

Synthesis, characterization and study on thermal stability, mechanical properties and thermal conductivity of UV-curable urethane acrylate-Clay (MMT) nanocomposites

Abbas Madhi^a, Behzad Shirkavand Hadavand^{b,*}, Ali Amoozadeh^a

^aFaculty of Chemistry, Semnan University, 35131-19111, Semnan, Iran

^bDepartment of Resin and Additives, Institute for Color Science and Technology, 1668814811, Tehran, Iran

Article history:

Received: 22/Aug/2017

Received in revised form: 06/Sep/2017

Accepted: 26/Sep/2017

Abstract

In this study, at first UV-curable urethane acrylate-Clay nanocomposites (UA/Clay) were synthesized, then the effects of nanoparticles on the thermal stability, mechanical properties and thermal conductivity of UA nanocomposites were investigated. FT-IR analysis confirmed the molecular structure of urethane acrylate oligomer. SEM images showed that the nanoparticles were dispersed uniformly in the polymer matrix. The thermal stability of samples was investigated by thermogravimetric analysis (DTG). DMTA study indicated significant improvement in the mechanical properties and thermal behavior of nanocomposites by adding a certain amount of Clay (3, 5 wt%) nanoparticles to polymer-matrix. Moreover, infrared thermography analysis showed that the thermal conductivity of the nanocomposites rise as filler content increased (3, 5 wt%).

Keywords: Nanocomposites, Nanoclay (MMT), Thermal stability, Mechanical properties, Thermal conductivity.

1. Introduction

In recent years, UV-curable resins have drawn a lot of attention because of their many advantages such as protection of environment, high speed cure, favorable mechanical characteristics, low cure temperature, free-solvent reactions, and high energy efficiency [1-3]. Urethane acrylates as one of the most significant UV-curable oligomers indicate some characteristics such as flexibility, chemical and thermal resistance [4]. UV-curable polyurethanes have drawn a lot of interests as electronic packaging materials due to the high flexibility that could decrease thermal stresses resulted of thermal shock [5-9]. However the low thermal conductivity ability in these materials is a significant

deficiency, because the generated heat of these devices could not be easily removed. Therefore the solid fillers including high innate thermal conductivity like as metal powders [10], carbon black, silica [11] and ceramic particles [5, 6, 10, 11] have been combined in polyurethanes. The reinforced polymeric coatings with organic and inorganic fillers, are commonly used to produce modified polymeric nanocomposites applied as thermal conductors or insulators with low thermal conductivity coefficient [12-18]. In order to analysis the coatings with low thermal conductivity coefficient, one method is the infrared thermography to study the measurement of temperature distribution on the different surfaces and materials, Moreira et al

*Corresponding author: E-mail address: shirkavand@icrc.ac.ir; Tel: +98 21 22956209

estimated the increasing of thermal resistance of polymeric nanocomposites using infrared thermography, they also studied the increasing of thermal resistance of polymeric nanocomposites made of thermoset polymers filled with metallic oxide nanoparticles. In addition they proved that nanocomposites showed very low thermal conductivity coefficient and in spite of the various amounts of nanoparticles in the samples, there is no remarkable difference in their thermal conductivity features [19, 20]. Polyurethane-Clay nanocomposites regardless of very low amount of organic Clay nanoparticles, represent good mechanical properties (glass transition temperature, storage modulus and loss modulus) [20, 21], thermal conductivity [21, 22], thermal stability and low flammability [23]. Montmorillonite (MMT) is combined of an octahedral aluminum layer located between two layers of silicon tetrahedral [24-26] that as the most common organic Clay is used for preparation of nanocomposites, having been used widely because of its natural origin and suitable cost. In this research, we attempt the preparation of UV-curable urethane acrylate-based nanocomposite coatings with improved thermal stability, mechanical properties (storage modulus, loss modulus and glass transition temperature), and thermal conductivity by using Clay (MMT) nanoparticles.

