

## Influence of Plasticizers on Mechanical, Thermal, and Migration Properties of Poly(Lactic Acid)/Zeolite Composites

Pei Qin<sup>1</sup>, Hyun-Mo Jung<sup>2</sup>, Dong-Soo Choi<sup>3</sup>, Sung-Wook Hwang<sup>1\*</sup>

### 〈Abstract〉

Poly(lactic acid) (PLA) is considered as one of the most promising bio-based polymers due to its high strength, high modulus, good processability, transparency after processing, and commercial availability. This study aimed to investigate the mechanical, thermal, and migration properties of poly(lactic acid)/zeolite (10 phr) composites prepared with various biocompatible plasticizers, such as triethyl citrate(TEC), tributyl citrate(TBC), and poly(ethylene glycol)(PEG400), through differential scanning calorimetry(DSC), thermo-gravimetric analysis(TGA) and standard tensile testing. The incorporation of PEG400 significantly increased the elongation at break, and DSC results showed that the addition of plasticizers drastically decreased the  $T_g$  of PLA/zeolite composites and improved the melt flow and processability. Besides, it was found from TGA results that PLA/zeolites composites plasticized by TEC and TBC were more easily to be thermally degraded than the composites plasticized by PEG400.

*Keywords : Poly(lactic acid), PLA, Plasticizer, Composites, Migration*

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1\* Corresponding Author, School of Chemical Engineering & Advanced Materials Engineering, Keimyung University, 1095 Dalgubeoldae-ro, Dalseo-gu, Daegu, 42601, Korea  
E-mail: swhwang@kmu.ac.kr

2 Dept. of Logistic Packaging, Kyongbuk Science College, Korea  
E-mail: hmjung@kbsc.ac.kr

3 Postharvest Engineering Division, National Institute of Agricultural Sciences, Korea  
E-mail: choi0ds@korea.kr

## 1. Introduction

In recent years, with increase of environmental awareness, bio-based polymers have attracted much attention due to their renewability, biocompatibility, and biodegradability. The most common bio-based polymers are poly(lactic acid)(PLA), polyhydroxy butyrate(PHB), polyhydroxyalkanoates (PHAs), polycaprolactone (PCL), and polybutylene adipate terephthalate (PBAT).[1] Among them, poly(lactic acid)(PLA) is considered as one of the most promising bio-based polymers due to its high strength and modulus, good processability, transparency after processing, and commercial availability.[2] Thanks to those advantages, PLA could be widely used in artificial bones, food packaging, disposable tableware, and other fields. Compounding with various nano/micro inorganic fillers could significantly enhance the mechanical, electrical, gas barrier, and thermal properties of PLA based composites. However, the brittleness at room temperature, extremely poor impact resistance, and weak crystallization ability of PLA limit its a variety of industrial applications. To overcome these drawbacks, many efforts have been made to improve PLA performance through different techniques such as modifications, adding reinforcing agents, and blending, alloying, and/or copolymerizing by realizing physical treatment, etc.[3]

Zeolites are hydrated alumina silicates of alkaline and alkaline earth elements having microporous crystal structures. It has been

extensively used as catalysts, adsorbents, and ion exchange reaction due to their regular pore structures and high thermal stability.[4,5] Zeolites are also used in active packaging systems particularly for fresh fruit and vegetables to extend shelf life, in which zeolites could provide an ability to separate specific molecules from the gas mixtures according to their selective pore dimension and polarity. The silver-loaded zeolites could be used as an antibacterial agent to be incorporated into the polymer matrix acting good anti-microbial packaging materials.[6,7] Therefore, the inclusion of zeolites into bio-based polymer, PLA may hold promise for a wide range of packaging applications. However, the addition of zeolite to compound with PLA still could not change the brittle nature. Lee et al.[8] studied the effect of Triethyl Citrate on the dispersibility and water vapor sorption behavior of PLA/zeolite composites. The mechanical properties of the PLA/zeolite composites without plasticizer was found to have the high tensile strength and brittleness, but the tensile strength of the composites added with plasticizers decreased, and the elongation at break considerably increased. This is because plasticizers could reduce the strong intramolecular attraction between polymer chains and increase the free volume within the polymer chains. It also was found that the plasticizer could cause uniform dispersion of the zeolite particles and increase its compatibility with the polymer.[8]

