

A Toughened PLA/Nanosilica Composite Obtained in the Presence of Epoxidized Soybean Oil

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ABSTRACT: In this manuscript, a toughened PLA/nanosilica composite with good storage stability was obtained in the presence of the epoxidized soybean oil (ESO). The composite was fabricated via a twin-screw extruder, and characterized by the FTIR, selective distribution test, and SEM. The surface of nanosilica was modified by the ESO through the chemical bonding, and this rendered the nanosilica to selectively localize in ESO droplets in the composite. As a result, the PLA/nanosilica composite was changed from brittleness to ductility with the addition of ESO. For example, the elongation and notched impact strength of the PLA/silica/ESO nanocomposite with 5 wt % nanosilica and 15 wt % ESO were $\sim 42\%$ and ~ 11 KJ/m², respectively, which were much higher than neat PLA or PLA/nanosilica composite without ESO. Furthermore, the change of the brittle fracture of PLA into ductile fracture was investigated by SEM micrographs in detail. A possible toughening mechanism was also proposed. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41220.

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INTRODUCTION

In recent years, environmental concerns and the shortage of petroleum resources have driven many efforts on the development and production of biodegradable or bio-based materials, which are known as “green materials.”¹ Among these materials, polylactide (PLA) is one of the most important biodegradable and bio-based polymers, and the monomers of which are generally derived from corn and sugar cane.² PLA is now not only used as biomedical materials in surgical sutures and controlled drug delivery systems but also used to substituted some conventional plastics to a certain extent due to its excellent mechanical strength and modulus.^{3,4} However, the inherent brittleness, poor heat resistance, low elongation at break ($<5\%$), and high price prevent it from being used in many applications.⁵

How to improve the toughness of PLA is a key study for both academic and industrial researchers.⁶ Plasticizers are frequently used not only to improve the process-ability of thermoplastics but also to increase the flexibility and ductility of glassy polymers.⁷ Although the toughness of PLA can be achieved by adding a plasticizer,^{8–11} the stiffness and modulus of PLA would greatly be decreased by the plasticizer. Inorganic filler is used to increase the stiffness of PLA, whereas no remarkable toughness can be obtained.

To overcome drawbacks resulting from the adding of only a plasticizer or an inorganic filler, a lot of work has been done on PLA/plasticizer/inorganic filler ternary systems, where both plasticizer and inorganic filler were used to enhance the toughness and stiffness.^{12–14} Unfortunately, due to the nonchemical reaction among PLA, plasticizers, and inorganic filler, plasticizers tend to migrate to the surface of the PLA and as a result the ductility of PLA composites eventually deteriorates due to the loss of plasticizers.¹⁵

To limit the migration of the low molecular weight plasticizers and toughen the PLA for a long time, chemical bond should be generated among the PLA, plasticizer, and filler. Recently, a series of studies have been done by our group on the utilization of reactively bio-based plant oil as plasticizers for PLA/starch blends.^{16–18} It was found that if the plant oil reacted with starch and formed a flexible interphase between PLA and starch, the ductility of PLA/starch blends could be increased. Based on this technology, the combination of plasticizer and filler via the chemical reaction is not only helpful to improve the overall mechanical properties but also to resolve the migration of plasticizers in the PLA/filler/plasticizer ternary system. However, the starch is belonged to the large-scale organic filler. The effect of the combination of starch and plasticizer on the improvement

of the mechanical properties of PLA/starch blends is not very obviously. Therefore, adding nanofillers and reactive plant oil plasticizers can represent an interesting way to extend and to improve the properties of PLA.

This article follows our previous papers on the utilization of plant oil as the reactive toughening agent for PLA/nanofiller composites. Meanwhile, the plant oil as the bio-based plasticizer is of current interest to toughen the bio-based PLA.^{19–22} As reported from these plant oils, the epoxidized soybean oil (ESO), with the nature of chain flexibility and reactivity of epoxy functional group with PLA,^{23–25} can be not only recognized as one of potential bio-based plant oil plasticizers to improve the toughness of PLA/nanofiller composites but also to produce some chemical reaction with nanofiller to limit its migration. As for the inorganic filler, the nanosilica has the potential reactive hydroxyl groups with ESO on its surface will be selected in the PLA/nanofiller/ESO ternary system. Moreover, the nanosilica used as a filler and crystallization nucleating agent to reinforce the PLA has been detailed investigated in other literatures.^{26–28} However, with our best knowledge, no reference has suggested a method of using the ESO to steadily toughen the PLA/nanosilica composite by chemical reaction during the simple melt-blending.

