Modification of Phenol Novolac Epoxy Resin and Unsaturated Polyester Using Sasobit and Silica Nanoparticles

Seyyed Mojtaba Mousavi[a], Seyyed Alireza Hashemi[b,], Sara Jahandideh[c], Sadegh Baseri[d], Maryam Zarei[e], and Sara Azadi[f]*

[a]Department of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran 713451789
[b]Department of Mechanical Engineering, Islamic Azad University, Najafabad Branch, Najafabad, Iran 8514143131
[c]Department of Polymer, Yazd University, Iran
[d]Department of Chemistry, Shahid Chamran, Ahvaz University
[e]Department of Engineering Sciences, Salman Farsi University, Kazerun, Iran
[f]Department of Chemistry, Bu-Ali Sina University, Hamedan, Iran

SUMMARY

Nanocomposites containing phenol novolac epoxy resin (PNER) were modified by unsaturated polyester resin (UPR) and then reinforced using sasobit and silica nanoparticles at different filler loadings via a multi-step manufacturing procedure. Afterward, effect of sasobit and silica loadings either on mechanical and thermal properties or on morphology of nanocomposites were examined. Results showed that increase in silica nanoparticles loading can improve both thermal and mechanical properties, but increase in silica loading more than 3 wt% can lead to decrease in the mechanical properties. In this case, addition of sasobit along with silica not only can improve the mechanical and thermal properties but also it can lead to improve in dispersion quality and morphology of nanocomposites. Eventually, with affordable and environmentally friendly materials such as sasobit, either production procedure or the overall quality and properties of nanocomposites can be improved.

*Corresponding author: Tel. 0098 939 843 25 09, Email: S.a.hashemi0@gmail.com and s.a.hashemi@smc.iaun.ac.ir (Seyyed Alireza Hashemi)

S.M. Mousavi, S.A. Hashemi, S. Jahandideh, S. Baseri, M. Zarei, and S. Azadi

INTRODUCTION

Epoxy resins (ER) are among most important thermoset polymers which extensively have used as matrix in various fields such as aerospace and surface coating industries [1]. Phenol novolac resin (PN) is a polymeric additive which can be used as a modifier for ER resins. PN is either easy to produce or low cost and cured PN shows excellent rigidity, dimensional stability and fire resistance. On the other hand, traditional PN suffers from brittleness, high shaping pressure and dark color due to the oxidation of phenolic groups [2]. Despite, Phenol novolac epoxy resins (PNER) have a good compatibility with unsaturated polyester resins (UPR). Widespread of UPR is due to its low cost, ease of processing, excellent interaction with fillers and wide variety of available grades. UPR is solution of unsaturated polyester with unsaturated coreactant diluent such as styrene. UPR suffers from brittleness and poor resistance to crack growth. Modification of ER with PN and UPR can cover their disadvantages and improve their tensile strength, toughness and thermal resistance and compatibility of PN and UPR with ER are due to their polar and functional groups [2, 3].

In a work by Bu et al. [2], they have used a silicone-contained bisphenol type monomer in order to modify PN as copolymerized with phenol and formaldehyde to gain modified phenolic resin. Besides, surface treated chopped sisal fiber was used in order to reinforce the phenolic resin. Result of this study showed that modification of phenolic resin with sisal fiber can lead to significant improvement in thermal and mechanical properties of final samples in comparison to net matrix.

In another work by Cherian et al. [3], they have modified ER with UPR. Results of this study showed that ER has good compatibility and miscibility with UPR which can lead to improvement in toughness and impact resistance. Besides, UPR not only can lead to improvement of toughness and impact resistance but also can improve thermal properties of modified epoxy resin. In addition, fiber reinforced UPR and PN can either lead to increase in mechanical and thermal resistance or improve in fire resistance, thermal stability and electrical conductivity [4, 5]. Furthermore, in some of researches, PNER was reinforced with silicon nanoparticles in order to increase its physical properties. Addition of conductive fillers along with silica nanoparticles, can lead to improvement of both electrical and mechanical properties of composites [6, 7]. In another work by Mousavi et al. [8], they have investigated the effect of modified UPR with cresol novolac epoxy resin (CNER) and silica nanoparticles on mechanical properties final samples. Based on their study, modification of UPR with CNER and silica nanoparticles can lead significant improvement in mechanical properties of final samples such as impact resistance and tensile strength.

Despite of that, in order to achieve more homogeneous suspension, viscosity of matrix have to be reduced. In this matter, usage of diluent agents can lead to decrease in overall viscosity of matrix, but this kind of additives can reduce the ultimate crosslink density of ER and affect the overall properties of fabricated composites [9, 10]. This aim can be achieved via usage of natural materials such as sasobit. Sasobit is an organic synthetic microcrystalline wax with long chain length of the aliphatic hydrocarbons with 40-114 carbon atoms and fine crystalline structure which can decrease the viscosity of matrix and improve the thermal resistance of composites due to its long aliphatic hydrocarbons chain. Chemical formula of sasobit is C_nH_{2n+2} and it can be obtained from sasol wax which can be find in South Africa and the common way for its fabrication is via Fischer-Tropsch method [11, 12].

