DOI: 10.32571/ijct.430058 **E-ISSN:2602-277X**

International Journal of Chemistry and Technology

http://dergipark.gov.tr/ijct

Research Article

Investigation of improvement of thermal and mechanical properties of polypropylene/nanoclay composites

Sameer A. AWAD[*], Eman M. KHALAF

on the last page

Department of Chemistry, College of Education for Pure Science, University of Anbar, Iraq

Received: 08 October 2018, Revised: 10 November 2018; Accepted: 12 November 2018

*Corresponding author e-mail: Sameer.msc1981@gmail.com

Citation: Awad, S. A.; Khalaf, E. M. *Int. J. Chem. Technol.* **2018**, 2 (2), 129-134.

ABSTRACT

This work aims to study the characterizations and modifications of systems based on polypropylene (PP) and nanoclay (NC). In this context, the effects of thermal and mechanical properties of the compsites of nanoclays with different loading of 1, 3, and 6% incorporated in PP matrix were investigated. The influences of thermal and mechanical properties on the preparation of polypropylene/nanoclay (PPNC) composite were investigated. The results of the thermogravimetric analysis (TGA) showed that thermal stability increased with higher loadings of nanoclay. The tensile properties of PP and PPNC were also studied. The tensile strength of PP with the higher loading of nanoclay increased by 24.40% compared to that of the pure PP matrix (27.5MPa). The modulus of elasticity of PPNC with higher loading of 6% NC was higher by 17.32% than that of pure PP. The elongation at break of PPNC reduced by 53%, by comparing with pure PP. The Tg of PNCC with higher loading of NC were higher by 8.6%. The degree of crystallinity of PPNC was higher by 27% than pure PP.

Keywords: Polypropylene, nanoclay, composite, thermal-mechanical properties.

Polipropilen/nanokil kompozitlerinin termal ve mekanik özelliklerinin iyileştirilmesinin incelenmesi

ÖZ

Bu çalışma polipropilen (PP) ve nanokil (NK) bazlı sitemlerin karakterizasyonlarını ve modifikasyonlarını incelemeyi amaçlamaktadır. Bu bağlamda, PP matrisine katılan % 1, 3 ve 6 oranında farklı yüklemelerle nanokil kompozitlerinin termal ve mekanik özelliklerinin etkileri araştırıldı. Polipropilen/nanokil (PPNK) kompozitin hazırlanmasının üzerine termal ve mekanik özelliklerin etkileri araştırıldı. Termogravimetrik analiz (TGA) sonuçları, termal karalılığın daha yüksek nanokil yüklenmsiyle arttığını gösterdi. PP ve PPNK'nin gerilme özellikleri de incelendi. PP'nin daha yüksek yükleme oranı ile PP'nin gerilme mukavemeti, saf PP matrisine (27,5 MPa) kıyasla % 24,40 artmıştır. Daha yüksek % 6 NK yüklü PPNK'nın esneklik modülü, saf PP'ninkinden % 17.32 oranında daha yüksekti. PPNK'nin kopma uzaması, saf PP'ye kıyasla % 53 oranında azaldı. Daha yüksek NK yüklemesiyle PNNK'nin Tg'si % 8,6 daha yüksekti. PPNK'nin kristallik derecesi, saf PP'ninkinden % 27 daha yüksekti.

Anahtar Kelimeler: Polipropilen, nanokil, kompozit, termal-mekanik özellikler.