To evaluate the influence of the chemical reaction between ESO and nanosilica on the mechanical properties of PLA, the three components are melt-blended by means of a two-screw extruder to fabricate the PLA/ESO/silica ternary nanocomposite. Furthermore, the distribution state of nanosilica and ESO in PLA matrix is systematically evaluated by SEM. The mechanical are characterized by tensile, impact, and DSC experiments to discuss the effects of ESO combined with nanosilica on PLA. Meanwhile, the toughening mechanism of the combination of ESO with nanosilica in PLA is investigated by the SEM. At last, the storage stability of the combination of ESO with nanosilica toughened PLA samples was evaluated by retesting their tensile and notched impact properties after 5 months.

EXPERIMENTAL

Materials

A semicrystalline extrusion grade, PLA 4032D was supplied by NatureWorks (Minnesota, USA). It was vacuum dried at 80°C for 8 h before use. The nanosilica (~30 nm) was bought from Shenzhen Yifeng Development Co., Ltd (Guangdong, China), and it was dried in a vacuum dryer for 24 h at 100°C before used. The chemical pure grade ESO was purchased from the Aladdin Reagent (Shanghai, China) and was used directly without further purification.

Preparation of the PLA Composites

PLA/nanosilica composites with and without ESO were firstly melt-blended in a Brabender twin-screw extruder (Brabender, Germany). The rotation rate and the mixing temperature were set at 40 rpm and 170°C/175°C/175°C/170°C/175°C, respectively. Where-after, the melting blends were water-cooled and sent to a LQ-25 granulator (Hengxi Machinery Manufacturing Co., Ltd, Taizhou, China) to make pellets. At last, the pellets of

PLA blends were dried at 85°C in a vacuum drying oven for 24 h before injection molding.

The FTIR Measurement

To prove the reaction between the silica and ESO, Extra-SiO₂-1 and Extra-SiO₂-2 were extracted from PLA/nanosilica composite (95/5) and PLA/nanosilica/ESO composite (80/5/15) by Soxhlet extraction, respectively. Extraction with chloroform at 85°C was continued for 1 week. The residual nanosilica white powders obtained by Soxhlet extraction were dried at 60°C for 24 h in the vacuum oven for the FTIR analysis. The FTIR (Nicolet FTIR 6700 infrared spectrophotometer, America, KBr powder) was used to characterize over a range of 4000–400 cm⁻¹.

Morphological Characterization

Microstructure of the fracture surfaces of samples with the dimension of 80 × 10 × 4 mm³ were recorded by a low expansion scanning electron microscope (SEM, Hitachi S-4800). The same SEM was also used to observe the tensile longitudinal fracture section and impact fracture section of neat processing PLA, PLA/nanosilica composite (95/5), PLA/ESO blend (85/15), and PLA/nanosilica/ESO ternary composite (80/5/15). To explore the toughening mechanism, the resulted tensile longitudinal sections of PLA with or without the filler were fractured in liquid nitrogen, respectively. Furthermore, the tensile longitudinal section of PLA/silica/ESO ternary nanocomposite with 25% elongation was fractured in liquid nitrogen to explore the detailed toughening mechanism of PLA. Moreover, the tensile and impact fractured surfaces were sputtered with gold before SEM examination. By these observations, the fracture mode of the materials can be revealed.

The Mechanical Properties Characterization

To measure the tensile properties of the neat PLA and PLA composites, the standard samples were firstly prepared by a HTF90W1 injection molding machine (Haitian Plastics Machinery, Ningbo, China). The temperatures of the injection molding were set at 180°C/185°C/185°C/185°C/180°C, respectively. The injection pressure was set at 65 MPa. The cooling time of the injection molding was 20 s. And then, according to ISO 527-2: 1996 (International Standards), the samples were injection molded into 1A type dumbbell-shaped samples with a thickness of 4.0 mm. The width of the narrow part and overall length for the dumbbell-shaped samples is 10.0 mm and 100.0 mm, respectively. Lastly, the tensile testing was carried out at a rate of 20 mm/min by a universal testing machine to investigate the tensile properties of the neat PLA and PLA composites. Four samples for each composite were tested. These samples were conditioned at room temperature for a period of 1 week prior of testing.

Based on the America standard of ISO179-1:1998 (International Standards), the samples were injection molded into a type of rectangular solid with a dimension of 80 × 10 × 4 mm³ for impacting test in a HTF90W1 injection molding machine (Haitian Plastics Machinery, Ningbo, China). To conduct the notch impact test, the samples were then notched on a WAY-240 universal sampling machine (Chengde Kecheng Testing Machine Co., Ltd, China), the depth of notch on these samples were arranged from 1.9 to 2.1 mm. The finally notch impact test was