Furthermore, addition of natural fillers such as nanobioceramic (the egg shell nanoparticle) and natural polymers (starch and glycerin) to PNER / UPR can lead to significant degradation under the soil and presence of egg shell nanoparticles in the cured PNER / UPR can improve the water absorption [13]. Besides, addition of montmorillonite nanoparticles to the ER not only can enhance the overall mechanical properties but also can enhance the thermal properties of nanocomposites [14]. Moreover, emission of electron beams to the linear low-density-polyethylene (LLDPE), ethylene-co-vinyl acetate (EVA) and clay nanoparticles can either enhance the mechanical or thermal properties of fabricated nanocomposites [15].

In addition, agglomeration of fillers throughout the matrix and also creation of bubble based voids in the matrix can highly reduce the overall mechanical and electrical properties of nanocomposites. In this case, removal of bubbles before the completion of curing process and also homogeneous dispersion of fillers throughout the matrix are very necessary for achieving a composite structure with optimal properties [16].

The aim of this work is to improve the overall properties of ER with PN and UPR in order to cover their disadvantages. Besides, with usage of natural and cost affordable fillers such as sasobit and silica nanoparticles, significant improvement in mechanical and thermal properties of final samples were achieved. In addition, sasobit is a multi-functional filler which can improve the dispersion quality of matrix as well as improve in thermal and mechanical properties.

MATERIALS AND METHODS

Materials and Equipment

PNER, UPR and their diethylene amine hardener were supplied by Mokarrar industrial group. Besides, acrylic acid and titanium dioxide were supplied by Merck & Co. and Sachtleben Chemie GmbH, respectively. Despite, Silica nanoparticles and sasobit were supplied by Sigma-Aldrich and Sasol Performance Chemical, respectively.

In addition, Impact (manufactured by ZWICK), Bending (manufactured by ZWICK), TGA (Thermal science division model PL-1500), DSC (Polymer Laboratories model PL-DSC) and SEM (TESCAN model VEGA3 SB) instruments were used in order to determine the overall properties of produced nanocomposites. Despite, with usage of particle size analyzer (PSA) (Horiba model LB 550), particle size distribution of silica nanoparticles was examined. **Figure 1** represent the PSA result for silica nanoparticles, as can be seen in this figure, particles size distribution vary between 50 – 100 nm. Optical images of sasobit nanoparticles were taken by digital optical microscope (RoHs model U1000x) and can be seen in **Figure 2**.

Production Procedure

Nanocomposites containing PNER and UPR were reinforced by titanium acrylic and silica nanoparticles and then subjected to different analysis. In this case, effects of increase in the weight percentage of silica nanoparticles and sasobit on the thermal, physical and mechanical properties of nanocomposites were examined. For the production of nanocomposites, first 15 wt% diluent agents, sasobit and silica nanoparticles were poured in the PNER and then
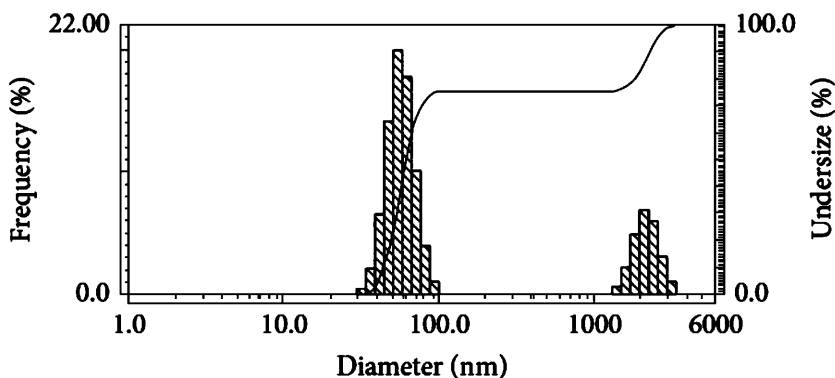

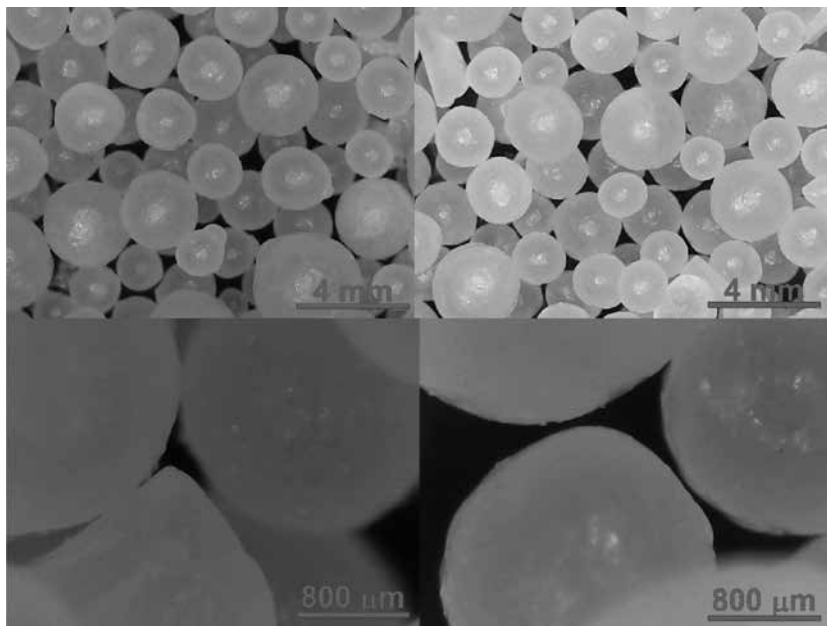**Figure 1.** *Particle size analyzer (PSA) of Sio$_2$ nanoparticles*