2. Experimental

2.1 Materials

The materials used in this research were isophorone diisocyanate (IPDI), 1,4-butanediol (BD), 2-hydroxyethyl methacrylate (HEMA), dibutyltin dilaurate (DBTDL), benzophenone, triethanolamine (TEA) and acetone purchased from Merck Co (Germany). Trimethylolpropane triacrylate (TMPTA) was purchased from Sigma-Aldrich Co (USA). Organically modified montmorillonite (MMT) nanoclay with the commercial name of Cloisite 30B which was modified with a quaternary ammonium salt containing one methyl, one tallow and two hydroxyethyl groups with particle size of 1-2 nm was

provided from US Research Nanomaterials (USA). All of the materials were used without further purification.

2.2 Preparation of urethane acrylate oligomer

Isophorone diisocyanate (0.1 mol, 22.23 g), 1,4-butanediol (0.05 mol, 4.5 g), 0.2 mL of DBTDL as a catalyst and 15 mL of acetone were charged into a three-necked flask equipped with a nitrogen inlet, a magnetic stirrer, a condenser and a thermometer. This mixture was stirred in an oil bath at 50 °C for 2 h by the magnetic stirrer. Then to the prepared pre-polymer, 0.2 mL of DBTDL, 0.1 mol (13.01 g) of 2-hydroxyethyl methacrylate and 15 mL of acetone were added. The mixture was stirred at 50 °C for 2 h until all NCO groups were completely removed and the UA oligomer was prepared. Finally, the synthesized UA oligomer was dried in the vacuum oven at ambient temperature for 1 h in order to remove the solvent. The completion of reaction was confirmed by FT-IR spectroscopy.

2.3 Preparation of nanocomposites

UA/Clay nanocomposites were prepared as following: at first, Clay (MMT) nanoparticles were dispersed in acetone by sonication for 30 min. Then, equal to 35 wt% of UA oligomer, trimethylolpropane triacrylate (TMPTA) as a reactive diluents for adjusting the viscosity was added to UA oligomer and 1, 3 and 5 wt% of the fillers were added to the UA resin separately. The mixtures were blended for 3 h using a magnetic stirrer until complete mixing was achieved. Next, equal to 2 wt% of UA resin, benzophenone as a photo-initiator and triethanolamine as a co-initiator were added to each mixture and mixed for 10 min. Finally, by a film applicator, 120µm thickness films of nanocomposites were prepared on the glass plates. The curing process of films was conducted by UV irradiation in a UV-curing device (1 kW Hg lamp, 80 w/cm) for 3 min. By changing the contents of nanoclay (MMT) in the range of 0, 1, 3 and 5 wt%, the groups of UA/Clay nanocomposites were prepared and encoded as Blank (UA/Clay (0%)), UA/Clay (1%), UA/Clay (3%) and UA/Clay (5%), respectively. The properties of the films were evaluated after UV irradiation curing.

The scheme of proposed reaction path has been shown in Figure 1.

Also in order to use in infrared thermography, 1, 3 and 5 wt% UA/Clay nanocomposites tablets were prepared in circular shapes with 25 mm diameter and 3 mm thickness by casting on glass molds and cured for 5 min at ambient temperature. The groups of UA/Clay and nanocomposites were prepared and encoded as Blank, UA/Clay 1 wt% (C1), UA/Clay 3 wt% (C2), UA/Clay 5 wt% (C3), respectively.

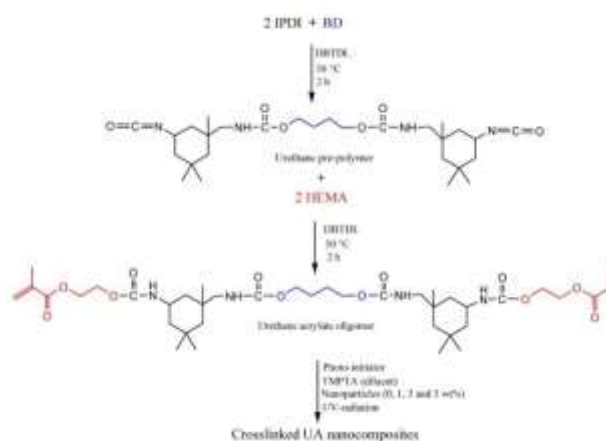


Fig.1. The scheme of proposed reaction path.