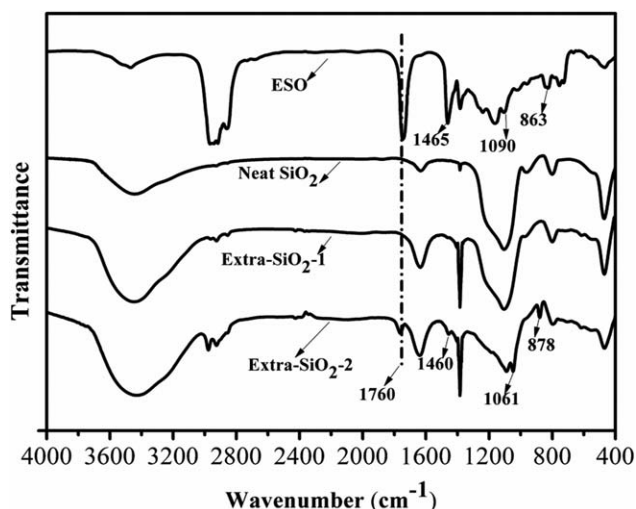


Figure 1. The FTIR spectra of ESO, neat silica, Extra-SiO₂-1, and Extra-SiO₂-2.

performed on a mechanical impact tester (XJ-50Z, Chengde Dahua Testing Machine Co. Ltd, Chengde, China). In the process of notch impact test, a 2.75 J pendulum was used to determine the notch impact strength. These samples were conditioned at room temperature for a period of 1 week before testing, and five samples for each composite were tested.

RESULTS AND DISCUSSION

The FTIR Analysis of the Extracted Nanosilica

To prove the reaction between ESO and nanosilica particles in the melted-blended process, the FTIR spectra of ESO, neat nanosilica, and two different kinds of extracted nanosilica, namely Extra-SiO₂-1 and Extra-SiO₂-2, were shown in Figure 1. The Extra-SiO₂-1 extracted from PLA/nanosilica (95/5) composites exhibited similar FTIR spectra with the neat nanosilica. Meanwhile, the peaks ranged from 1700 cm⁻¹ to 1800 cm⁻¹, which could be attributed to carboxyl (—C=O—) group, did not appear in the FTIR spectra of neat nanosilica and Extra-SiO₂-1. Thus, it could be inferred that there was no chemical change in Extra-SiO₂-1 particles and their surface could not have been modified by PLA. While the Extra-SiO₂-2 particles extracted from the PLA/nanosilica/ESO ternary (80/5/15) composite were measured by FTIR. Interestingly, it is observed that the peak at 1760 cm⁻¹ attributed to carboxyl

(—C=O—) group appeared in the FTIR spectra. Meanwhile, the peaks at 1465, 1090, and 863 cm⁻¹ in the spectra of ESO appeared in the relevant positions of Extra-SiO₂-2 FTIR spectra (1460, 1061, and 878 cm⁻¹). Moreover, the intensity of alkyl (—CH₃—/—CH₂—) peaks in the spectra was greatly enhanced in contrast with Extra-SiO₂-1. Thus, during the melt-blending, the surface of nanosilica particles was mainly bonded by ESO molecules grafting via the chemical reaction between ESO and nanosilica.

Morphology Analysis

To investigate the effect of ESO on the existing state of nanosilica in the PLA matrix, morphologies of PLA and PLA nanocomposites were observed by SEM, respectively. It was noteworthy that many nanosilica aggregate particles were dispersed in the PLA matrix [Figure 2(a)], indicating the poor dispersion of silica in PLA. Meanwhile, the morphology can be obviously changed by the addition of ESO. In Figure 2(b), similar with our previous and Ali's researches,^{16,23} it can be found that many ESO was dispersed in PLA matrix with the formation of droplets.

However, while the three components PLA, nanosilica, and ESO were melt-blended together, it was observed that many of the ESO droplets contained many nanosilica granules inside [Figure 2(c)]. Meanwhile, the volume of ESO droplets was enlarged by the immigrated of nanosilica particles. It seems that the nanosilica particles were inclined to localize dispersion in ESO droplets, and formed some mixture of ESO/nanosilica in the PLA matrix.

Moreover, the nanosilica particles in PLA/nanosilica composites with and without ESO were extracted out and marked as Extra-SiO₂-1 and Extra-SiO₂-2, respectively. The dispersed stability of 0.03 g Extra-SiO₂-1 and 0.03 g Extra-SiO₂-2 in 1.2 g water and 0.12 g ESO were shown in Figure 3, respectively. It could be observed that the Extra-SiO₂-1 was homogeneously dispersed in water but precipitated in ESO, whereas, the dispersion of Extra SiO₂-2 was in opposite to that of Extra SiO₂-1. It was indicated that the nanosilica in PLA/nanosilica composite was hydrophilic, but it is oleophilic in PLA/nanosilica/ESO ternary composite. Thereof, it was reasonably believed that the dispersion of nanosilica in PLA matrix was different with the addition of ESO. Maybe, in the PLA/nanosilica/ESO ternary composite, the nanosilica particles were inclined to localize in ESO phase, but not in the PLA phase, which similar with the phenomenon in Figure 3.