Selection of plasticizers for PLA composites used in food packaging is required to consider many conditions: compatibility, low volatility, anti-migration, extraction within the service life, non-toxic, etc.[9] Several compounds have been studied as plasticizers for PLA to improve the ductility, such as triacetin[10], citrate esters [10,11], glycerol [12], oligomers lactic acid [13], poly(ethylene glycol) (PEG) [14,15], poly(propylene glycol) (PPG) [16] and epoxidized soybean oil [17], etc. It has been reported that due to the polar interaction between the ester group of PLA and the citrate plasticizer, PLA has good solubility in the citrate plasticizer.[18] Wang et al.[19] analyzed the plasticization effect of PLA by using a poly(ethylene glycol)(PEG) and found that the introduction of PEG reduces the intermolecular force and enhances the mobility of PLA chains, thus improving the crystallization capacity and flexibility of PLA.

However, In case that the content of PEG above 10 wt%, the phase separation would occur in the miscible PLA/PEG blend system.

In this study, the influence of several plasticizers such as triethyl citrate, tributyl citrate, and PEG400 on the physical, mechanical, and thermal properties of the PLA/zeolite composites was investigated, and the migration behavior of plasticizer from PLA/zeolite composites was also assessed.

## 2. Materials and Methods

### 2.1 Materials

PLA resin (2003D grade, 6 g/10 min of the melt flow index at 210°C) was supplied by NatureWorks (Minnetonka, MN, USA). The

**Table 1. Chemical structure and properties of materials**

Material	Supplier	Chemical structure	General properties
PLA	NatureWorks		T <sub>g</sub> : 58°C, T <sub>m</sub> : 150°C~160°C Mw: 120000g/mol, MFI: 6g/10min
Zeolite	Sigma Aldrich	Na <sub>86</sub> [AlO <sub>2</sub> ] <sub>86</sub> (SiO <sub>2</sub> ) <sub>106</sub> · xH <sub>2</sub> O	Mw: 60.08g/mol Appearance: white powder
TBC	Sigma Aldrich		Density: 1.043g/mL, Mw: 360.45g/mol Boiling point: 170°C, Appearance: Oily liquid
TEC	Sigma Aldrich		Density: 1.137g/mL, Mw: 276.28g/mol Boiling point: 294°C, Appearance: Oily liquid
PEG400	Sigma Aldrich		Density: 1.128g/mL, Boiling point: 290°C Mw: 380-420g/mol, Appearance: Oily liquid

**Table 2. Thermal characteristics and the degree of crystallinity of PLA/zeolite composites plasticized by different plasticizers**

Sample	T <sub>g</sub> (°C)	T <sub>cc</sub> (°C)	ΔH <sub>cc</sub> (J/g)	T <sub>m</sub> (°C)		ΔH <sub>m</sub> (J/g)	X <sub>c</sub> (%)
PZ	60.2	117.9	21.36	149.2		23.51	2.54
PZ TEC 5phr	55.6	110.8	19.86	146.4		20.58	0.89
PZ TEC 10phr	47.3	107.8	19.87	142.7	149.6	20.78	1.17
PZ TEC 15phr	38.0	97.9	19.97	137.1	147.0	20.32	0.47
PZ TBC 5phr	52.1	110.2	19.26	145.4		20.03	0.95
PZ TBC 10phr	42.7	100.0	20.34	146.3	149.1	20.49	0.19
PZ TBC 15phr	35.5	92.8	20.27	136.7	147.3	20.51	0.32
PZ PEG400 5phr	55.9	109.9	22.80	146.3	153.0	23.46	0.82
PZ PEG400 10phr	41.1	91.3	23.13	137.9	149.8	25.61	3.20
PZ PEG400 15phr	36.9	88.1	19.92	137.0	150.2	24.06	5.56