Figure 2. *Optical images of sasobit particles*

stirred (500 rpm) for 4 h under indirect heat about 50-60°C. Then, after each 4 h stirring, resulting suspension was mixed with ultra-sonic mixer with 100 W power for 15 min. Afterward, 10 phr diethylene triamine with ratio 100:60 was added to the suspension and then stirred (200 rpm) for further 5 min. Moreover, the suspension was poured in related molds and subjected to the vacuum with magnitude 50 cmHg. Then samples were cured in two different stages, each time for 1 h under 70°C for primary and post cure, respectively. A view of manufacturing procedure can be seen in **Figure 3**. Despite, specification of each nanocomposite and filler loadings can be seen in **Table 1**.

RESULTS AND DISCUSSIONS

Impact Test (Izod)

In order to examine the effect of sasobit nanoparticles at different filler loadings on the impact strength, samples A_2 and B_2 were compared with each other. Despite, samples E_2, C_2, C_3, C_4 and D_4 were examined and compared with sample E_5 (net resin) in order to evaluate the effect of silica nanoparticles and sasobit on the overall amount of impact resistance. In **Figure 4**, impact
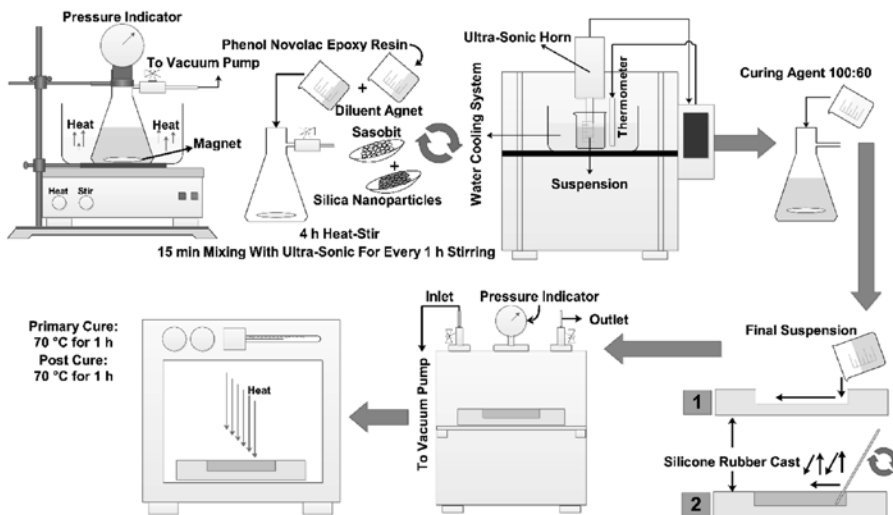
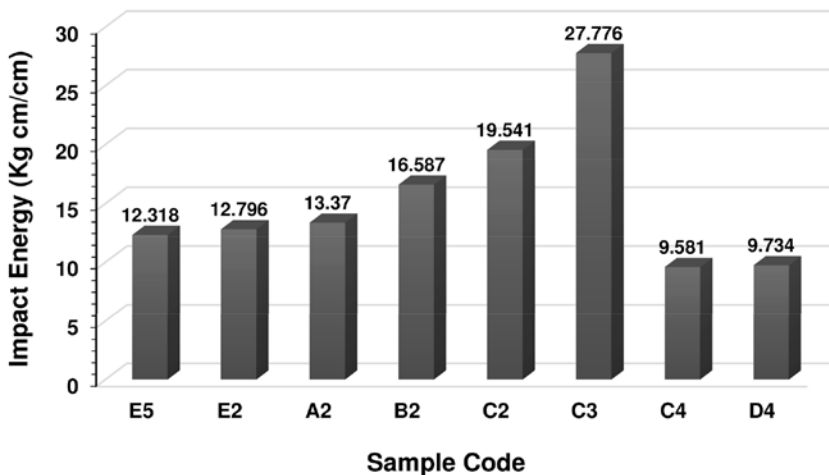**Figure 3.** *A view of manufacturing procedure*

Figure 4. *Impact resistance results for nanocomposites at different filler loadings*

resistance of different samples with various filler loadings can be seen. As can be seen in this figure, by increase in the weight percentage of sasobit, chain strength and consequently impact resistance of composite samples were increased through the formation of an active complex between acrylic acid and the reactive oxygen of PNER. Moreover, the impact resistance of nanocomposites was increased due to the increase in weight percentages of silica nanoparticles. In addition, these results are due to the strengthening