1. INTRODUCTION

Polypropylene is an appropriate thermoplastic, and it is one of the most widely used polymers in injection-moulded products with a suitable balance between processing and performance. Also, it has been utilized widely for different applications such as packaging, technical automotive parts and compounds due to its low cost, thermal stability and corrosion resistance.[1-3] Fusion temperature of polypropylene is about 162-165°C and is high enough to resist hot water. It is not easy to make thermoforming. It is used highly for different applications due to its low cost, low density and high thermal stability, and corrosion resistance.[4-6] Nanoclays consist of the nanoparticles of layered mineral silicates with layered structural units that can form complex clay crystallites.[7-9] An individual layer unit is composed of octahedral and tetrahedral sheets. Nanocaly particle is one of the essential nanoparticles utilized in polymeric materials as polymer nanocomposites with a wide variety. Also, the improvement of mechanical properties for thermoplastics due to the reinforcement by the clay nanolayers makes them significance to be investigated.[10-12] Nanoclays have a great research interest due to its unique features which are including very high aspect ratio, and its ability to be dispersed within the polymer matrix.[13-15] The thermoplastic polymer-inorganic nanocomposites have been studied abundantly, and one of the characteristics in obtaining them is that they significantly enhance the thermal and mechanical properties of the polymer.[16-18] The influence of nanoclay additives on the properties of PP has been investigated by a few earlier studies.[19-24] Continual studies have showed the improvements in overall properties for final products of polymer reinforced nanoclay with lower contents 0.5 wt % compared to conventional composites with a large amount of micron size fillers such as wood particles, glass, and metals.[25] Some of the recent studies showed that polypropylene-nanoclay (PPNC) nanocomposites had gained a significant attention for their improvement on high modulus, strength, and heat resistance. The addition of nanoclay in PP and PP increases the melt flow viscosity and also enhances the improvements of the rate of crystallinity and thermal stability.[27] This work aims to investigate the effect of nanoclay with different concentrations on the thermal, mechanical, morphology properties of PP/nanoclay composites.

2. MATERIALS AND METHODS

2.1. Materials

Polypropylene particles were provided by Saudi Polymer Company (HGZ-120SP). Polypropylene polymer has a melt flow index of 4g·30 min^{-1} at 237°C with the density of 0.921 g·cm^{-3}. The nanoclay utilized was type Calsite 30B and was procured from Southern Clay Products (USA). Nanoclay (Calsite30B) consists of organically modified nanometer scale which layered by magnesium aluminium silicate platelets. Moisture content is ≤ 2%, particle zize is about 2 µm.

2.2. PPNC preparation

The PPNC films were prepared by adding the PP with different ratios of 1, 3, and 6% of nanoclay using an internal mixer type (Haake HBI system 90, 300 cc, fill factor 0.8). Before melt mixing, the PP and the NC were preheated in a vacuum oven at 80°C for 8 hours. PP was fed into the twin screw extruder at the rate of 8 kg per hour and the NC was added regularly at the melting zone The samples were then continuously mixed for 15minutes at 170ºC with a rotor speed of 50 rpm. The PP nanocomposite was pressed under 30 MPa at 190°C for 8 min and then cooled down at room temperature for 4 hours.

2.3. Characterization

2.3.1. DSC tests

Thermal properties were analyzed using the differential scanning calorimeter (model JADE, Perkin Elmer, USA). The weights of the samples used in this study were about ±7.9 mg. The samples were assessed with a thermal scan with temperatures from 30 to 300°C at a heating rate of 10°C·min^{-1}, under a nitrogen atmosphere. In the process, heat flow versus temperature change was monitored. The degrees of crystallinity (Xc) of PP and PPNC were calculated from the heat of fusion (ΔH_m) of the second heating cycle from the following equation: [28]

$$Xc = \frac{\Delta H_m}{(1-\emptyset)\Delta H_m^{\circ}} \times 100\%$$

where, ΔH^o_m is the fusion heat for 100% crystalline PP, which is 209 J·g^{-1}. Φ is the weight fraction of NC filer in PPNC composites.

2.3.2. Thermal analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTG) measurements were carried out using a Perkin-Elmer thermal analyzer (Waltham, MA, USA). The mass of the samples was between 5 to 10 mg. The samples were heated in the range 30-500ºC with a flow heating rate 10ºC·min^{-1} under a nitrogen atmosphere.

2.3.3. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) analyses were carried out to test the surface modification of PP and PPNC samples using SEM device (JCM-6000PLUS NeoScope). The samples were synthesized and coated with a gold coating.

2.3.4. Tensile tests

Tensile measurements of the samples were carried out at the room temperature using a device equipped with a 10 KN load cell (a Universal Instron Machine, UK. Model AT/CT M500). Dog-bone-shaped samples with overall dimensions of 16.3 × 1.9 × 0.5 cm were prepared, the tests were done according to the American Society

DOI: 10.32571/ijct.430058 **E-ISSN:2602-277X**

for Testing and Materials (ASTM) standard D638. Tensile tests were performed by a crosshead pulling at a rate of 2 mm·min^{-1} until the failure of the samples. Four samples were tested for each analysis of samples.