Characterization techniques

The FT-IR results were recorded on a Perkin Elmer (Spectrum 1, USA) apparatus in the wave number range of 400-4000 cm^{-1} . FT-IR spectra of the samples were performed in KBr disk on the spectrophotometer. The SEM images were used to study morphological features on LEO 1455VP (Germany) scanning electron microscope. The thermal stability of the samples was studied from DTG curves employing Perkin Elmer Pyris Diamond (USA). The samples were heated from 25 °C to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere. The dynamic mechanical properties such as storage modulus, loss modulus and loss tangent as functions of temperature were measured by a dynamic mechanical thermal analyzer (DMA, 242 C, Netzch Co, Germany) with a modulus range of 10^3 to 10^6 MPa. The thermal conductivity of samples was measured by TEMP spectroscopy (2000 A, USA) range of 3-35 μm

and in the range of 8-15 μm by the Testo infrared camera (875-2, Germany) (ASTM-E903-96).

3. Results and discussion

3.1 Characterization of UA oligomer

The FT-IR spectra of pre-polymer and UA oligomer are shown in Figure 2. The pre-polymer (IPDI + BD mixture) spectrum shows a sharp absorption band for NCO groups at 2268 cm^{-1} . The pre-polymer + HEMA mixture represents a sharp peak between 2917 and 2956 cm^{-1} due to the C-H stretching vibrations of alkyl chains. An absorption peak at 3342 cm^{-1} is related to the N-H stretching vibrations. The peak at 1534 cm^{-1} indicates N-H bending vibration. Also, there exist another absorption bands around 1459 and 1638 cm^{-1} that are related to the C=C stretching vibrations. In addition, the observed peaks at 1719, 1241, 1170 and 1044 cm^{-1} are assigned to the stretching vibrations of C=O, C-N of urethane, C-O of urethane and C-O in HEMA respectively, as well as the peaks at 1454 and 1386 are attributed to bending vibrations of C-H in CH₂ and C-H in CH₃ of HEMA. These results prove the successful synthesis of the UA oligomer. One could mention that the absorption peak of NCO groups observed at 2268 cm^{-1} disappeared indicating the completion of the reaction.

Morphology of nanocomposites

Scanning electron microscopy (SEM) was used for investigation of fracture surfaces of UA (blank) and UA/Clay (1, 3 and 5 wt%) (Figure 3 a-d). The cross-sectional area of UA was smooth and aggregate without pores or channels. The gray colored regions indicated the bulk of the UA matrix and the brighter regions indicated the distribution of Clay nanoparticles within the UA coating. The number of bright nanoparticles enhanced with the increasing Clay nanoparticles contents. Due to the uniform dispersion of the nanoclay in the polymer matrix the UA/Clay (3%) surface was completely rough. The reason behind this could be the chemical interactions between the polar nanoclay surfaces and polar UA bonds which were present in the segments of the UA matrix. These results clearly demonstrated some physical interactions

between Clay nanoparticles and UA matrix as well as the good dispersion led to improved mechanical properties and thermal conductivity of the nanocomposites.

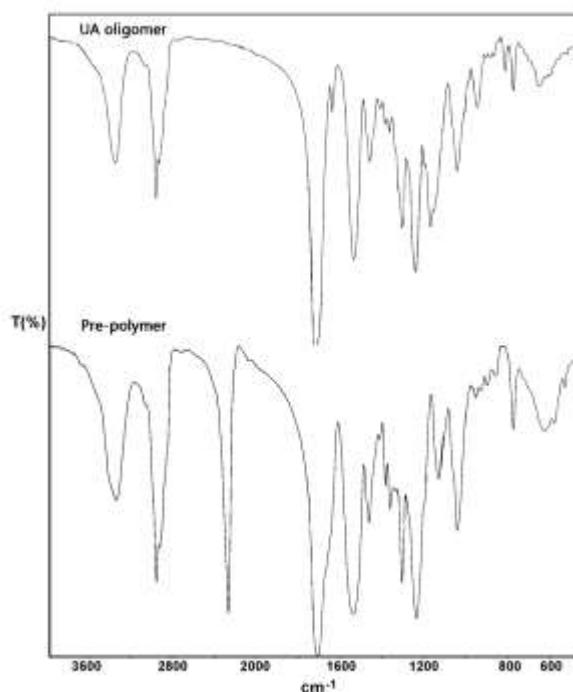


Fig. 2. The FT-IR spectra of pre-polymer and UA oligomer.