Table 1. Characterization of each nanocomposite

Categories	Sample Code	Silica Nanoparticle Weight Percentage (wt%)
A: PNER and UPR with 1 wt% Sasobit	A_1	1 wt%
	A_2	2 wt%
	A_3	3 wt %
	A_4	4 wt %
	A_5	0 wt%
B: PNER and UPR with 3 wt% Sasobit	B_1	1 wt%
	B_2	2 wt%
	B_3	3 wt %
	B_4	4 wt %
	B_5	0 wt%
C: PNER and UPR with 5 wt% Sasobit	C_1	1 wt%
	C_2	2 wt%
	C_3	3 wt %
	C_4	4 wt %
	C_5	0 wt%
D: PNER and UPR with 7 wt% Sasobit	D_1	1 wt%
	D_2	2 wt%
	D_3	3 wt %
	D_4	4 wt %
	D_5	0 wt%
E: PNER and UPR	E_1	1 wt%
	E_2	2 wt%
	E_3	3 wt %
	E_4	4 wt %
	E_5	0 wt%

properties of nanoparticles penetrating into the continuous phase of resin which was increased the flexibility of nanocomposites and made their fraction harder by increase in their strength. However, this strengthening properties can lead to opposite results by increase in the silica nanoparticles weight percentage to 4 wt%. Experimental evidence has indicated that this rate of filler loading can created a weak point in the matrix. In this case, the reason lies in the fact that one of the problems with usage of spherical silica nanoparticles is the agglomeration of nanoparticles which can be solved by usage of ultra-sonic mixer in the production procedure. However, by increase in the filler loading from 3 wt% to 4 wt%, even by using ultra-sonic mixer, the agglomeration

problem could not be solved. This method can only improve particle distribution in the content of matrix, but due to the large size of nanoparticles, interaction between them would increase. Thus, most of this agglomerations and defects in nanocomposites fracture becomes inevitable, which can cause decrease in the fracture energy and impact resistance of nanocomposites.

Bending Test

In this section, effect of sasobit and silica nanoparticles loadings on the overall amount of bending strength were evaluated. In this case, stress-strain diagram for samples E_5, E_2, A_2 and B_2 can be seen in **Figure 5**. Besides, in **Figure 6**, stress-strain diagram for samples C_2, C_3 and C_4 can be seen. As can be seen in **Figure 5a** and **b**, addition of silica nanoparticles to the matrix can improve the bending strength. In **Figure 5a**, **c** and **d**, it can clearly be seen that reinforcing the net matrix with sasobit and silica nanoparticles as well as increase in weight percentage of sasobit, can improve the bending strength. As can be seen in **Figure 6**, increase in weight percentage of silica
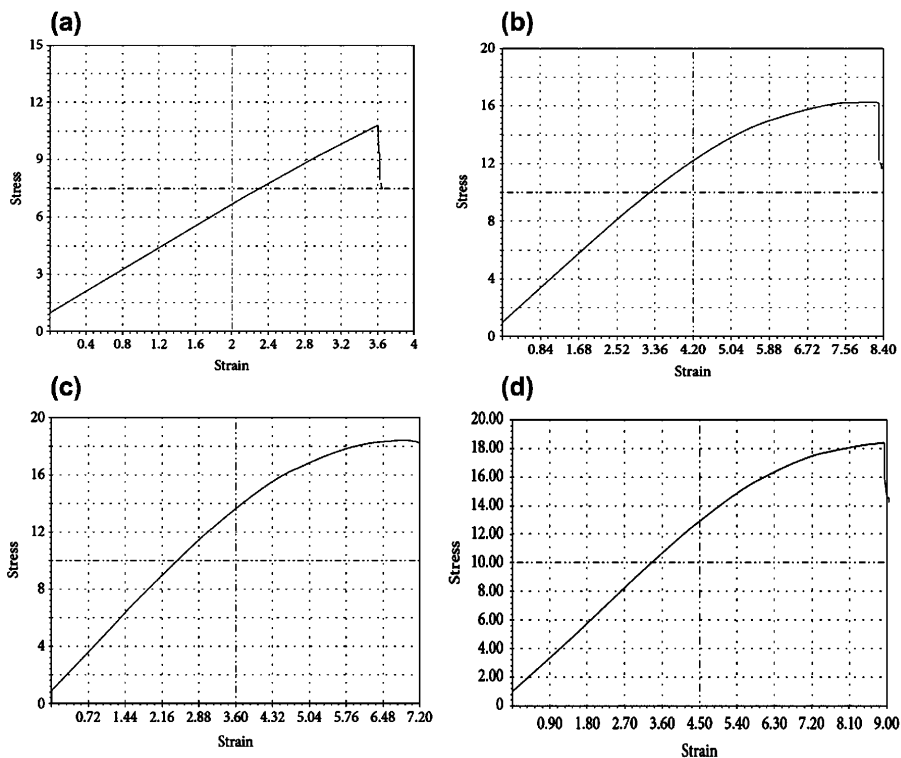