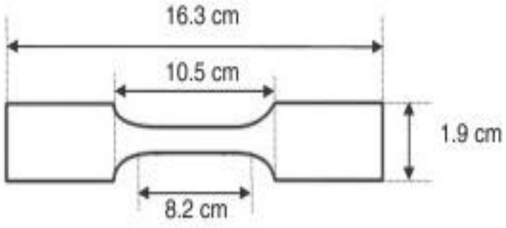

Figure. 1 The Dog-bone-shaped specimens of tensile samples.

2.3.5. Hardness test

Hardness tests were carried out using a Shimadzu testing machine (G21 series). Rockwell R method was used for the tests. Three samples with dimensions of 12.6 cm × 1.2 cm × 0.4 cm were measured for each composite. The samples were dipped by utilizing a steel sphere with a load of 90 kg. The average of recorded data was stated as the Rockwell R hardness and the measurements made according to the standard ASTM E18.

3. RESULTS AND DISCUSSION

3.1. Differential Scanning Calorimetry (DSC)

Table 1 summarizes the DSC heating and cooling curves for PP and the PP/nanoclay composites. The melting temperatures of the PP composites are higher than that of pure PP (Table 1). The melting temperature with higher loading of 6% nanoclay (172.8±0.7ºC) is higher than that of pure PP (159.5±0.8 ºC). The glass transition temperature (T_g) shifted toward the higher temperature with PPNC in comparison with the PP matrix. While T_g values were 63.7±0.5ºC for PP, for PP/nanoclay composites were 64.4±0.2ºC, 65.1±0.3ºC, and 69.2±0.2ºC with nanoclay loading 1, 3, and 6%, respectively. Furthermore, all crystallization degree of PPNC is slightly higher than that of PP. The crystallization degree with higher loading of nanoclay (6%) in PP was 48.9% once compared with PP (38.5%). Moreover, the melting temperature (T_m) values of PPNC shifted slightly toward the higher temperature, compared to that of pure PP. The crystallized temperature (Tc) of PPNC with higher loading showed a higher value (120.6±0.8 ºC), compared to that of pure PP (114.5±0.7ºC). Previous study shows the glass transition temperature increases as the NC loadings increased in the PP matrix.[29-31]

Table 1. DSC results of all the investigated PP and PP/NC composite samples

Samples	**T_g (ºC)**	**T_m (ºC)**	**Tc (ºC)**	**X_c %**
Pure PP	63.7±0.5	159.5±0.8	114.5±0.7	38.5
PP/1%NC	64.4±0.2	162.7±0.6	114.7±0.5	41.2
PP/3%NC	65.1±0.3	166.4±1.2	120.6±0.8	43.5
PP/6%NC	69.2±0.2	172.8±0.7	130.5±1.1	48.9

3.2. Thermal analysis (TGA/DTG)

Pure PP and PP nanocomposites showed a single degradation step. The increase in thermal stability of the PP nanocomposites is occurred probably because of the presence of the nanoclay additives. TGA thermograms of pure PP and PP nanocomposites are displayed in Figure 2. The onset of degradation (T_i) gives more information according to TGA curves in Figure 2. The maximum temperature was calculated from the DTG curves in Figure 3. The summary of the thermal stability for each samples explaining the onset temperature (T_{ons}), the temperature at 50% weight loss (T_{50}), the maximum temperature (T_{max}), and residue for each sample are exhibited in Table 2.