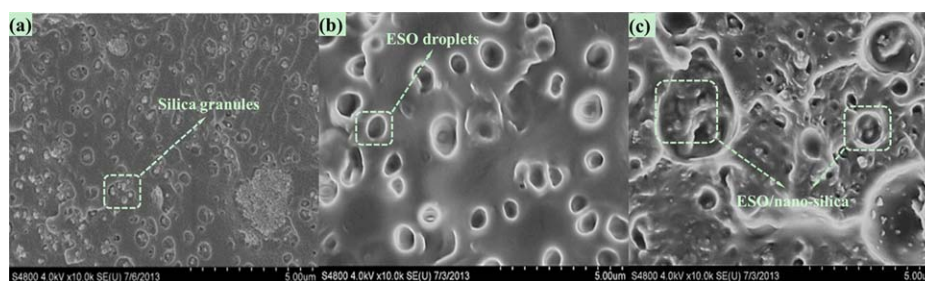


Figure 2. Morphology of the PLA/silica nanocomposites and PLA/ESO blend. (a) PLA/silica nanocomposite (95/5), (b) PLA/ESO blend (85/15), and (c) PLA/silica/ESO ternary nanocomposite (80/5/15). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

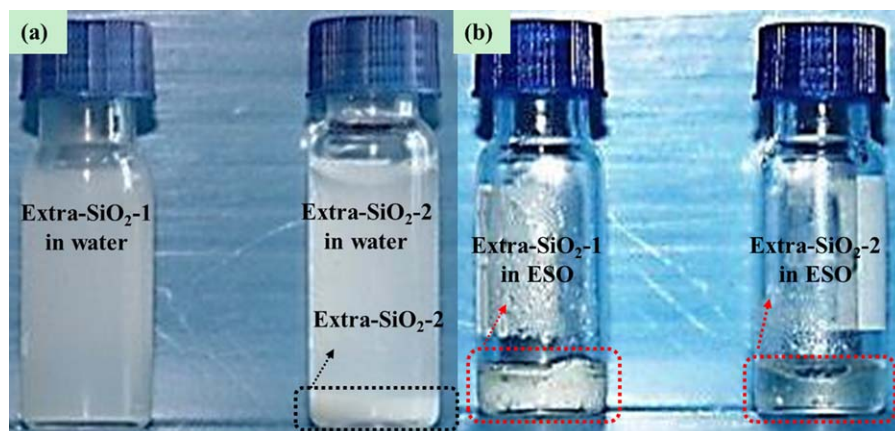


Figure 3. The dispersion of Extra-SiO₂-1 and Extra-SiO₂-2 in water (a) and ESO (b) for 10 min, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thus, as proved in Figure 1 and Figure 3, the possible inner structure of PLA/nanosilica/ESO ternary composite in Figure 2(c) could be illustrated in Figure 4. During the melt-blending process, the oleophilic characteristic of the pristine nanosilica was produced by the grafting of ESO on its surface. As a result, the nanosilica particles were inclined to selectively localize in ESO droplets, and formed some mixture of ESO/nanosilica in the PLA matrix. This localization of nanosilica was also investigated in other immiscible polymer blended systems with its hydrophilic character changing.^{29–31} But, with our best knowledge, no direct reference has been reported the combination of nanosilica and ESO could be formed in the PLA matrix via the simple melt-blending.

Mechanical Properties

Pure PLA is a fairly rigid material with a high tensile modulus (~ 3399 MPa) and tensile strength (~ 66 MPa), but it is very brittle with very low elongation at break ($\sim 3\%$) and weak impact strength (~ 3 KJ/m²), as shown in Figure 5. The addition of nanosilica particles induced an increase in tensile modulus of PLA, but it had no obvious effect on the tensile strength, elongation at break, and impact strength. Clearly, the inorganic nanosilica particles can only enhance the stiffness of PLA. When the ESO is blended with PLA, it does not function as a plasticizer and cannot tune PLA from rigid to ductile (Figure 5). Even higher content of ESO seems not to influence the mechanical properties of PLA at all, which also proved by Broström.²³