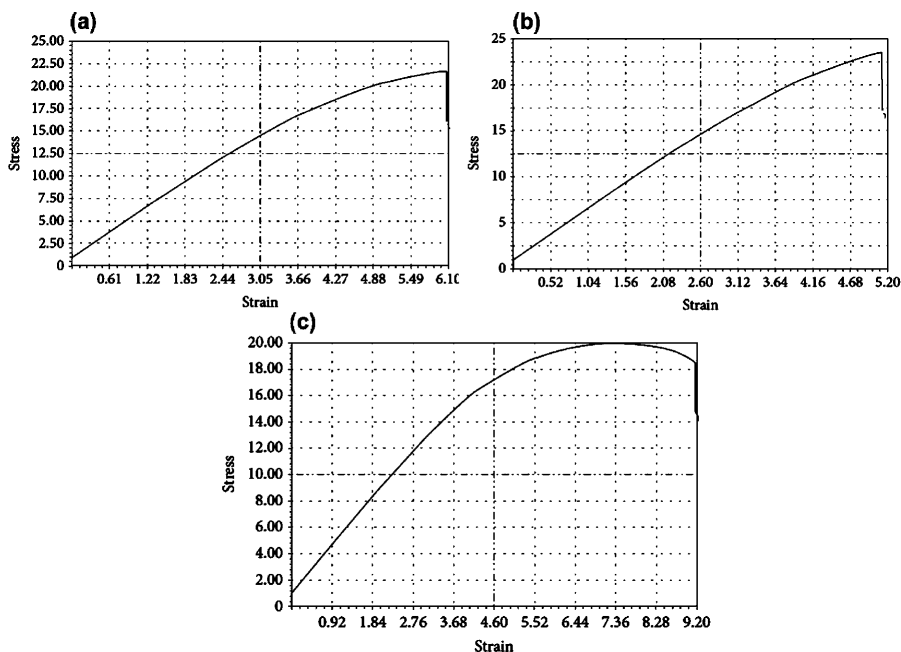**Figure 5.** *stress-strain diagram of samples (a) E_5, (b) E_2, (c) A_2, (d) B_2*

Figure 6. *Stress-strain diagram of samples (a) C_2, (b) C_3 and (c) C_4*

nanoparticles with presence of sasobit (with constant weight percentage) can lead to improve in bending strength, but increase in silica weight percentage more than 3 wt% can lead to significant decrease in the bending strength which is due to the agglomeration of silica nanoparticles at higher weight percentages. Moreover, formation of a fully active complex of sasobit with the phenolic oxygen of PNER can lead to increase in the flexibility and entanglement of chains. Despite, after increase in the weight percentage of silica nanoparticles from 3 wt% to 4 wt%, agglomeration rate of fillers were increased which can be due to the increase in the attraction forces between nanoparticles that were dominated the interaction with matrix. In this case, agglomeration of fillers can lead to the creation of stress concentration areas that can highly affect the overall properties of nanocomposites. Therefore, the energy required for samples fracture will decrease. A view of this fact can clearly be seen in **Figures 5** and **6**. Furthermore, bending test results for samples at different filler loadings can be seen in **Table 2**. In addition, **Figure 7** represent the bending test results for samples at different filler loadings.

Table 2. Three point bending test data

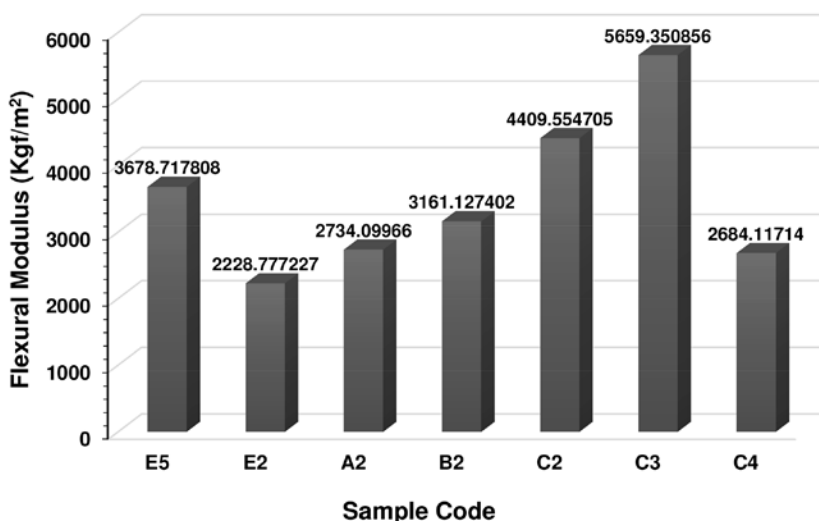| Sample code	Maximum stress (Kgf)	Point of fracture (mm)	Elastic modulus (Kgf/m^2)	Energy (J)	Yield point (Kgf)
E$_5$	10.56	3.620	17433351.576	0.215	9.098
E$_2$	16.252	8.972	1811379.736	0.884	14.068
A$_2$	18.437	8.298	2328025.568	0.862	16.159
B$_2$	18.460	7.186	15630215.849	1.033	16.439
C$_2$	21.694	6.054	3058632.104	0.800	18.519
C$_3$	23.492	5.108	3546546.677	0.688	21.030
C$_4$	19.978	9.159	2668893.735	1.306	17.786

