

그래핀/폴리카보네이트 복합재료를 함유한 POSS의 합성 및 열적 특성의 분석

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Synthesis, Characterization and Investigation of Thermal Properties of POSS Containing Graphene/Polycaprolactone Composites

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Abstract: In this study, it has been demonstrated that polyhedral oligomeric silsesquioxane (POSS) based graphene-poly-caprolactone nanocomposites (POSS-G-PCL) were successfully prepared by using ring opening polymerization method. For this purpose, first, graphene-POSS composite (GP) was synthesized with graphene oxide and aminopropylsbutyl POSS (POSS-NH₂). Second, POSS containing graphene-polycaprolactone composite (PCL-G-POSS) was synthesized by using ϵ -caprolactone, graphene-POSS, and Tin(II) octanoate as initiator in DMF at 110 °C. This reaction was repeated without of solvent (PCL-G-POSS in bulk) and by using different amount of caprolactone (PCL*-G-POSS). The synthesized composites and polymers were characterized by nuclear magnetic resonance (¹H NMR), gel permeation chromatography (GPC), and fourier transform infrared spectroscopy (FTIR). Thermal behaviors of molecules were analyzed by thermogravimetry (TG). The surface morphologies of composites were analyzed by scanning electron microscope (SEM). The results of TG and GPC analyses showed that the thermal stability and molecular weight of the composites were increased with the addition of POSS.

Keywords: polyhedral oligomeric silsesquioxane (POSS), polycaprolactone, graphene, composite, thermal properties.

Introduction

Nowadays, developing technology that can respond to the growing needs of the pursuit of superior materials continues to increase. Hybrid materials are very important in these related studies because they carry the properties of both organic and inorganic materials. Being used as organic fraction in the hybrid materials, polymers bring flexibility, lightness, easy processability and durability to product. Thermal, mechanical and chemical resistance can be gained to the product by using advanced technology polymers such as polyester and polyamide. Metal, ceramic or silicate structures can be used as inorganic matrix. However, the use of ceramic-derived materials as matrix cause to low thermal conductivity,¹⁻³ low ox-

idation resistance,^{4,5} low density, and many features like these.⁶⁻⁸ So that, different composites can be prepared between a hybrid molecule called as POSS (polyhedral oligomeric silsesquioxane) and commercial polymers like ϵ -caprolactone by using several methods (radical polymerization, click chemistry, controlled polymerization techniques, and ring opening polymerization). POSS is a relatively new type of organic-inorganic hybrid molecules. POSS has great potential in the synthesis of organic-inorganic composites and has attracted much interest in recent years.⁹ Also, it is known that PCL is synthetic polyester obtained by the self-condensation of the cyclic ester caprolactone.^{10,11} PCL has unique properties that make it attractive for biomaterials applications. Like most synthetic polymers, it has excellent water-resistant properties. At the same time, like most natural polymers, it has excellent biodegradability and biocompatibility properties. These properties have made it possible for PCL to be used in a variety of biomaterial

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applications including drug release,¹² medical devices,¹³ cell cultivation/cell culture,¹⁴ and biodegradable packaging materials.¹⁵⁻¹⁷

Also, inorganic particles are widely used as reinforcement materials for polymers.¹⁸⁻²⁰ Among inorganic materials, graphite oxide (GO) has recently attracted much research attention as a composite with polymers. GO is layer-structured compound and can be obtained by the oxidation of natural graphite.^{21,22} Recently, the improvements of other physical properties of PCL such as electrical properties and crystallization behaviors have attracted considerable interest.²³⁻²⁵ There are several preparation methods to obtain polymer-GO composite.²⁶⁻²⁸ One of them can be prepared by solution intercalation method. This is based on a solvent system in which the polymer is solubilized and GOs are dispersed in a suitable solvent, such as water, acetone, chloroform, tetrahydrofuran (THF), dimethyl formamide (DMF) or toluene, owing to the weak forces that stack the layers together. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated, the sheets reassemble, sandwiching the polymer to form the composite-nanocomposites.²⁹