Table 2. TGA results of PP and PP/nanosilica composites

Samples %	**T_{onset} (±0.1 ºC)**	**T_{50} (±0.1 ºC)**	**T_{max} (±0.1 ºC)**	**Residual yield %**
PP	355	370	383.6	5.5
PP/1% nanoclay	368	373	385.7	6.8
PP/3% nanoclay	375	388	388.1	7.2
PP/6% nanoclay	382	391.5	390.5	9.5

The decrease in mass loss between 300-500ºC was observed with increasing the nanocaly content. The onset temperature (T_{ons}) and the maximum temperature (T_{max}) increased by 27ºC and 7ºC, respectively, compared to that of pure PP. The residual yield of PPNC with higher 6% NC loading was higher (9.5%) than that of lower loading of NC (1% and 3%), and pure PP that were 6.8 and 7.2%, and 5.5%, respectively. When compared to early studies that we performed on the thermal stability of PNCC, these studies showed that thermal decomposition of nanoclay incorporated in PP polymer was shifted the decomposition to a higher temperature by comparing with PP.[10,12,22,29,32]

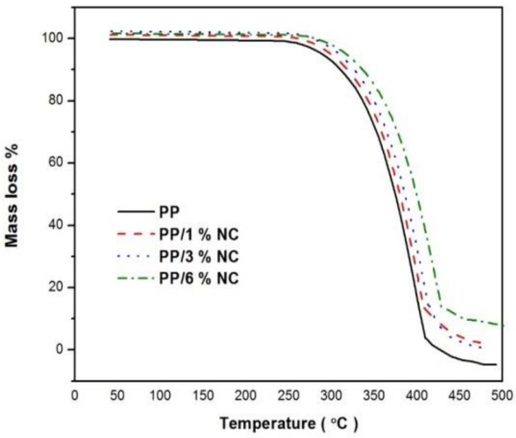

Figure 2. TGA thermograms of PP/nanoclay composites recorded at different loading ratios of 1, 3, and 6 % of nanoclays.

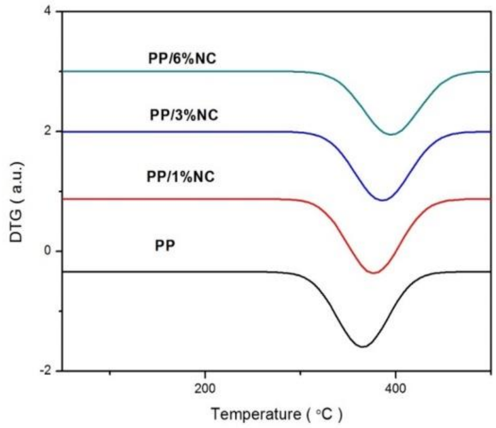

Figure 3. DTG thermograms of PP/nanoclay composites recorded at different loading ratios 1, 3, and 6 % of nanoclays.

3.3. Mechanical properties of PPNC

To further analyze the influence the content of nanoclay filler on the mechanical properties of the PP, the composite samples were tested by the tensile instruments. The summary of tensile tests for PP and PP nanocomposites is exhibited in Table 3. Accordingly, nanoclay content in PP increased tensile strength and reduced elongation at break.

The addition of nanoclay fillers of 1 wt. %, 3 wt. %, and 6 wt. % to the PP composite induced a rise in tensile strength 29.2±0.2 MPa, 31.8±0.4 MPa, and 34.2±0.2 MPa, respectively, once compared with the tensile strength of pure PP (27.5±0.3MPa) (Table 3). The modulus increased upon nanoclay addition to the PP. The modulus with higher loading of nanoclay in PP was higher by 17.32% than pure PP. The elongation exhibited a slight reducing with nanoclay incorporated in PP. The elongation at break of PP/6% nanoclay composite was decreased by 53%, compared to that of pure PP (Table 3). The results of mechanical properties indicated that the higher dispersion with the addition of nanoclay (6 wt. %) improved the mechanical properties of the PP. The interfacial properties between PP and nanoclay fillers were enhanced in tensile strength and contributed to the slight increase in average tensile strength of their corresponded composites. As seen from Table 3, the hardness values increased by 16.2% compared to that of pure PP. Previous study on the propylene-clay nanocomposite exhibited significant improvement in the tensile properties. The improvement of tensile strength for PPNC is up to 50%.[31]

Table 3. Mechanical properties of PP and PPNC

Samples	Tensile strength MPa	Young's modulus MPa	Elongation %	Hardness
PP	27.5±0.3	1480±25	15±1.2	66. 8±5.7
PP/1 % NC	29.2±0.2	1510±33	14.5±0.9	67.6±4.82
PP/3% NC	31.8±0.4	1602±35	12.2±0.7	73.8±5.92
PP/6% NC	34.2±0.2	1790±40	9.8±0.9	79.5±7.2

3.4. Morphology properties of PPNC

Figure 4a and 4b show SEM micrographs of pure PP and PPNC with 6% NC loading. Figure 4b showed that the NC with higher loading (6%) has well saturated dispersed in PP by comparing with PP matrix (Figure 6a) that exhibited little voids and nets on the surface random heterogeneous agglomerates.