3.1 Thermogravimetric analysis

Thermogravimetric derivative (DTG) curves of UA/Clay (3 wt%) and UA films are shown in Figure 4. There were three major peaks on the DTG curves. The first peak, which appeared around 100-170 °C, was related to evaporation of water, solvent and un-reacted materials. The nanocomposite was degraded in two steps; in the first step, a weight loss approximately 50% weight occurred around 350-400 °C, which was related to the degradation of the polymer chains. The second degradation step was a severe weight loss between 450-500 °C attributed to separation of the inorganic parts of polymer and ultimately the nanocomposite was degraded completely. The DTG results for UA and UA/Clay 3 wt% films are summarized in Table 1. According to Table 1, as temperature increases, weight loss of UA becomes higher than that of UA/Clay 3 wt%. Results prove that loading of nanoclay leads to enhancement of thermal stability of polymer. Also,

increased thermal stability is due to the good dispersion of nanoparticles in polymer-matrix and strong chemical interactions between Clay (MMT) nanoparticles and the polymeric matrix.

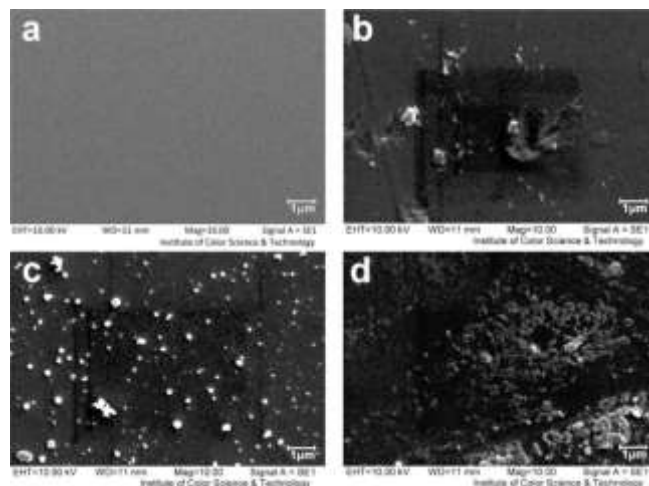


Fig.3.SEM images of UA/Claynanocomposites. (a)UA, (b)1%, (c)3% and (d)5%.

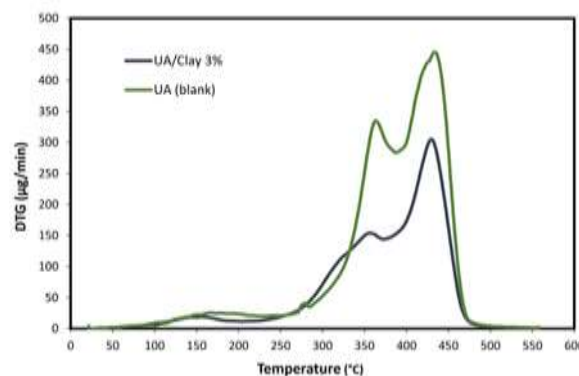


Fig. 4. DTG curves of UA and UA/Clay (3 wt%) nanocomposite.

3.1. Dynamic mechanical thermal analysis (DMTA)

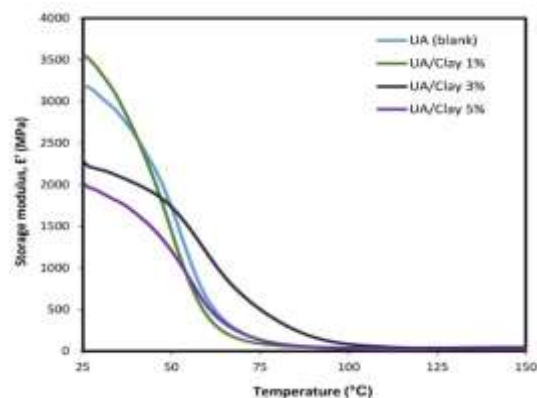
Viscoelastic properties such as storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) as functions of temperature were measured in a dynamic mechanical thermal analyzer. The storage modulus indicates the elastic modulus and loss modulus is related to the lost energy due to the friction associated with the polymer chains. The loss tangent can be demonstrated as the quotient of the loss and storage module.

Table 1. DTG analysis results of UA and UA/Clay (3 wt%) nanocomposite.