In this study, we successfully synthesized POSS based graphene-polycaprolactone nanocomposite (PCL-G-POSS) by using ring opening polymerization. We could not find any detail of thermal behavior and the other characteristic features of this composite in literature. Also, it was considered that the characteristic features of poly(ϵ -caprolactone)/graphite oxide composite such as high degradation temperature, higher T_g , thermal conductivity restriction, oxidation stability were improved so we expect that this study will contribute to the literature and application areas for the POSS composites and it can play an important role as a source for studies on the POSS composites in the future.

Experimental

Materials. Tin (II) 2-ethyl-hexanoate ($\text{Sn}(\text{Oct})_2$, Aldrich, 95%, UK) were used as received. Epsilon-caprolactone (CL, Aldrich, 97%, UK) was vacuum distilled over calcium hydride. Other solvents and chemicals were purified by conventional drying and distillation procedures. The graphite powder (Sigma Aldrich Lot: BCBC7679W, USA), the potassium permanganate (Merck 99%), sulfuric acid (>96%), nitric acid, and hydrogen peroxide were purchased from Sigma-Aldrich and used as received. Aminopropylisobutylposs ($\geq 97.0\%$, Hybrid Plastics, USA), dimethylformamide (DMF) anhydrous

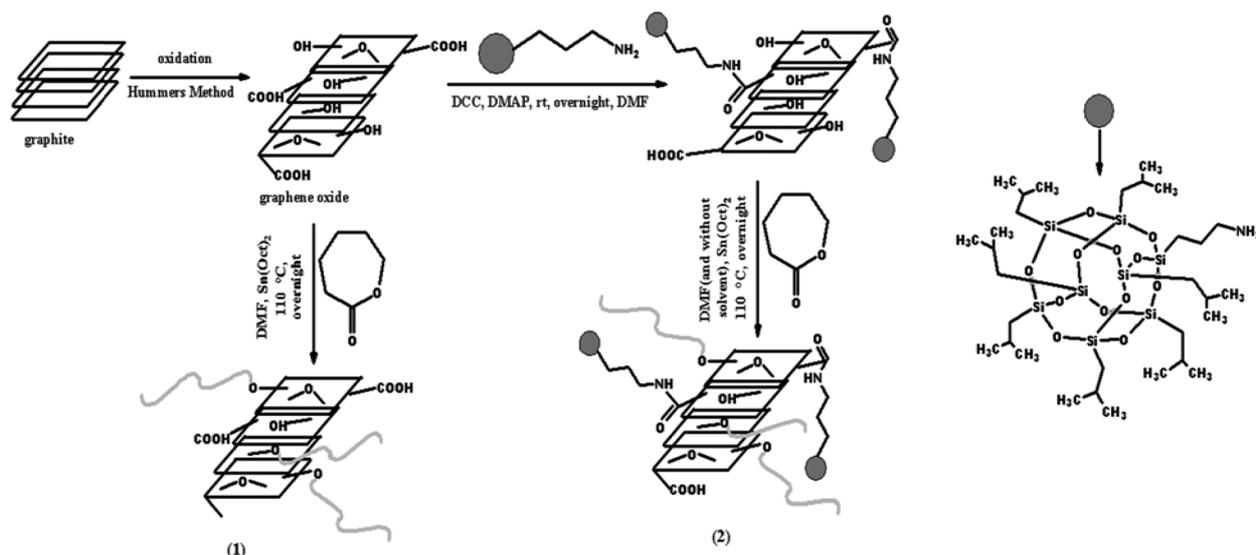
($\geq 99.9\%$, Sigma-Aldrich, UK), dicyclohexylcarbodiimide (DCC) ($\geq 99.9\%$, Sigma-Aldrich, UK), and 4-(dimethylamino)pyridine ($\geq 99.9\%$, Sigma-Aldrich, UK) were used in the experiments.