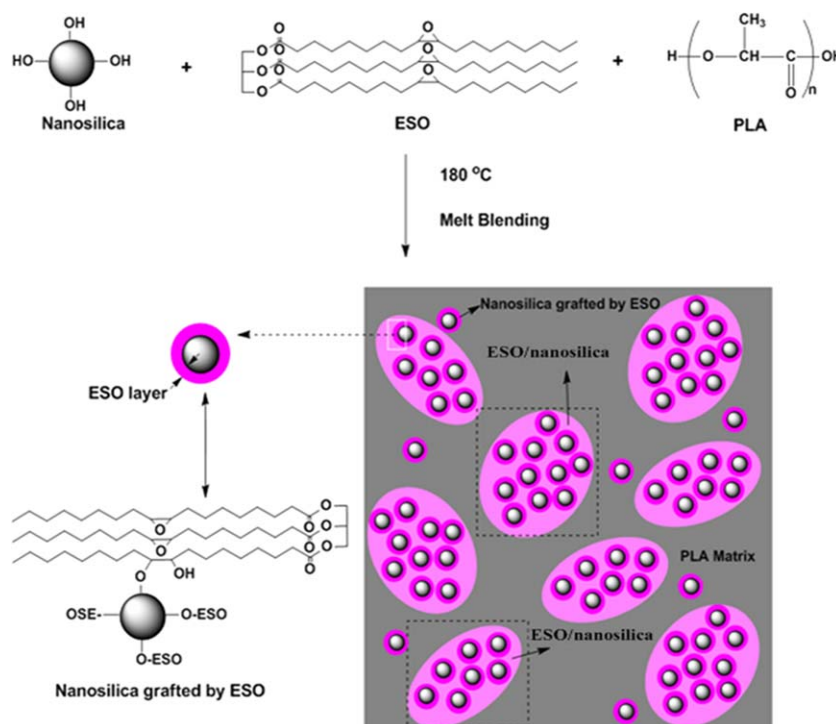


Figure 4. The possible inner structure of PLA/silica/ESO ternary nanocomposite during melt-blending process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

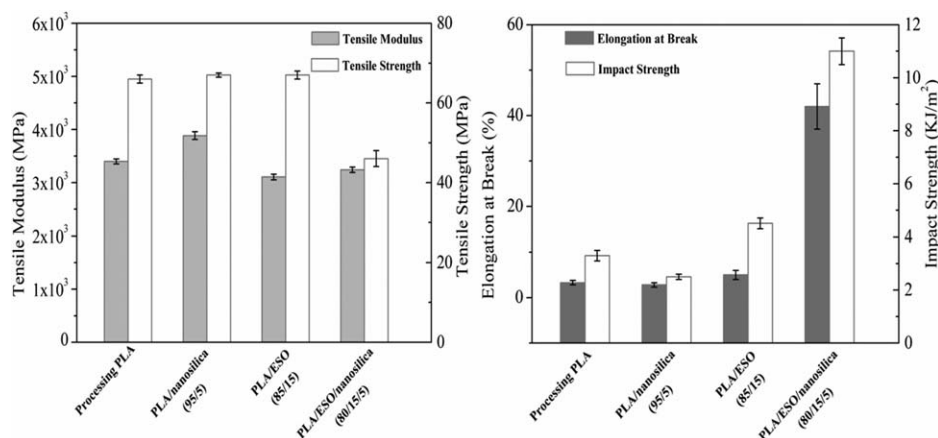


Figure 5. Mechanical properties of PLA, PLA/ESO, PLA/silica, and PLA/silica/ESO nanocomposites.

However, the addition of ESO to PLA/nanosilica composite could considerably improve the mechanical properties of PLA/nanosilica binary composite (Figure 5). With 15 wt % ESO in PLA/nanosilica composite, the elongation at break and notched impact strength increased to $\sim 42\%$ and ~ 11 KJ/m², respectively. Meanwhile, its tensile modulus and tensile strength could also reach up ~ 3300 MPa and ~ 46 MPa, respectively. All of the mechanical properties change above revealed that the combination of ESO and nanosilica could tune the brittle PLA from rigid to ductile state. Moreover, the stiffness and tensile strength of PLA could also reach a high level with the combination of ESO and nanosilica. Thus, the combination of ESO with nano-

silica will offer a simple method to toughen PLA with balanced stiffness via the melt blending.

Toughening Mechanism of the Combination of Nanosilica with ESO

To further explore the toughening mechanism of PLA with or without the combination of ESO with nanosilica, SEM analysis was conducted. The tensile and fracture SEM micrographs are shown in Figure 6. It was shown that the tensile and impact fracture behavior of the PLA/ESO or PLA/nanosilica did not have any change after drawing and impacting, which could be attributed to the PLA' brittle failure according to Yan's work.³²