Samples			
UA		UA/Clay 3%	
Temperature (°C)	Lost weight (µg/min)	Temperature (°C)	Lost weight (µg/min)
100	9.2	100	5.6
150	22.3	150	18.4
200	23	200	11
250	20	250	19
300	72	300	53
350	252	350	149
400	300	400	173
450	283	450	160
500	4.2	500	3.5

3.1.1 Storage modulus (E')

The variations of storage modulus of UA/Clay (1, 3 and 5%) nanocomposites are shown in Figure 5. UA/Clay (1 wt%) at 25 °C has the maximum value of storage modulus compared with other samples. The increase of the storage modulus is not constant and as temperature increases one could observe a decreasing trend of the storage modulus. When temperature goes higher than 50 °C the storage modulus drops significantly. Among UA/Clay nanocomposites the highest E' is related to the sample including 3 wt% nanoclay at temperature of 50-100 °C, this is due to the good dispersion and attachment between Clay nanoparticles and UA matrix in comparison with the 1 and 5 wt% samples. As temperature increases above 50 °C, UA/Clay nanocomposites indicate higher E' than UA (blank) suggesting strong interactions between the UA matrix and Clay nanoparticles. The values of storage modulus (E') in the temperature range of 25 and 50-100 °C for UA, UA/Clay nanocomposites are shown in Table 2.

**Fig. 5.** Storage modulus (E') dependence on temperature for UA and UA/Clay nanocomposites.**Table 2.** Comparison of storage modulus (E') for UA and UA/Clay nanocomposites.

T (°C)	E' (MPa)			
	UA	UA/Clay 1%	UA/Clay 3%	UA/Clay 5%
25	3188	3554	2261	2005
50	1665	1371	1709	1174
60	598	398	1146	519
70	208	128	654	203
80	84	65	350	87
90	44	48	163	50
100	29	41	81	36

UA/Clay (3 wt%) shows the lowest loss modulus due to the good dispersion and lacking of nanoparticles aggregation in the polymer-matrix. This signifies the barrier effects of nanoparticles that cause the movements of polymeric chains to be limited in the UA matrix indicating a great interaction at the interfaces between nanoparticles and polymer matrix [27].

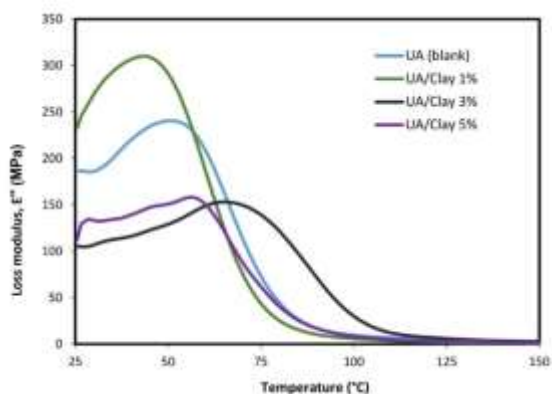


Fig. 6. Loss modulus (E'') dependence on temperature for UA and UA/Clay nanocomposites.

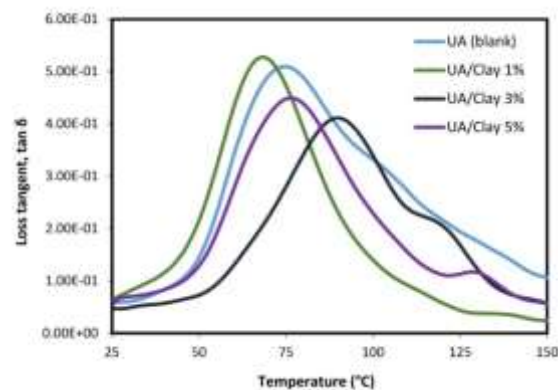


Fig.7. Loss tangent ($\tan \delta$) dependence on temperature for UA and UA/Clay nanocomposites.