Instrumentation. ^1H NMR (NMR, nuclear magnetic resonance) measurements were recorded in CDCl_3 (deuterium chloroform) with $\text{Si}(\text{CH}_3)_4$ as internal standard, using Varian AS-400 (400 MHz) instrument (USA). Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a PerkinElmer FTIR Spectrum One-B spectrometer (USA). Molecular weights were determined by gel permeation chromatography (GPC) instrument equipped with a Waters styragel column (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 1 mL/min and a Waters 410 differential refractometer detector (UK). All SEM images were obtained by using a field emission scanning electron microscope Zeiss FE-SEM Supra 25 microscope (Germany) under high vacuum at a voltage of 15.0 kV with a working distance of 6.0 mm.

TG measurements of polymer powder samples were obtained on PerkinElmer Diamond TA/TGA(USA) from 25 to 600 °C at 10 °C heating rate under constant flow rate of 100 mL/min of nitrogen atmosphere. The sample weights for all the experiments were taken in the range of 8-10 mg.

Preparation of Graphene Oxide (GO). GO was prepared by following modified Hummers method.²² In the typical procedure, graphite (1.0 g) was mixed with 23 mL of H_2SO_4 (95%) and the mixture was stirred for 30 min within an ice bath. Potassium permanganate (6.0 g) was added very slowly in the suspension with vigorous stirring while maintaining a reaction temperature of 20 °C. The ice bath was, then, removed, and the reaction mixture was stirred overnight at 35 °C. In the next step, water was added to the pasty solution with constant agitation. Thereupon, the color of the solution changed to yellowish brown. After 2 h of vigorous stirring, 25 mL of 30% H_2O_2 was added and immediately the color turned golden yellow. The mixture was washed several times with 5% HCl and then deionized (DI) water until the solution became acid free. Then the reaction mixture was filtered and dried under vacuum at 65 °C. The GO was obtained as a black-gray powder.

Synthesis of Graphene-POSS (GP) Composite. Graphene oxide (1 mg) was mixed with 0.11 mmol (0.1 g) POSS-NH₂ and 2 mL DMF. The mixture was sonicated for 2 h. The resulting solution was charged to a 10 mL round-bottom flask and DCC (0.057 mmol, 0.0117 g), DMAP (0.057 mmol, 0.007 g) were added into the mixture. The solution was stirred over-



Scheme 1. Synthesis of POSS based graphene-polycaprolactone (PCL-G-POSS) composite.

night at room temperature. The mixture was precipitated in water and it was dried under vacuum overnight (all reaction steps can be seen at Scheme 1).

Synthesis of Graphene-Polycaprolactone (PCL-G) Composite. The ROP (ring opening polymerization) of CL was proceed with OH groups on the surface of the GO as the initiators. The desired amount of GO (1.0 mg), monomer caprolactone (CL) (18 mmol) and DMF (2 mL) were loaded into a dried three-necked flask equipped with a magnetic stirring bar. Then, the desired amount of catalysts $\text{Sn}(\text{Oct})_2$, was added into the mixture. The three-necked flask was put into an oil bath at 110 °C. Under nitrogen atmosphere with vigorous stirring and then cooled to the room temperature after reaction for 24 h. The obtained polymer was precipitated in methanol, and then washed with methanol to remove unreacted CL. Finally the PCL-G was dried in the vacuum oven at 40 °C.