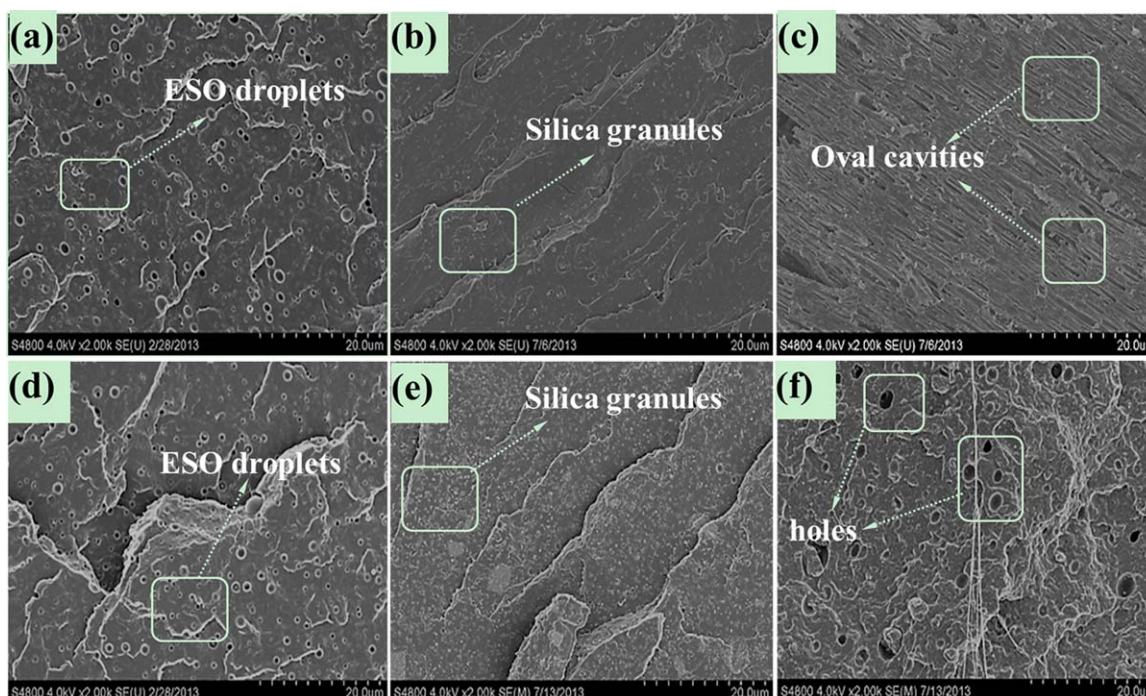


Figure 6. Tensile SEM micrographs of (a) PLA/ESO blend (85/15), (b) PLA/silica nanocomposite (95/5), and (c) PLA/silica/ESO ternary nanocomposite (80/5/15) tensile in the tensile direction and their corresponding SEM micrographs for impact fracture surfaces (d-f). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

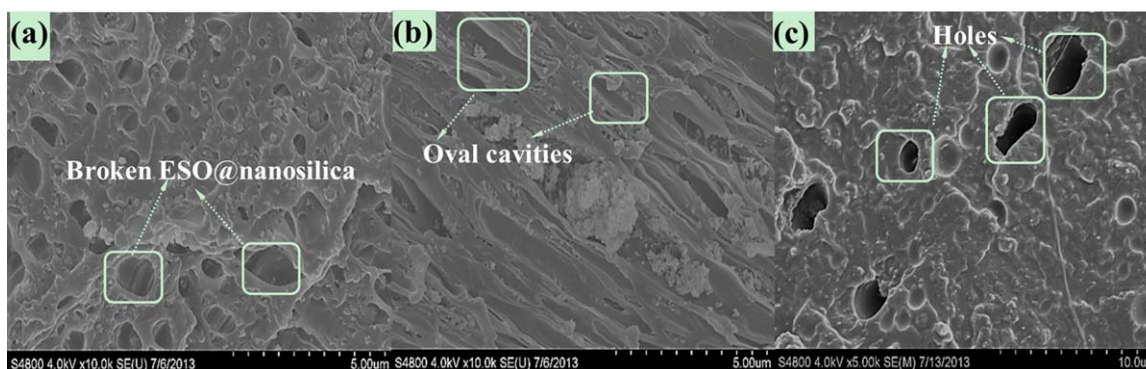


Figure 7. Tensile and impact SEM micrographs of PLA/nanosilica/ESO (80/5/15) composite, (a) with $\sim 25\%$ elongation (unbroken), (b) with $\sim 40\%$ elongation at break, (c) notched impact fracture surface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thereof, it was concluded that neither ESO nor nanosilica could change the fracture brittle behavior of PLA in terms of tensile and impact experiments.

However, while the combination of ESO with nanosilica existed in PLA matrix, the composite which had the highest elongation at break [Figure 6] could experience tremendous plastic deformation in the stress direction [Figure 6(c)]. Many long oval cavities were visible [Figure 6(c)], which was obviously different from the fracture surface before drawing [Figure 2(c)]. Moreover, the fracture surface of PLA/nanosilica/ESO ternary composite which had the highest impact strength also underwent an obvious change [Figure 5(f)]. Some holes occurred in the PLA matrix after impacting, which indicated the detaching of nanosilica/ESO phases from PLA matrix in the impacting process. As obtained from the tensile and impact fracture of toughened polymer systems,^{33–36} it was well known that crazing, cavitation, shear banding, crack bridging, and shear yielding have been identified as important energy dissipation processes. Thereof, the results mentioned above showed that the great toughness improvement of ternary composite might be ascribed to the cavitation effect produced by the combination of nanosilica with ESO under stretching and impacting. However, the mechanism of the oval cavities or holes produced by the nanosilica/ESO mixture under stretching or impacting is not very clear.

