range. The degradation of neat nylon 6,6 started at about 380 °C and completed at about 460 °C. Clay/nylon 6,6 nanocomposite show slight resistance to degradation (30-50°C higher than neat polymer) as compared to neat nylon 6,6. The TG curve of 3 wt% clay/nylon 6,6 nanocomposites showed that the degradation started from 390 and completed at about 495 °C. While in the case of 15 wt% clay/nylon 6,6 nanocomposites, the TG curve start dipping from 400-510 °C. Similarly, the Orellana et al reported that the thermal stability

of polypropylene matrix was increased by the addition of silica, alumina and titania nanoparticles [17].

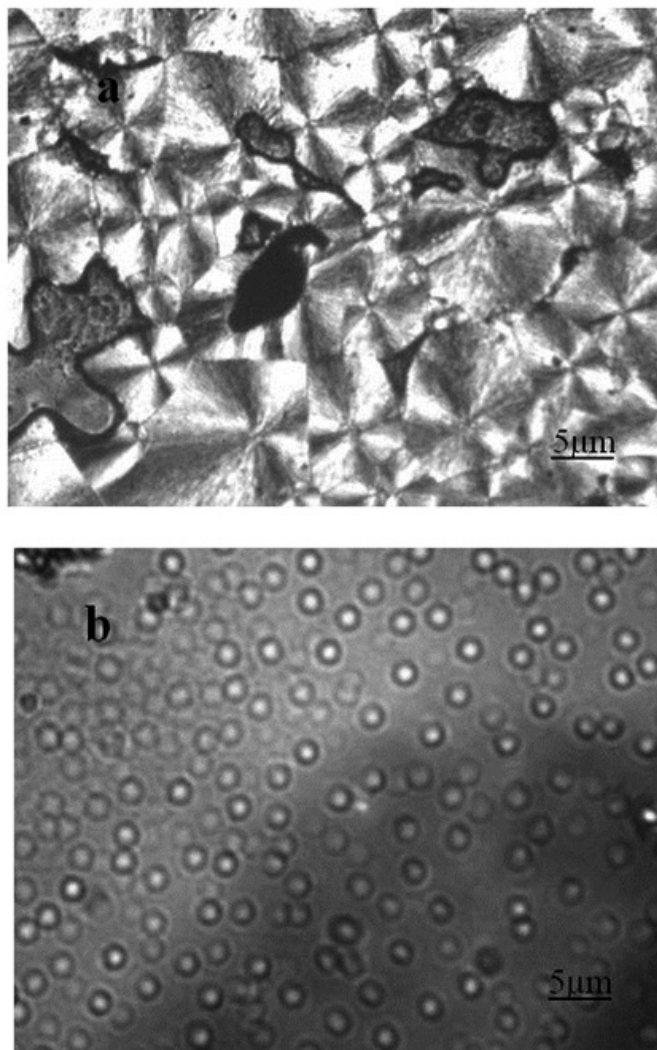


Figure 2: POM images of (a) neat nylon 6,6 and (b) 5 wt% clay/nylon 6,6.

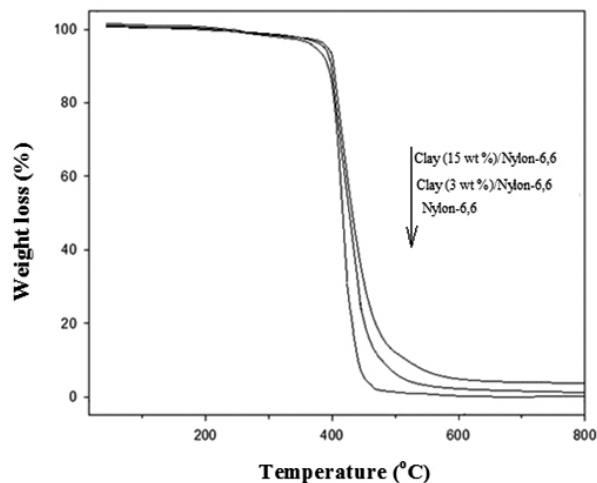


Figure 3: TGA thermograms of neat nylon 6,6, 5 and 15 wt% clay/nylon 6,6 nanocomposites.