General Procedure for the Synthesis of POSS Based Graphene-Polycaprolactone (PCL-G-POSS) Composite. In the typical experiment, the desired amount of graphene POSS (GP) (26.3 mg), monomer CL (2 mL, 18.04 mmol), DMF (2 mL, 28.83 mmol) were loaded into a dried three-necked flask equipped with a magnetic stirring bar. Then, the desired amount of catalysts $\text{Sn}(\text{Oct})_2$, was added into the mixture. The three-necked flask was put into an oil bath at 110 °C. Under nitrogen atmosphere, the mixture was vigorously stirred and then cooled to the room temperature after reaction for 2 h. The obtained polymer was diluted by chloroform (10 mL) and precipitated in methanol, then washed with methanol to

Table 1. Molecular Weight, PDI and %Yield of PCL-G and PCL-G-POSS Composites

Composites	M_w	M_n	PDI	%Yield
PCL-G	7800	6500	1.2	65
PCL-G-POSS	10800	8400	1.2	70
PCL*-G-POSS	11500	9000	1.2	70
PCL-G-POSS in bulk	15000	9500	1.5	70

remove unreacted CL. Finally the PCL-G-POSS (grey-white powder) was dried in the vacuum oven at 40 °C. The reaction was repeated without solvent (under reduced pressure, bulk reaction). Also the same reaction was tried to using 1 mL (9.02 mmol) caprolactone (PCL*-G-POSS) under the same conditions. Molecular weight of samples were listed in Table 1.

Results and Discussion

In our study, we first synthesized GO and GP. Following experiment was carried out for graphene-polycaprolactone composite and POSS based graphene-polycaprolactone composite (PCL-G and PCL-G-POSS). These composite polymers were synthesized via ring opening polymerization. Chemical structure of both esters and polymers were identified by several techniques (FTIR, ^1H NMR, GPC, TG, and SEM).

It was proved by FTIR (Figure 1) and ^1H NMR (Figure 2) spectroscopy that the polymerization has occurred. As seen in Figure 1, the FTIR absorption bands for C=O bond of the

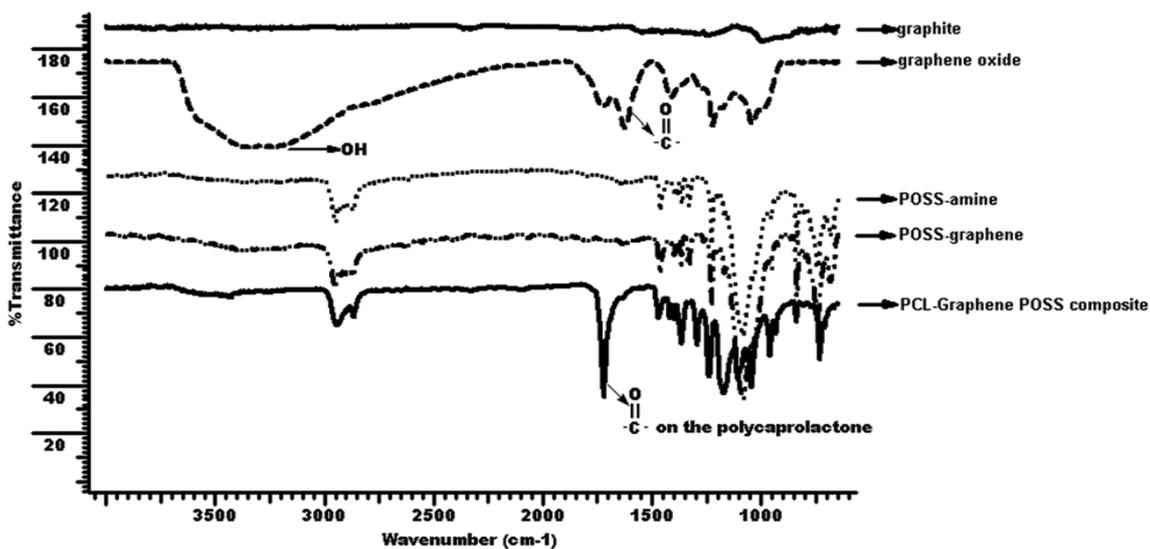


Figure 1. FTIR spectra of graphite, GO, POSS-NH₂, POSS-graphene, and PCL-G-POSS.