Furthermore, the morphology of PLA/silica/ESO ternary nanocomposite with 25% elongation in the tensile direction was investigated to explore the detailed process of cavities generation. It could be seen that under stretching, some oval cavities and deformed and fractured nanosilica/ESO mixture simultaneously appeared in the PLA matrix [Figure 7(a)]. With the stretching lasting, the cavities might be initiated from the fractured location of nanosilica/ESO mixture and gradually propagated in the stress direction with the deformation of the PLA matrix. At last, the long cavities appeared in the PLA matrix and many broken ESO/nanosilica mixtures were found surrounding the cavities. As a result, the mechanical energy was locally released by the formation of cavities and shear yielding was then allowed, which resulted in the improved elongations of the PLA.

Meanwhile, some holes under impacting [Figure 7(c)] were visibly occurred in the PLA matrix because of some nanosilica/ESO mixtures debonding from the PLA matrix under impacting. After that, the impact strength of the PLA/nanosilica/ESO composite was increased. The similar results were also reported in the poly(lactic acid)/poly(butylene adipate-*co*-terephthalate)/nanoparticle ternary composites via the formation of holes or cavitation in PLA matrix.³⁶ Overall, the toughened mechanism of PLA under drawing and impacting was related with the combination of ESO with nanosilica in PLA.

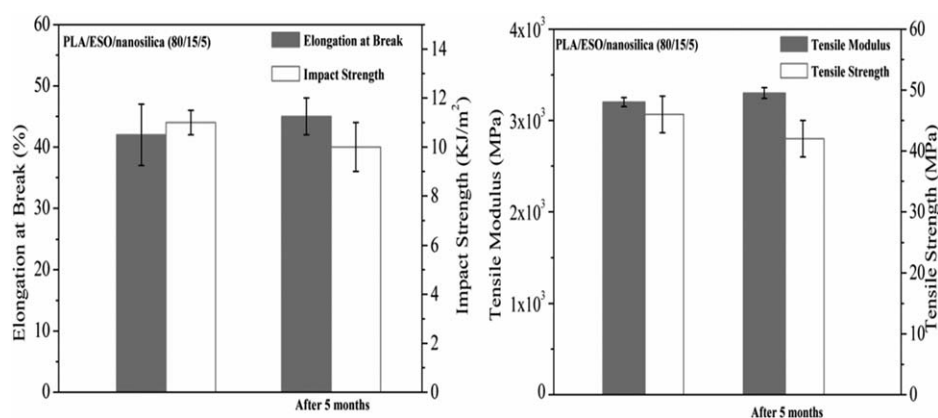


Figure 8. The tensile and notched impact testing of PLA/nanosilica/ESO ternary composite (80/5/15).

Time Stability of the Toughened PLA with the Addition of ESO and Nanosilica

Based on the researches of Höglund' group,¹⁵ the plasticizers without any reactive groups reacting with PLA or fillers could easily migrate from the PLA matrixes and resulted in the properties of PLA deterioration. To assess the stability of nanosilica/ESO mixtures toughening the PLA, the tensile and notched impact testing of the PLA/nanosilica/ESO ternary composite (80/5/15) was investigated after 5 months. As shown in Figure 8, the elongations and notched impact strength of the PLA/nanosilica/ESO ternary composite could still reach ~45% and ~10 KJ/m², which had not much change after 5 months. Meanwhile, in Figure 8, the tensile modulus and strength neither changed too much in contrast with its originated state. Based on these results, it indicated that the ESO with reactive groups could form a stable nanosilica/ESO mixture to toughen the PLA with the balanced stiffness via the melt blending.

CONCLUSIONS

PLA, ESO, and nanosilica were melt-blended via a twin screw extruder to successfully prepare a toughened and stiff PLA ternary composite. During the melt-blending process, the ESO could chemically bond onto the surface of silica particles via the ready reaction of ESO with silica, and then brought the modified silica particles to selectively localize in ESO droplets and formed some nanosilica/ESO mixtures in the PLA matrix. With the combination of nanosilica with ESO in the PLA matrix, it could induce cavitation to consume the energy produced under the stretching and impacting, which resulted in the toughness of PLA obviously improved. Moreover, through the combination of ESO and nanosilica, the stiffness of PLA was not decreased much by ESO. Meanwhile, after 5 months, the mechanical properties of PLA/ESO/nanosilica ternary composite including its elongation and impact strength remained unchanged, which reflected the good storage stability of PLA composite promoted by the combination of ESO with nanosilica. This article offers an effective method to fabricate an ESO/nanosilica mixture to toughen the brittle PLA with a balanced stiffness via the melt blending.