The DTA scan of neat nylon 6,6, 3 and 15 wt% clay/nylon 6,6 nanocomposites shows distinct endotherms (figure 4). A single broad melting endotherm around 250 – 290 °C represents two stable crystalline polymorphic phases (monoclinic  $\alpha$ - phase and  $\gamma$ - phase) of nylon 6,6. These phases arise as a result of transformation due to intermolecular hydrogen bonding [18]. This transformation is prevented by clay filling and a weak endothermic peak was observed for clay/nylon 6,6 nanocomposites. Two small endothermic peaks around 450 – 510 °C represent a two stage degradation process [19]. Incorporation of clay reduced degradation temperature and thus these endothermic peaks are shifted to slightly lower temperature in clay/nylon 6,6 nanocomposites. The height of peaks increase gradually as the clay content increased. The stronger endothermic peaks for 15 wt% clay/nylon 6,6 around 250 °C and 430 °C is due to the fact that the interaction between clay and polymer results more stable morphology by heterogeneous nucleation mechanism of the induce silicate crystal [20].

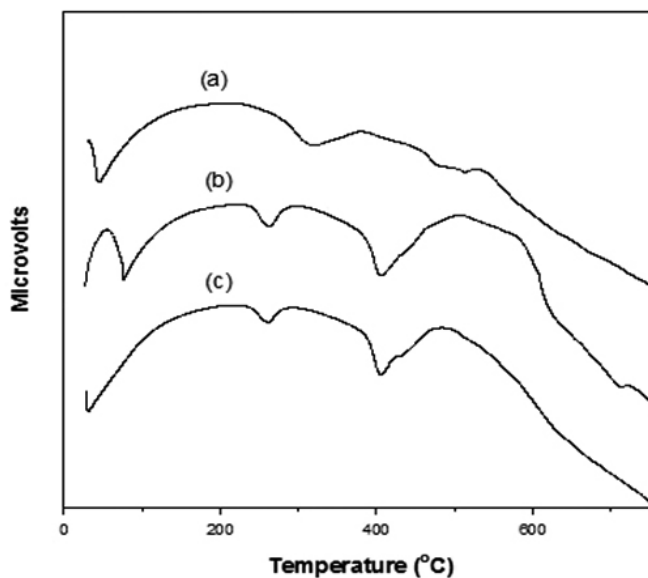


Figure 4: DTA curves of (a) neat nylon 6,6, (b) 5 wt% clay/nylon 6,6 and (c) 15 wt% clay/nylon 6,6 nanocomposites

#### Mechanical properties of neat nylon 6,6 and clay/nylon 6,6 nanocomposites

Table 1 shows mechanical properties of neat nylon 6,6, 3, 10 and 15 wt% clay/ nylon 6,6 nanocomposites. The tensile stress and modulus of neat nylon 6,6 of 1.6 and 172 N/mm<sup>2</sup>. While the mechanical properties of the clay/ nylon 6,6 composites was decreased gradually as increased the clay content in polymer matrix. The tensile stress values decreases from 1.6 N/mm<sup>2</sup> (neat nylon 6,6) to 0.94 N/mm<sup>2</sup> (15 wt% clay/nylon 6,6) and modulus values decreases from 172N/mm<sup>2</sup> (neat polymer) to 79 N/mm<sup>2</sup> (15 wt% clay/polymer composites). The decrease in mechanical properties in the case of clay/nylon 6,6 composites is might be due to the less compatibility between the clay and nylon 6,6.

Table 1: Mechanical properties of neat nylon 6,6 and clay/nylon 6,6 nanocomposites.

Samples	Stress Yield (N/mm <sup>2</sup> )	Young Modulus (N/mm <sup>2</sup> )
Neat nylon 6,6	1.6 ± 0.3	172.4 ± 3.1
5 wt% clay/nylon 6,6	1.4 ± 0.2	110.3 ± 21.4
10 wt% clay/nylon 6,6	0.93 ± 0.04	84.2 ± 12.2
15 wt% clay/nylon 6,6	0.94 ± 0.3	79.9 ± 33.6

#### Solvent uptake study of neat nylon 6,6 and clay/nylon 6,6 nanocomposites

The solvent uptake of neat nylon 6,6 and clay/nylon 6,6 nanocomposites were studied in solvents like distilled water, chloroform, 2M HNO<sub>3</sub> and

Kerosene oil. The data is arranged as percent swelling in tables 2 - 5. Percent swelling was observed to increase initially, after some time reach to equilibrium. Water uptake was found more rapid than all other solvent. It was also found that the increase in clay contents causes a decrease in solvent uptake. Solvent uptake of neat nylon 6,6 and clay/nylon 6,6 nanocomposites is in the following order neat nylon 6,6 > 3 wt% clay/nylon 6,6 > 10 wt% clay/nylon 6,6 > 15 wt% clay/nylon 6,6.