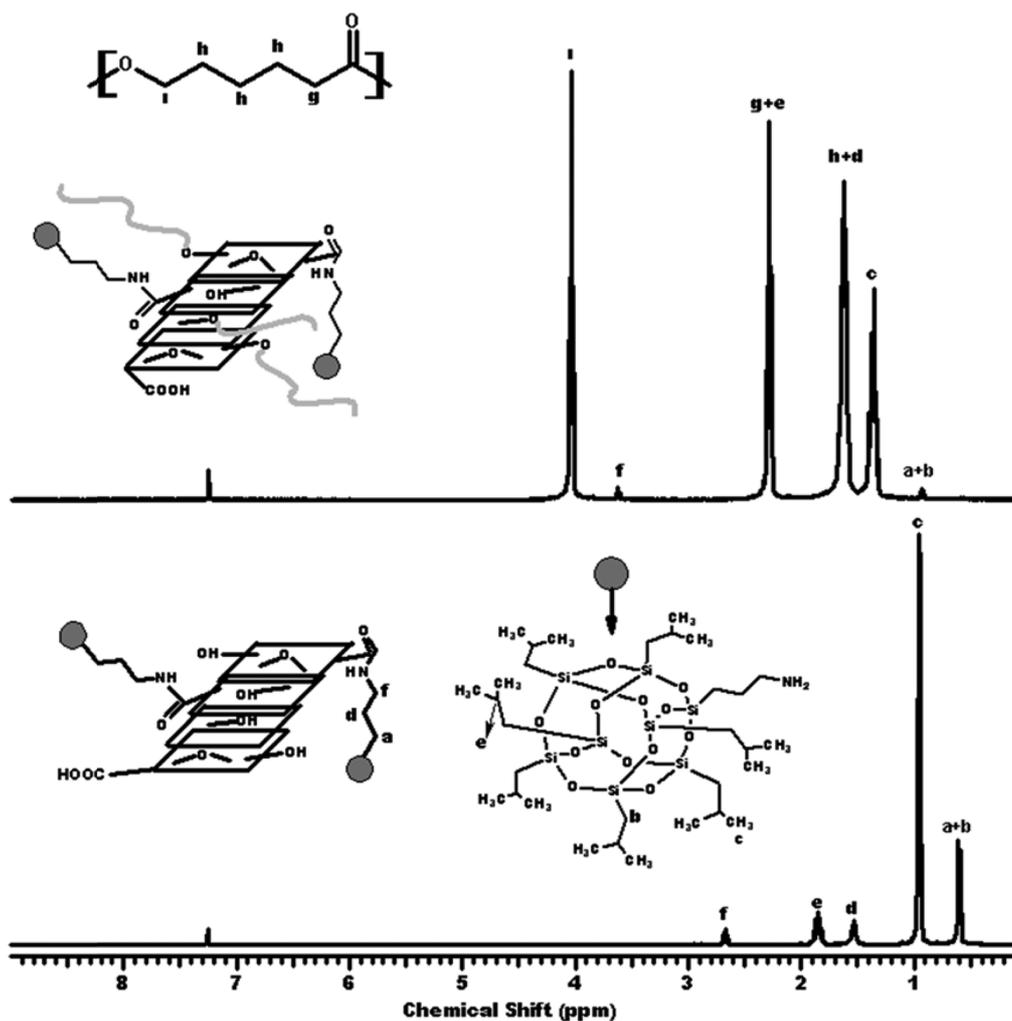


Figure 2. ¹H NMR spectrums of graphene-POSS and PCL-G-POSS.