Figure 7. Bending test results for samples at different filler loadings

Thermal Properties of Fabricated Nanocomposites

In this section, thermal properties of fabricated nanocomposites at different filler loadings were evaluated. In this case, with usage of differential scanning calorimetry (DSC) test, glass transition temperature of nanocomposites and also their thermal stability based on heat flow were evaluated. A view of DSC analysis for nanocomposites at different filler loadings can be seen in **Figure 8**. Besides, as can be seen in **Figure 8**, different amounts of sasobit was not significantly changed the glass transition temperature of nanocomposites which can be due to the compatibility of ER at same amounts of nanofiller. In addition, after the comparison between sample containing pure matrix

and other samples, it was observed that with increase in the nanofiller concentration, the order of the crystal crosslink was disrupted and glass transition temperature decreased.
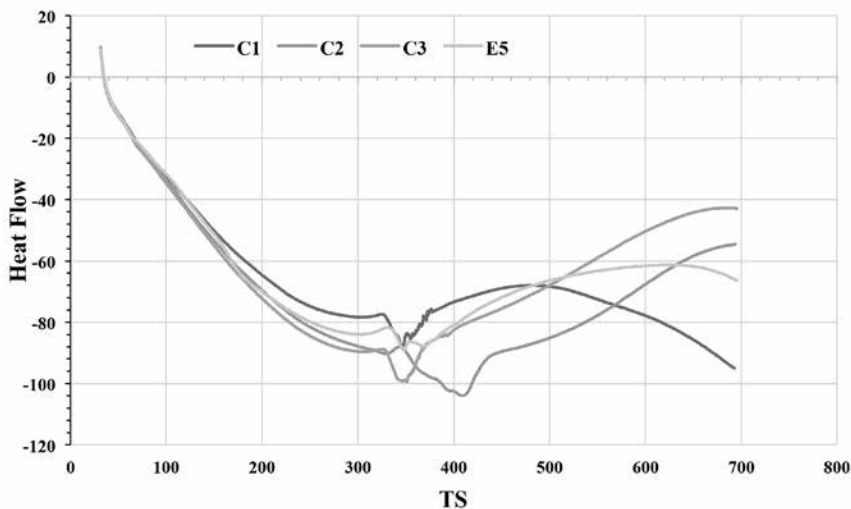

Figure 8. *Comparison between differential scanning calorimetry (DSC) test for samples E_5, C_1, C_2, C_3*

In addition, with usage thermo gravimetric analysis (TGA), effect of temperature on the weight stability of nanocomposites were examined, a view of these results for different samples can be seen in **Figure 9**. These diagrams indicated a significant increase in the thermal stability of nanocomposites containing 3 wt% silica nanoparticles in comparison with other samples. In addition, improvement in the thermal stability of nanocomposites can be attributed to the barrier effect of layered silicate structure and sasobit which retained the small molecules, generated during the thermal decomposition process thereby preventing a quick heat expansion and limiting any further degradation. Long chain length of the hydrocarbons with 45-115 carbon atoms in sasobit can extend the plastic limit and increase the range of melting temperature in blends [12, 17, 18]. Besides, the melting temperature of sasobit is 100 and at tempratures below its melting point, sasobit forms a lattice structure in blends which can provide better stability within the matrix and prevents the movement of molecules in the modified blend and thus increase in the viscosity of blend at low and intermediate temperatures [11]. On the other hand, sasobit act as a Newtonian and non-Newtonian fluid at temperatures higher and lower than its melting temperature, respectively. Eq. (1) shows sasobit's rheological sweep temperature at frequency of 1 Hz in complex hear modulus testing [19]:

$$G^* = \begin{cases} 10^6 \ Pa & 30 \leq T \leq 95 \\ -38732T + 4{\times}10^6 & 95 \leq T \leq 120 \quad R^2 = 86\% \\ 0.5 \ Pa & 120 \leq T \leq 180 \end{cases} \tag{1}$$

Where T is temperature in °C. Eq. (1) indicated that decreased significantly in temperature range of 95-120°C (around sasobit melting point of 100°C), while in temperatures below 95°C and above 120°C its remain relatively constant. Despite, thermal degradation of sasobit occurs at temperature between range of 350-520°C and its weight loss Eq. is as follows:

$$\text{Sasobit weight loss} = \begin{cases} 100\% & 50 \leq T \leq 350 \\ 0.0009T^2 - 1.34T + 472.36 & 350 \leq T \leq 550 \end{cases} \tag{2}$$

Which Ta is temperature in and is equal to 94 %. Eventually, sasobit act as a shield against the heat and in heating range more than 350°C, its degradation occurs and sasobit will lose weight.
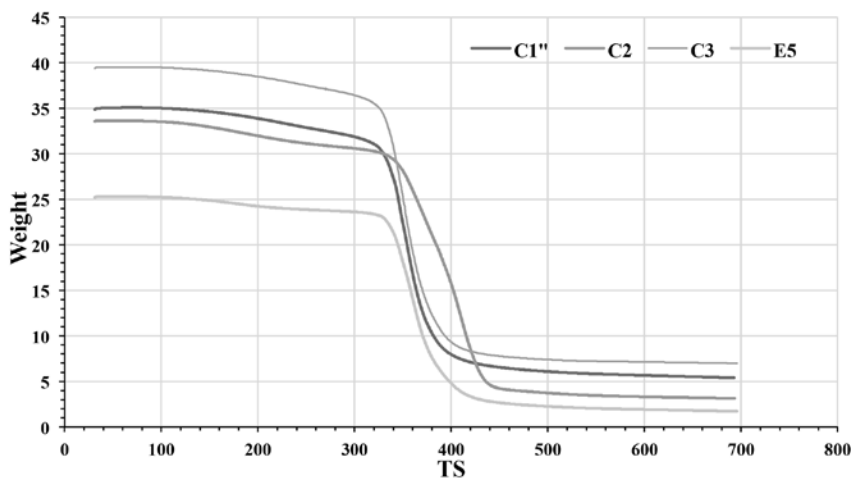