The decrease of solvent uptake by clay/polyimide nanocomposite was also reported by Mansoori *et al.* [21]. They suggested that there is a strong interaction between polyimide and montmorillonite and the excellent barrier properties of the large aspect ratio silicate, which enhanced the available surface area of the fillers. The strong interaction between the clay and polymer results in the formation of bound polymer (polymer in close proximity to the filler), which is either physisorbed or chemisorbed, and that might restrict the solvent uptake.

**Table 2:** % water uptake by neat nylon 6,6 and clay/nylon 6,6 composites.

Time (h)	Nylon 6,6	5 wt% clay/nylon 6,6	10 wt% clay/nylon 6,6	15 wt% clay/nylon 6,6
½	200.00	166.00	150.00	114.28
1	216.00	200.00	166.67	142.85
2	266.67	233.33	183.33	157.14
3	300.00	266.67	200.00	171.42
6	316.67	300.00	216.67	185.71
12	366.67	333.33	250.00	200.00
24	400.00	366.67	266.67	214.28
48	416.67	400.00	283.33	242.85
72	416.67	400.00	316.67	257.14

## EXPERIMENTAL

### Materials

Nylon 6,6 was purchased from sigma Aldrich chemical company. The filler Kaolin clay(china clay) was kindly provided by local china clay plant Swat Pakistan. Formic acid was purchased from BDH chemical company and used as received.

### Thermal treatment of kaolin clay

Kaolin clay was heated in a furnace to 350 °C in the presence of oxygen. This thermal treatment results dehydrated kaolin but does not leads to any structural change [22]. Thermal treatment may also cause the degradation of organic matter present in the clay. At temperature above 350 °C (~400 °C) dehydroxylation of kaolin takes place which cause various structural changes in the clay.<sup>23</sup> Thus to avoid these structural changes clay is heated up to 350 °C in this study.

**Table 3:** % kerosene uptake by neat nylon 6,6 and clay/nylon 6,6 composites.

Time (h)	Nylon 6,6	5 wt% clay/nylon 6,6	10 wt% clay/nylon 6,6	15 wt% clay/nylon 6,6
½	233.33	200.00	187.50	166.67
1	250.00	208.33	200.00	188.89
2	266.67	216.67	212.50	200.00
3	283.34	216.67	212.50	200.00
6	300.01	233.33	225.00	211.11
12	316.68	241.67	237.50	222.22
24	333.35	250.00	237.50	233.33
48	350.02	258.33	250.00	244.44
72	350.02	258.33	250.00	244.44

### Preparation of samples

Neat nylon 6,6 and 5, 10, and 15 wt% clay/nylon 6,6 nanocomposite samples were prepared via solution casting method. For neat nylon 6,6 sample

one gram of the polymer was dissolved in formic acid by continuous stirring with magnetic stirrer and obtain a thick homogenous solution. Thin films of nylon 6,6 were made from this clear solution via solution casting technique. For clay/nylon 6,6 samples, calculated amount of nylon 6,6 was dissolved in formic acid as in the case of neat sample. At the same time calculated amount of clay was also dispersed in formic acid. The two solutions were then mixed together in a beaker, stirred well and sonicated for about 40 min and then thin films of the nanocomposites were prepared via solution casting technique. The attached solvent was removed by washing the films rapidly with distilled water.

**Table 4:** % chloroform uptake by neat nylon 6,6 and clay/nylon 6,6 composites.

Time (h)	Nylon 6,6	5 wt% clay/nylon 6,6	10 wt% clay/nylon 6,6	15 wt% clay/nylon 6,6
½	350.00	266.66	220.00	211.11
1	400.00	300.00	240.00	233.33
2	425.00	333.33	280.00	255.55
3	450.00	366.67	300.00	277.77
6	475.00	400.00	320.00	288.88
12	525.00	433.33	340.00	311.11
24	575.00	466.67	360.00	322.22
48	600.00	466.67	360.00	333.33
72	600.00	400.00	360.00	333.33

### Instrumentation

Morphology of gold-coated nylon 6,6 and clay/nylon 6,6 nanocomposites were analyzed in liquid nitrogen using scanning electron microscope (SEM) model JEOL, JSM-5910. Crystallization pattern of nylon 6,6 and clay/nylon 6,6 nanocomposites were analyzed using polarized optical microscope(POM) modal Optika B-600 POL. The samples were melted on hot plate, squeeze between two glass slides and analyzed under POM. Thermal properties (TGA and DTA) were studied under nitrogen atmosphere at heating rate of 20 °C/ min from room temperature to 800 °C using TG/DTA, Perkin Elmer instrument. The mechanical properties (tensile strength and modulus) nylon 6,6 and clay/nylon 6,6 nanocomposites were examined using universal testing machine (UTM), Model 100-500 KN, Iestomeric Inc. The solvent uptake capacity of nylon 6,6, and clay/nylon 6,6, were studied in selected solvents like distilled water, 2M HNO<sub>3</sub> solution, chloroform and kerosene oil. Small dry rectangular strips of the samples were weighed and then immersed in vials containing about 10 mL solvents. Percent swelling is determined by the following equation [23].