PCL-G-POSS composite takes place around 1700 cm^{-1} while the characteristic strong absorption band of the ether group appears at 1100 cm^{-1} , and two bands for C-H bending appear at 1233 and 855 cm^{-1} . $^1\text{H NMR}$ spectra are belong to POSS-graphene and PCL-G-POSS. The characteristic peaks for $-\text{NH}-\text{CH}_2$ protons between 2.55 and 2.6 ppm. Additionally, CH_3 protons were detectable as a sharp signal at 1 ppm. Some parts of the CH_2 group protons are observed at 0.6 ppm because of the neighboring silisium. The other parts of CH_2 are seen about 1.5 ppm. The characteristic signal for the $(\text{CH}_3)_2\text{CHCH}_2$ is observed at $1.8-1.9$ ppm. All of proton signals are showed in Figure 2.

Figure 3 and Figure 4 show the TG thermograms of PCL-G, PCL-G-POSS, PCL-G-POSS in bulk, PCL*-G-POSS under argon atmosphere and air over a temperature range 30 to $600\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Synthesized polymers has degraded in one stage in under argon unlike to air. When the decomposition in argon atmosphere was compared with in the air atmosphere, it has been observed that thermal stability of polymers has increased. Because of oxidation thermal degradation behavior of polymer composites are similar to each other but according to data obtained from TG studies, it is clear that char yield of the the composites (PCL-G-POSS) is enhanced when compared with PCL-G. This result shows that POSS molecule gains stability to the composite. This is because the G-POSS is a hybrid molecule and $-\text{Si}-\text{O}-$ and $-\text{Si}-\text{C}-$ bonds have higher energy than others. A similar result that POSS increase thermal stability has been reported in literatures.³⁰ Also, caprolactone ratio in composite (PCL*-G-POSS) was reduced to observe the change of thermal behavior of composite but it did not change significantly.

M_n (number-average molecular weight), M_w (weight-average molecular weight), and the polydispersity index (PDI) of synthesized polymer composites were measured by GPC as the results are showed in Table 1. According to Table 1, PCL-G-

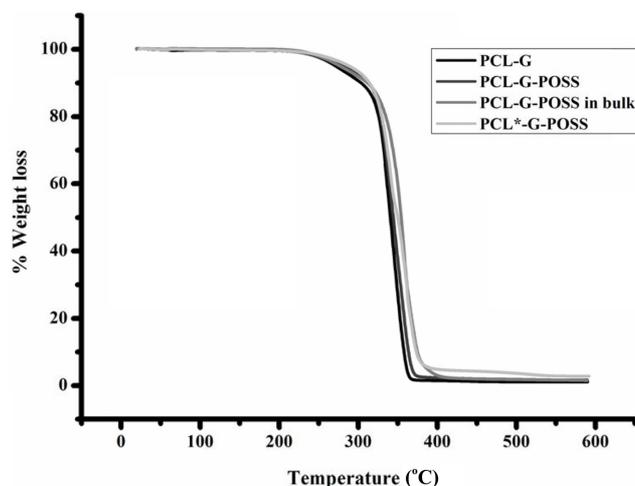


Figure 3. TG thermograms of PCL-G, PCL-G-POSS, PCL-G-POSS in bulk, PCL*-G-POSS under argon atmosphere.

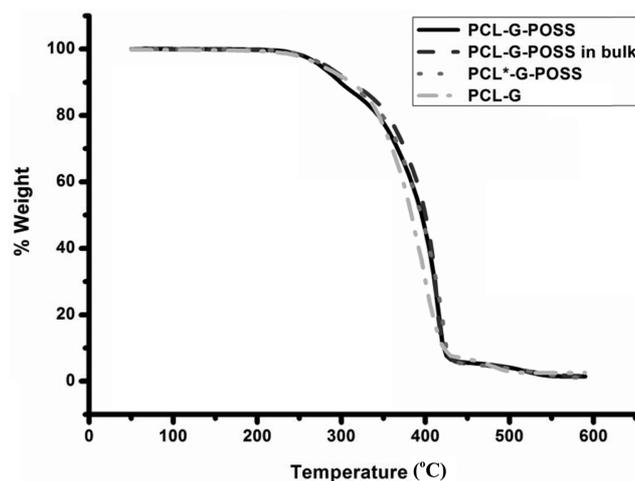


Figure 4. TG thermograms of PCL-G, PCL-G-POSS, PCL-G-POSS in bulk, PCL*-G-POSS under air.