Figure 9. *Thermal gravimetric analysis test for samples E_5, C_1, C_2, C_3*

Scanning Electron Microscopy (SEM)

With usage of SEM images, surface and morphology of nanocomposites were examined. In this case, SEM analysis for different sample can be seen in **Figure 10**. **Figure 10a**, **b** and **c** shows the morphology of samples E2, B2 and C3, respectively. As mentioned, sasobit can improve the dispersion quality of fillers within the matrix [11]. As can be seen in **Figure 10a-c**, increase in sasobit loading not only can decrease the agglomeration rate of fillers but also it can improve nanocomposites morphology. In **Figure 10a** and **b**, it can

clearly be seen that fillers were agglomerated throughout the matrix but in **Figure 10c**, morphology of nanocomposite and dispersion of fillers within the matrix have improved which is due to the increase in sasobit loading.
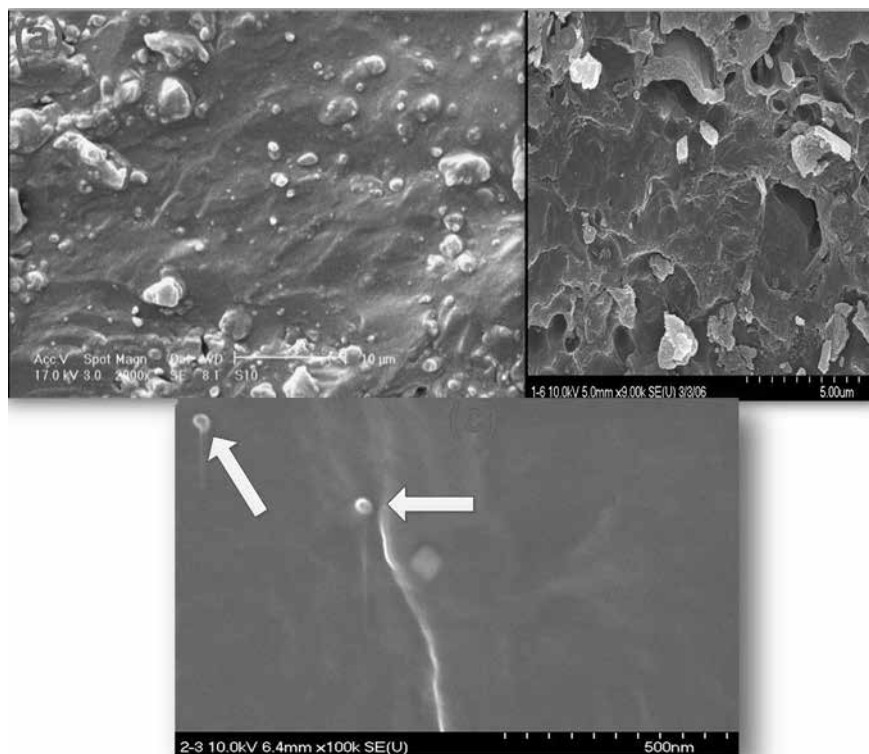

Figure 10. *SEM images of samples (a) E_2, (b) B_2 and (c) C_3*

CONCLUSIONS

In this study, with the use of a multi-step manufacturing procedure, nanocomposites containing silica nanoparticles, sasobit, UPR and PNER at different filler loadings were fabricated. In this case, the effect of sasobit and silica loadings on the mechanical, thermal and morphology of nanocomposites were evaluated. Results showed that improvement of ER with PN and UPR can improve both mechanical and thermal properties of matrix. In addition, increase in silica nanoparticles loading can lead to improve in thermal and mechanical properties of nanocomposites, but increase in silica nanoparticles loading to more than 3 wt% can improve the agglomeration rate of fillers within the matrix and thus increase in stress concentration areas which can lead to significant decrease in the mechanical properties of nanocomposites.

On the other hand, addition of sasobit along with silica nanoparticles can either improve mechanical or thermal properties of nanocomposites. Sasobit can improve the dispersion quality of fillers within the matrix and decrease the overall rate of defects throughout nanocomposites which can lead to significant improvement in nanocomposites morphology and quality. Results of this study showed that with the use of cost affordable materials such as sasobit, along with silica nanoparticles, nanocomposites with suitable thermal and mechanical properties can be achieved.

REFERENCES

1. P. Kasemsiri, A. Neramittagapong, P. Chindaprasirt, Curing kinetic, thermal and adhesive properties of epoxy resin cured with cashew nut shell liquid, *Thermochimica Acta* **600** (2015) 20-27.