DOI: 10.32571/ijct.430058 E-ISSN:2602-277X

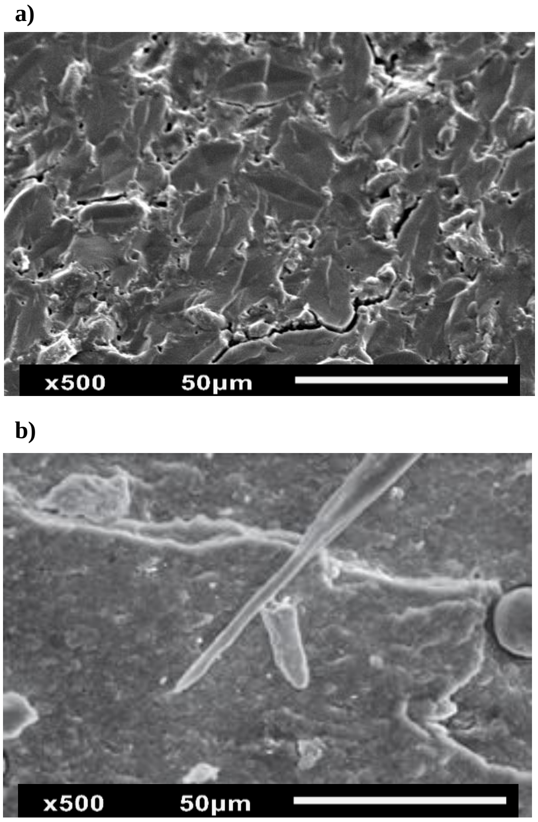

Figure 4. SEM micrographs of a) pure PP, b) PPNC with 6% NC loading.

4. CONCLUSIONS

Addition of NC to PP matrix has significant improvements in the properties of PPNC composites. The results of DSC showed that Tg of PNCC increased by 19.5%, compared to that of PP that exhibited no significant changes in T_g value and PPNC displayed the highest degree of the crystallinity (48.9%) compared to that of PP. The results of TGA displayed that the PPNC exhibited higher thermal stability as the NC loading increased in PP matrix. The maximum decomposition showed a higher resistant of thermal decomposition with a higher temperature (390.5±0.1℃). The residual yield of PPNC (9.5%) was higher than that of pure PP (5.5%). The results of mechanical tests showed significant improvements as the NC content increased. Tensile strength and modulus of elasticity increased with the addition of nanoclay up to 6 wt%, and elongation at break reduced. The hardness of PPNC also increased with increasing nanoclay content. The morphology results showed good and homogenous dispersion on the surface of PPNC with higher loading.

Conflict of interest

Authors declare that there is no conflict of interest to declare.