POSS composites have higher molecular weight than PCL-G composite. This can attribute a direct result of presence of POSS in composite. PDI ratios are the same except for the

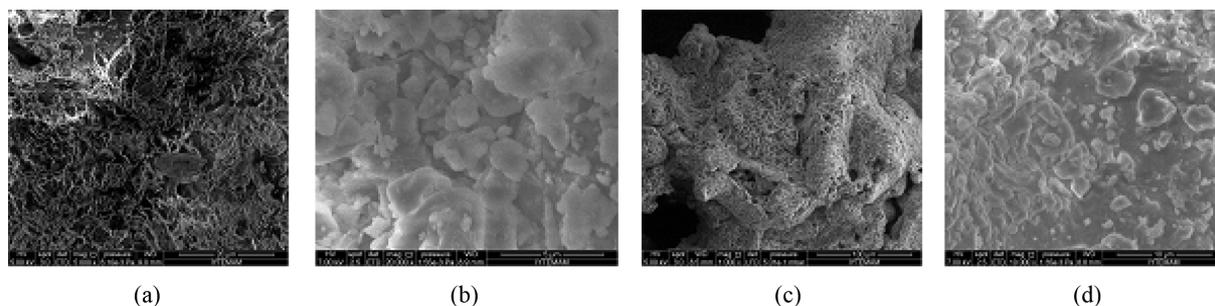


Figure 5. SEM images of (a) PCL-G-POSS; (b) POSS-graphene; (c) PCL; (d) POSS-NH₂.

PCL-G-POSS in bulk. As compared to other composites which they were synthesized in solvent, the reason of high PDI of PCL-G-POSS (in bulk) can be related with intense of POSS in polymer-composite chain because it increased in volume per gram so weight-average molecular weight (M_w) increased more than the other composites.

Figure 5 shows five SEM images of the surface of synthesized composites. In Figure 5(a), POSS-graphene is embedded in the PCL matrix, and rough interfaces between POSS-graphene and PCL are observed. As shown in the SEM image of Figure 5(b), many entangled clusters of POSS-NH₂ are observed. If insufficient dispersion and poor interfacial adhesion between filler and matrix occur, it is really difficult to find the individually embedded POSS in the polymer matrix. SEM images of POSS, PCL-graphene oxide, and synthesized composites are similar to literatures.^{31,32}

Conclusions

POSS-G-PCL composites were prepared by ring-opening polymerization method. As a result, the molecular weight of graphene-POSS composite increased with the POSS contents. FTIR spectroscopy supported the generation of new composite between graphene-POSS and PCL. Syntheses of composites were supported by ¹H NMR. On the other hand, the SEM image showed both the embedment of POSS containing graphene composite within the PCL matrix and the thicker diameter of POSS-graphene after polymerization, implying semi-homogeneous morphological characteristics, and good compatibility. According to data obtained from TG, the presence of POSS plays important role for thermal stability.