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REFERENCES

1. Mohanty, A. K.; Misra, M.; Drzal, L. T. *J. Polym. Environ.* **2002**, *10*, 19.
2. Södergard, A.; Stolt, M. *Prog. Polym. Sci.* **2002**, *27*, 1123.
3. Fambri, L.; Pegoretti, A.; Fenner, R.; Incardona, S. D.; Migliaresi, C. *Polymer* **1997**, *38*, 79.
4. Ma, Z.; Gao, C.; Gong, Y.; Shen, J. *Biomaterials* **2005**, *26*, 1123.
5. Hiljanen-Vainio, M.; Varpomaa, P.; Seppala, J.; Tormala, P. *Macromol. Chem. Phys.* **1997**, *197*, 1503.
6. Anderson, K. S.; Schreck, K. M.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 85.
7. Mascia, L.; Xanthos, L. *Adv. Polym. Tech.* **1992**, *11*, 237.
8. Ljungberg, N.; Wesslen, B. *Polymer* **2003**, *44*, 7679.
9. Anderson, K. S.; Hillmyer, M. A. *Polymer* **2004**, *45*, 8809.
10. Labrecque, L. V.; Kumar, R. A.; Dave, V. J. *Appl. Polym. Sci.* **1997**, *66*, 1507.
11. Jacobsen, S.; Fritz, H. G. *Polym. Eng. Sci.* **1999**, *39*, 1303.
12. Gao, X.; Qu, C.; Zhang, Q. *Macromol. Mater. Eng.* **2004**, *289*, 41.
13. Li, H.; Huneault, M. A. *Polymer* **2007**, *48*, 6855.
14. Odent, J.; Habibi, Y.; Raquez, J. M. *Compos. Sci. Technol.* **2013**, *84*, 86.
15. Höglund, A.; Hakkarainen, M.; Albertsson, A. C. *Biomacromolecules* **2009**, *11*, 277.
16. Xiong, Z.; Li, C.; Ma, S. Q.; Feng, J. X.; Yang, Y.; Zhang, R. Y. *Carbohydr. Polym.* **2013**, *95*, 77.
17. Xiong, Z.; Yang, Y.; Feng, J. X.; Zhang, X. M.; Zhang, C. Z.; Tang, Z. B. *Carbohydr. Polym.* **2013**, *92*, 810.
18. Xiong, Z.; Zhang, L. S.; Ma, S. Q.; Yang, Y.; Zhang, C. Z.; Tang, Z. B. *Carbohydr. Polym.* **2013**, *94*, 235.
19. Chang, K.; Robertson, M. L.; Hillmyer, M. A. *ACS. Appl. Mater. Interfaces* **2009**, *10*, 2390.
20. Gramlich, W. M.; Robertson, M. L.; Hillmyer, M. A. *Macromolecules* **2010**, *43*, 2313.
21. Robertson, M. L.; Chang, C. K.; Gramlich, W. M.; Hillmyer, M. A. *Macromolecules* **2010**, *43*, 1807.
22. Robertson, M. L.; Paxton, J. M.; Hillmyer, M. A. *ACS. Appl. Mater. Interface* **2011**, *3*, 3402.
23. Broström, J.; Boss, A.; Chronakis, I. S. *Biomacromolecules* **2004**, *5*, 1124.
24. Xu, Y. Q.; Qu, J. P. *J. Appl. Polym. Sci.* **2009**, *112*, 3185.
25. Ali, F.; Chang, Y. W.; Kang, S. C. *Polym. Bull.* **2009**, *62*, 91.
26. Ji, G.; Zhai, W.; Lin, D. *Ind. Eng. Chem. Res.* **2013**, *52*, 6390.
27. Wu, J. H.; Yen, M. S.; Kuo, M. C.; Chen, B. H. *Mater. Chem. Phys.* **2013**, *142*, 726.
28. Papageorgiou, G. Z.; Achilias, D. S.; Nanaki, S. *Thermochim. Acta* **2010**, *511*, 129.
29. Fenouillot, F.; Cassagau, P.; Majesté, J. C. *Polymer* **2009**, *50*, 1333.
30. Elias, L.; Fenouillot, F.; Majesté, J. C.; Cassagnau, P. *Polymer* **2007**, *48*, 6029.
31. Li, P.; Huang, Y. J.; Kong, M. Q.; Lv, Y. D.; Luo, Y.; Yang, Q.; Li, G. X. *Colloid. Polym. Sci.* **2013**, *291*, 1693.
32. Yan, S.; Yin, J.; Yang, Y. *Polymer* **2007**, *48*, 1688.
33. Johnsen, B. B.; Kinloch, A. J.; Mohammed, R. D. *Polymer* **2007**, *48*, 530.
34. Kim, G. M.; Michler, G. H. *Polymer* **1998**, *39*, 5699.
35. Jiang, L.; Wolcott, M. P.; Zhang, J. *Biomacromolecules* **2006**, *7*, 199.
36. Jiang, L.; Liu, B.; Zhang, J. *ACS Ind. Eng. Chem. Res.* **2009**, *48*, 7594.