3.1.2 Loss tangent ($\tan \delta$)

Figure 7 shows the loss tangent that is dependent on temperature. The glass transition temperature (T_g) is determined by the peak of $\tan \delta$ curve. When temperature goes higher than 50 °C, a transition from a glassy to a soft elastic region is observed in the nanocomposite samples. With increasing flexibility of the nanocomposites, T_g decreases. UA/Clay 1 wt% indicates lower glass transition temperature and higher flexibility than the other samples, that the reasons behind this are attributed to its flexibility ability, reduction of chains interactions and the weakened intermolecular forces due to the orientation of Clay layers in the nanocomposites. Therefore, UA/Clay 1 wt% has the lowest T_g and highest flexibility against UA/Clay 3 wt% with the highest T_g and lowest flexibility. The T_g values of all samples are shown in Table 3. Adding 1, 3 and 5 wt% Clay nanoparticles to the UA matrix leads to some changes in the loss tangent curves. UA/Clay 3 wt% represents lower height of $\tan \delta$ peak compared with UA/Clay (1 and 5 wt%). The damping peak of UA matrix is shifted to higher temperatures (from 70 to 100 °C) with adding 3 wt% of nano Clay, which is attributed to the reinforced effect in which the nanoparticles have limited the mobility of polymeric chains. The UA/Clay 3 wt% sample compared with other samples suggests lower and wider height of $\tan \delta$ peak.

Table 3. T_g values of UA and UA/Clay nanocomposites.

Samples	T_g (°C)
UA	74.6
UA/Clay1%	68
UA/Clay3%	90.3
UA/Clay5%	77.3

3.2 Thermal conductivity

Thermal conductivity coefficient of UA nanocomposites including 1, 3 and 5 wt% in comparison with UA (blank) has been studied. Finding results from infrared thermography and surface temperature of samples have been presented in Figure 8 and Table 4. Results signify that with increase of fillers content (3 and 5 wt%), both of surface reflection coefficient and temperature of samples surface decrease (Blank: 42.2 °C, UA/Clay 1 wt% (C1): 40.9 °C, UA/Clay 3 wt% (C2): 42.5 °C, UA/Clay 5 wt% (C3): 43.8 °C). As surface reflection coefficient increases, surface temperature decreases and this reduction causes thermal conductivity to decrease, consequently energy consumption reduces. Therefore one could point that UA/Clay 1 wt% plays a thermal barrier role, as well as UA/Clay 3 and 5 wt% have an ability of thermal conductivity and also a higher thermal conductivity coefficient. In other word, thermal conductivity of the sample containing 1 wt% reduces, however by increase of Clay nanoparticles (3 and 5 wt%) loading, thermal conductivity increases.

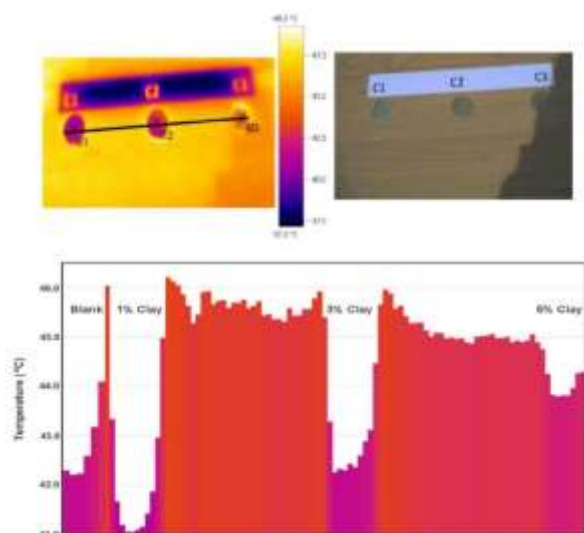


Fig.8. Infrared thermography resulted of UA and UA/Clay nanocomposites.

Table 4. Surface temperature of UA and UA/Clay nanocomposites.

Samples	Temperature (°C)
UA	42.2
UA/Clay 1%	40.9
UA/Clay 3%	42.5
UA/Clay 5%	43.8

4. Conclusions

In this research a series of UV-curable urethane acrylate nanocomposites with high storage modulus and low loss modulus were synthesized. The nanocomposites contained Clay (MMT) nanoparticles and urethane acrylate resin. The synthesis of the UA oligomer was confirmed by FT-IR spectroscopy. SEM images from fracture surface showed proper dispersion of Clay nanoparticles. Thermogravimetric analysis results suggested that loading of Clay nanoparticles to UA matrix leads to increase of thermal stability of polymer. DMTA results showed that higher value of stiffness was achieved with increasing of Clay nanoparticles content in the UA matrix corresponding to the higher values of storage modulus. However, the reduction of the loss modulus and loss tangent of the UA matrix with increasing filler contents showed the reinforcing effect created by the act of clay