2. Z. Bu, J. Hu, B. Li, Novel silicon-modified phenolic novolac resins: Non-isothermal curing kinetics, and mechanical and thermal properties of their biofiber-reinforced composites, *Thermochimica Acta* **575** (2014) 244-253.

3. A. Benny Cherian, A.V. Lity, T. Eby Thomas, Epoxy-modified, unsaturated polyester hybrid networks, *European Polymer Journal* **43** (2007) 1460-1469.

4. B.K. Kandola, L. Krishnan, D. Deli, J.R. Ebdon, Blends of unsaturated polyester and phenolic resins for application as fire-resistant matrices in fibre-reinforced composites. Part 2: effects of resin structure, compatibility and composition on fire performance, *Polymer Degradation and Stability* **113** (2015) 154-167.

5. C. Li, H. Fan, D.-Y. Wang, J. Hu, J. Wan, B. Li, Novel silicon-modified phenolic novolacs and their biofiber-reinforced composites: Preparation, characterization and performance, *Composites Science and Technology* **87** (2013) 189-195.

6. M. Endo, Y.A. Kim, M. Ezaka, K. Osada, T. Yanagisawa, T. Hayashi, M. Terrones, M.S. Dresselhaus, Selective and efficient impregnation of metal nanoparticles on cup-stacked-type carbon nanofibers, *Nano Letters* **3**(6) (2003) 723-726.

7. F. Hussain, M. Hojjati, M. Okamoto, R.E. Gorga, Review article: polymer-matrix nanocomposites, processing, manufacturing, and application: an overview, *Journal of Composite Materials* **40**(17) (2006) 1511-1575.

8. S.M. Mousavi, N. Goudarzian, S.A. Hashemi, Unsaturated Polyester Resins Modified With Cresol Novolac Epoxy and Silica Nanoparticles: Processing and Mechanical Properties, I*nternational Journal of Chemical and Petroleum Sciences* **5**(1) (2016) 13-26.

9. H.D. Wagner, R.A. Vaia, Nanocomposites: issues at the interface, *Materials Today* **7**(11) (2004) 38-42.

10.   L.R. Xu, V. Bhamidipati, W.-H. Zhong, J. Li, C.M. Lukehart, E. Lara-Curzio, K.C. Liu, M.J. Lance, Mechanical property characterization of a polymeric nanocomposite reinforced by graphitic nanofibers with reactive linkers, J*ournal of Composite Materials* **38**(18) (2004) 1563-1582.

11.   A. Jamshidi, M.O. Hamzah, Z. You, Performance of warm mix asphalt containing Sasobit®: State-of-the-art, *Construction and Building Materials* **38** (2013) 530-553.

12.   A. Syroezhko, M. Baranov, S. Ivanov, N. Maidanova, Influence of natural additives and those synthesized by the Fischer-Tropsch method on the properties of petroleum bitumen and quality of floated asphalt, *Coke and Chemistry* **54**(1) (2011) 26-31.

13.   S. Mousavi, H. Esmaeili, O. Arjmand, S. Karimi, S. Hashemi, Biodegradation Study of Nanocomposites of Phenol Novolac Epoxy/Unsaturated Polyester Resin/Egg Shell Nanoparticles Using Natural Polymers, *Journal of Materials* 2015 (2015).

14.   S. Mousavi, O. Arjmand, S. Hashemi, N. Banaei, Modification of the Epoxy Resin Mechanical and Thermal Properties with Silicon Acrylate and Montmorillonite Nanoparticles, *Polymers from Renewable Resources* **7**(3) (2016) 101.

15.   S. Mousavi, A. Aghili, S. Hashemi, N. Goudarzian, Z. Bakhoda, S. Baseri, Improved Morphology and Properties of Nanocomposites, Linear Low Density Polyethylene, Ethylene-co-vinyl Acetate and Nano Clay Particles by Electron Beam, *Polymers from Renewable Resources* **7**(4) (2016) 135.

16.   S.A. Hashemi, S.M. Mousavi, Effect of bubble based degradation on the physical properties of Single Wall Carbon Nanotube/Epoxy Resin composite and new approach in bubbles reduction, *Composites Part A: Applied Science and Manufacturing* **90** (2016) 457-469.

17.   N. Wasiuddin, N. Saltibus, L. Mohammad, Effects of a wax-based warm mix additive on cohesive strengths of asphalt binders, Transportation and Development Institute Congress 2011: Integrated Transportation and Development for a Better Tomorrow, 2011, pp. 528-537.

18.   N.M. Wasiuddin, R. Saha, J. King, William, Effects of a wax-based warm mix additive on lower Compaction Temperatures, Geo-Frontiers 2011: Advances in Geotechnical Engineering 2011, pp. 4614-4623.

19.   H.M. Silva, J.R. Oliveira, C.I. Ferreira, P.A. Pereira, Assessment of the performance of warm mix asphalts in road pavements, *International Journal of Pavement Research and Technology* **3**(3) (2010) 119-127.

S.M. Mousavi, S.A. Hashemi, S. Jahandideh, S. Baseri, M. Zarei, and S. Azadi