$$\text{Solvent uptake (\%)} = \frac{W_0 - W}{W} \times 100$$

Where “W” is the weight of dry sample and “W<sub>0</sub>” is the weight of wet sample in solvents.

## CONCLUSION

Dispersion of clay particles in the polymeric matrix was confirmed by SEM analysis. Nucleation effect reduces the size of spherulite in clay/polymer as confirm from POM images. Incorporation of clay greatly improve the thermal properties nylon 6,6 where temperature stability up to 50 °C may be achieved. However, mechanical properties of nylon 6,6 were not much affected by clay filling. The solvent uptake was found to increase with time and after some time equilibrium is establish, after which solvent uptake decreases. The solvent uptake also decreases as clay content increases. The degradation of the clay nanocomposites in HNO<sub>3</sub> and chloroform was also observed.

## REFERENCES

- Giannelis, E. P. *Adv. Mater.*, **8**, 29-35 (1996).
- Figiel, L. *Computational Mater. Sci.*, **84**, 244–254 (2014).
- LeBaron, P. C.; Wang, Z.; Pinnavaia, T. J. *J. Appl. Clay. Sci.*, **15**, 11-29 (1999).
- Vaia, R. A.; Price, G.; Ruth, P. N.; Nguyen, H. T.; Lichtenhan, J. *J. Appl. Clay. Sci.*, **15**, 67-92 (1999).

5. Biswas, M.; Ray, S. S. *Adv. Polym. Sci.*, **155**, 167-221 (2001).
6. Giannelis, E. P.; *Appl. Organomet. Chem.*, **12**, 675-680 (1998).
7. Xu, R.; Manias, E.; Snyder, A. J.; Runt, J. *Macromolecules*, **34**, 337-339 (2001).
8. Madakbas, S.; Akmakc, E.; Kahraman, M.V.; Esmer, K. *Chemical Papers*, **67**, 1048-1053 (2013).
9. Agag, T.; Takeichi, T. *Polymer*, **41**, 7083-7090 (2000).
10. Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.*, **8**, 1179-1184 (1993).
11. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T. *Mater. Res.*, **8**, 1185-1189 (1993).
12. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J. Appl. Polym. Sci.*, **49**, 1259-1264 (1993).
13. Gilman, J. W.; Kashiwagi, T.; Lichtenhan, J. D. *SAMPE J.*, **33**, 40-46 (1997).
14. Okada, A.; Usuki, A. *Mater. Sci. Eng. C.*, **3**, 109-115 (1995).
15. Sepulveda, M. J.; Vallyathan, V.; Attfield, M. D.; Piacitelli, L.; Tucker, J. H. *Am. Rev. Respir. Dis.*, **127**, 231-235 (1983).
16. Grim, R. E. *Clay mineralogy*, 2<sup>nd</sup> Edd. New York, McGraw-Hill, **1968**, p. 596.
17. Orellana, F.; Lisperguer, J.; Nuñez, C. *J. Chil. Chem. Soc.*, **59**, 2389-2393 (2014).
18. Wan, T.; Du, T.; Wang, B.; Zeng, W.; Clifford, M. *Polym. Compos.*, **2012**, 33, 2271-2276.
19. Rathi, S.; dahiya, J. B. *Indian J. Chem.*, **51A**, 1677-1685(2012).
20. Venkataramani, S.; Lee, J. H.; Park, M. G.; Kim, S. C. *J. Macromol. Sci. Part A. Pure Appl. Chem.*, **46**, 65-73 (2009).
21. Mansoori, Y.; Sanaei, S. S.; Zamanloo, M.-R.; Imanzadeh, G.; Atghia, S. V. *Bull. Mater. Sci.*, **36**, 789-798 (2013).
22. Bellotto, M.; gualtieri, A.; Artioli, G.; clark, S. M. *Phys. Chem. Minerals.*, **22**, 207-217 (1995).
23. Saeed, K.; Khan, I. *Iran. Polym. J.*, **23**, 53-58 (2014).