nanoparticles. Also, as filler contents increased, T_g values of the UA matrix rise indicating an improvement in the thermal behavior of the UA matrix. The infrared thermography analysis showed UA/Clay 1 wt% was a thermal barrier, however higher loading of Clay nanoparticles (3, 5 wt%) content into UA matrix led to increase of thermal conductivity. The results proved that adding Clay nanoparticles to the polymeric matrix caused improvement of thermal stability, mechanical properties and thermal conductivity.

References

- [1] C. Decker, *Pigment & Resin Technology.*, **30** (2001) 278.
- [2] A. Srivastava, D. Agarwal, S. Mistry, *Pigment& Resin Technology.*, **37** (2008) 217.
- [3] Alavi Nikche MM, Ghavidel kelshimi R, Akbar R and Vakili M, *Journal of Applied Chemistry.*, **10** (2015) 9.
- [4] F. Wang, J. Q. Hu, W. P. Tu, *Prog. Org. Coat.*, **62** (2008) 245.
- [5] Lu X, Xu GJ, *J Appl Polym Sci.*, **65** (1997) 2733.
- [6] Lu X, Xu G, Hofstra PG, Bajcar RC, *J Polym Sci, Part B:Polym Phys.*, **36** (1998) 2259.
- [7] Ho TH, Wang CS, *Polymer.*, **37** (1996) 2733.
- [8] Figovsky OL, Sklyarsky LS, Sklyarsky ON, *J Adhes Sci Technol.*, **14** (2000)915.

- [9] Tey JN, Soutar AM, Mhaisalkar SG, Yu H, Hew KM, *ThinSolid Films*, **504** (2006)384.
- [10] Mamunya YP, Davydenko VV, Pissis P, Lebedev EV, *Eur Polym J*, **38** (2002)1887.
- [11] Benli S, Yilmazer Ü, Pekel F, Özkar S, *J Appl Polym Sci*, **68**(1998)1057.
- [12] M. J. Hodgin, R. H. Estes, *NEPCO WEST Conference, Anaheim, CA*, (1999) 359.
- [13] D. Kumlutas, I. H. Tavman, M.T. Coban, *Compos. Sci. Technol*, **63** (2003) 113.
- [14] H. Lee, S. Eun, *American Composites Manufacturers Association, Tampa, Florida*, (2004).
- [15] C. Liu, T. Mather, *Society of Plastic Engineers*, (2004) 3080.
- [16] H.Ishidax, *S.Heights, US Patent* (1999) 5.900.
- [17] R. D. Hermansen, *EP*, (2001) 754 741 B1.
- [18] I. H. Tavman, *Academic Book Publication, Dordrecht, Netherlands*, **169** (2004) 449.
- [19] H. R. Frank, D. S. Phillip, *EP*,**0**(2002) 794.
- [20] D. C. Moreira, M. C. O. Telles, L. C. S. Nunes, L. A. Sphaier, J. M. L. Reis *14th Brazilian Congress of Thermal Sciences and Engineering, RJ, Brazil, November (2012)* 18.
- [21] Y. W. C. Yang, H. C. Yang, G. J. Li , Y. K. Li, *J. Polym. Res.*, **11** (2004) 275.
- [22] W. J. Choi, S. H. Kim, Y. J. Kim, S. C. Kim, *Polymer.*, **45** (2004) 6045.
- [23] M. Berta, A. Saiani, C. Lindsay, R. Gunaratne, *J. Appl. Polym.Sci.*, **112** (2009) 2847.
- [24] V. Selvakumar and N. Manoharan, *Indian Journal of Science and Technology.*, **7** (2014) 136.
- [25] Ahmadi SJ, Huang YD, Li.W. Review Synthetic routes, properties and future applications of polymer-layered silicate nanocomposites. *J Mater Sci.*, **39** (2004) 1919.
- [26] Elhami S and Mohmedi N, *Journal of Applied Chemistry.*, **11** (2017) 59.
- [27] Moayad HF, Sahrim H, Aziz H and Shamsul B, *Composites Part B.*, **52** (2013) 334.