REFERENCES

1. Hegde, R. R.; Bhat, G. S. *J. Appl. Polym. Sci.* **2010,** 118 (6), 3141-3155.

2. Asl, D. H.; Abdouss, M.; Angaji, T. M.; Haji, A. *Chem. Ind. Chem. Eng.* **2013,** 19 (3), 441-448.

3. Awad, S.; Khalaf, E. *Eng. Technol. J.* **2017**, 35, 845-848.

4. Yuan, Q.; Awate, S.; Misra, R. *Eur. Polym. J.* **2006,** 42 (9), 1994-2002.

5. Awad, S.; Khalaf, E. *Usak University J. Eng. Sci.* **2018,** 1 (1), 38-46.

6. Hedayatnasab, Z.; Eslami-Farsani, R.; Khalili, S.; Soleimani, N. *Fiber Polym.* **2013,** 14 (10), 1650-1656.

7. Khalaf, E.; Awad, S. *J. Adv. Chem.Sci.* **2017**, 3(1), 426-427.

8. Komatsu, L.; Oliani, W.; Lugao, A.; Parra, D. *Radiat. Phy. Chem.* **2014,** 97, 233-238.

9. Abareshi, M.; Zebarjad, S. M.; Goharshadi, E. K. *J. Vinyl. Addit. Technol.* **2016,** 22 (3), 285-292.

10. Kumar, V.; Singh, A. *Rev. Chem. Eng.* **2013,** 29 (6), 439-448.

11. Awad, S. A; Khalaf, E. M. *Usak University J. Mater. Sci.* **2017**, 6 (1/2), 15-25

12. Soleimani, N.; Khalili, S. M.; Farsani, R. E.; Nasab, Z. H. *J. Reinf. Plast. Compos.* **2012,** 31 (14), 967-976.

13. Morales, A. R.; Paiva, L. B. d.; Zattarelli, D.; Guimarães, T. R. *Polímeros* **2012,** 22 (1), 54-60.

14. Stoeffler, K.; Lafleur, P. G.; Perrin-Sarazin, F.; Bureau, M. N.; Denault, J. *Compos. A: Appl. Sci. Manufactur.* **2011,** 42 (8), 916-925.

15. Awad, S. A.; Khalaf, E. M. *Bull. Mater. Sci.* **2018,** 41 (3), 67.

16. Yuan, Q.; Misra, R. *Polymer* **2006,** 47 (12), 4421-4428.

DOI: 10.32571/ijct.430058 E-ISSN:2602-277X

17. Zhu, S.; Chen, J.; Li, H.; Cao, Y. *J. Appl.Polym. Sci.* **2013,** 128 (6), 3876-3885.

18. Khalaf, E.; Awad, S. *Int. J. Mater. Sci. Applications* **2016**, 5, 297-301.

19. Sharma, B.; Mahajan, S.; Chhibber, R.; Mehta, R. *Procedia Chem*. **2012,** *4*, 39-46.

20. Picard, E.; Vermogen, A.; Gérard, J.-F.; Espuche, E. *J. Member. Sci.* **2007,** 292 (1-2), 133-144.

21. Wang, K.; Zhao, P.; Yang, H.; Liang, S.; Zhang, Q.; Du, R.; Fu, Q.; Yu, Z.; Chen, E. *Polymer* **2006,** 47 (20), 7103-7110.

22. Dimitry, O. I.; Abdeen, Z. I.; Ismail, E.; Saad, A. *J. Polym. Res.* **2010,** 17 (6), 801-813.

23. Awad, S. A.; Khalaf, E. M. *J. Thermoplast. Compos. Mater.* **2018**, 0892705718804585.

24. Xie, S.; Zhang, S.; Zhao, B.; Qin, H.; Wang, F.; Yang, M. *Polym. Int.* **2005,** 54 (12), 1673-1680.

25. Hegde, R. R.; Spruiell, J. E.; Bhat, G. S. *Polym. Int.* **2014,** 63 (6), 1112-1121.

26. Hegde, R. R.; Bhat, G. S.; Spruiell, J. E.; Benson, R. *J. Polym. Res.* **2013,** 20 (12), 323.

27. Saminathan, K.; Selvakumar, P.; Bhatnagar, N. *Polym. Test.* **2008,** 27 (3), 296-307.

28. Lertwimolnun, W.; Vergnes, B. *Polymer* **2005,** 46 (10), 3462-3471.

29. Taşdemir, M.; Caneba, G. T.; Tıwarı, R.; Wang, B. *Polymer-Plast. Technol. Eng.* **2011,** 50 (10), 1064-1070.

30. Ramsaroop, A.; Kanny, K.; Mohan, T. *Mater. Sci. Appl.* **2010,** 1 (05), 301.

31. Rane, A.; Abitha, V. *J. Mater. Environ. Sci.* **2015,** 6 (1), 60-69.

32. Fitaroni, L. B.; de Lima, J. A.; Cruz, S. A .; Waldman, W. R. *Polym. Degrad. Stabil.* **2015,** 111, 102-108.

ORCID

ID 0000-0002-9194-719X (S. A. Awad)

ID 0000-0001-7887-6158 (E. M. Khalaf)