References

- G. Kickelbick, *Prog. Polym. Sci.*, **28**, 83 (2003).
- J. Pyun and K. Matyjaszewski, *Chem. Mater.*, **13**, 3436 (2001).
- H. Althues, J. Henle, and S. Kaskel, *Chem. Soc. Rev.*, **36**, 1454 (2007).
- T. Kuilla, S. Bhadra, D. Yao, N. H. Kim, S. Bose, and J. H. Lee, *Prog. Polym. Sci.*, **35**, 1350 (2010).
- D. Gnanasekaran, K. Madhavan, and B. S. R. Reddy, *J. Sci. Indus. Res.*, **68**, 437 (2009).
- B. Janowski and K. Pielichowski, *Polimery*, **53**, 87 (2008).
- S. W. Kuo and F. C. Chang, *Prog. Polym. Sci.*, **36**, 1649 (2011).
- V. V. Shevchenko, A. V. Stryutskii, V. N. Bliznyuk, N. S. Klimenko, A. V. Shevchuk, E. A. Lysenkov, and Y. P. Gomza, *Polym. Sci. Ser. B*, **56**, 216 (2014).
- K. Tanaka and Y. Chujo, *J. Mater. Chem.*, **22**, 1733 (2012).
- Z. Q. Ai, Q. L. Zhou, R. Guang, and H. T. Zhang, *J. Appl. Polym. Sci.*, **96**, 1405 (2005).
- Y. Yildirim, B. Doğan, S. Muğlalı, F. Saltan, M. Özkan, and H. Akat, *J. Appl. Polym. Sci.*, **126**, 1236 (2012).
- J. Bei, W. Wang, Z. Wan, and S. Wang, *Polym. Adv. Technol.*, **7**, 104 (1996).
- M. Yasin and B. Tighe, *Biomaterials*, **13**, 9 (1992).
- L. Rouxhet, F. Duhoux, O. Borecky, R. Legras, and Y. J. Schneider, *J. Biomater. Sci. Polym. Ed.*, **9**, 1279 (1998).
- M. F. Koenig and S. J. Huang, *Polymer*, **36**, 1877 (1995).
- M. A. Tasdelen, *Eur. Polym. J.*, **47**, 937 (2011).
- G. Biresaw and C. J. Carriere, *J. Appl. Polym. Sci.*, **83**, 3145 (2002).
- I. J. Arvanitoyannis, *Macromol. Sci. Polym. Rev.*, **39**, 205 (1999).
- I. Arvanitoyannis, E. Psomiadou, N. Yamamoto, and J. M. V. Blanshard, *Polymer*, **36**, 493 (1995).
- I. Arvanitoyannis, E. Psomiadou, N. Yamamoto, and J. M. V. Blanshard, *J. Appl. Polym. Sci.*, **56**, 1045 (1995).
- B. C. Brodie, *Phil. Trans. R. Soc. A*, **149**, 249 (1859).
- W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, **80**, 1339 (1958).
- T. Kuill, S. Bhadra, D. Yao, N. H. Kim, S. Bose, and J. H. Lee, *Prog. Polym. Sci.*, **35**, 1350 (2010).
- R. Jeffrey, A. Potts, R. Daniel, B. Dreyer, W. Christopher, B. Bielawski, S. Rodney, and A. Ruoff, *Polymer*, **52**, 5 (2011).
- R. Daniel, A. Dreyer, P. B. Sungjin, W. Christopher, A. Bielawski, S. Rodney, and B. Ruoff, *Chem. Soc. Rev.*, **39**, 228 (2010).
- K. Zahra, K. Sepideh, and S. S. Naser, *Iran. Polym. J.*, **24**, 203 (2015).
- A. Lerf, H. He, M. Forster, and J. Klinowski, *J. Phys. Chem. B*, **102**, 4477 (1998).
- P. Liu, K. Gong, P. Xiao, and M. Xiao, *J. Mater. Chem.*, **36**, 933 (2010).
- W. D. Lee, *J. Polym. Sci., Part B: Polym. Phys.*, **45**, 28 (2007).
- L. Kuo, L. Shaorong, H. Bin, and W. Chun, *Iran. Polym. J.*, **21**, 497 (2012).
- S. Sepidar, M. Eoin, C. T. Brianna, G. Sanjeev, L. O. David, and G. W. Gordon, *Carbon*, **52**, 296 (2013).
- N. Toktam, T. Aaron, and M. S. Alexander, *J. Colloid Inter. Sci.*, **435**, 145 (2014).