zeolite(Molecular sieves 13X, powder type: 2 μm average particle size)was purchased from Sigma Aldrich (St. Louis, Missouri, USA). The plasticizers selected for this study were purchased from Sigma Aldrich (St. Louis, Missouri, USA). The choice of these plasticizers was based on requisites such as environmental friendly and biocompatibility. The characteristics of these materials are listed in Table 1 and 2.

## 2.2 Composites preparation

PLA/zeolite composites with various plasticizers were prepared according to a two-step procedures. The PLA resin and the additives were first dried in a vacuum oven at 60°C for 24 hrs. Varying amounts of each plasticizers (5, 10 and 15 phr) were mixed together with 10 phr of zeolite and PLA within an internal mixer (Brabender, Germany) at a barrel temperature of 180°C and a

rotation speed of 50 rpm for 7 min. The composition was selected based on the authors previous study for comparison.[8] In the second step, the PLA/zeolite/plasticizers composites were compression-molded using a QMESYS hot press (QMESYS, Korea) at 180°C (3 min pre-melting, 3 min pressing and 5 min cooling) to obtain sheets/films for further characterizations. All of the samples were dried at 60°C for 12 hrs in a vacuum oven before the experiments.

## 2.3 Characterization

### 2.3.1 Mechanical properties

Tensile testing was carried out at room temperature with a universal test machine QM100SE(QMESYS, Korea) by following the ASTM D882-01 Standard.[20] The cross-head speed was of 12.5 mm/min. The test specimens were dried at 60°C for 12 hrs in a

vacuum oven before the experiments.

### 2.3.2 Thermal properties

The thermal stability of composites were obtained from Simultaneous Thermo-gravimetry and Differential Thermal Analyzer, DTG-60 (Shimadzu, Japan). Samples of approximately 10mg were heated at 10°C/min from 30°C to 800°C under nitrogen atmosphere (flow rate 10mL/min). Differential scanning calorimetry (DSC) analysis were carried out by using a DSC25 (TA, USA) under nitrogen atmosphere (flow rate 50ml/min). Samples (around 5 mg) were sealed in aluminum pans and heated from 0°C to 200°C, cooled to 0°C and heated again to 200°C at 10°C/min. Glass transition temperature ( $T_g$ ), Cold crystallization temperature ( $T_{cc}$ ) and melting temperature ( $T_m$ ) were determined during the second heating scan. The degree of crystallinity ( $X_c$ ) was calculated using the following equation [21]:

$$X_c = \frac{\Delta H_{m,PLA} - \Delta H_{cc,PLA}}{\Delta H_{m,PLA}^o \cdot x_{PLA}}$$

Where  $\Delta H_m$  is the enthalpy of melting,  $\Delta H_{cc}$  is the enthalpy of cold crystallization,  $\Delta H_m^o$  is the enthalpy of fusion of 100% crystalline PLA (93.6 J/g)[22], and  $x_{PLA}$  is the weight fraction of PLA in the composite.

### 2.3.3 Migration tests

Films prepared by compression-molding were used for the additives migration tests. The migration property of each PLA/zeolite

composites were tested by a Simultaneous Thermo-gravimetry/Differential Thermal Analyzers (TGA). Samples of approximately 10mg were heated at 20°C/min from 30°C to 110°C, and maintained it at 110°C for 300 min under nitrogen atmosphere (flow rate 20 mL/min).

## 3. Results and Discussion

### 3.1 Mechanical properties

It is well known that PLA has a high tensile and modulus, with a low elongation at break. With the addition of plasticizers, changes in mechanical properties were identified by the tensile test. Figure 1 shows the typical stress-strain curves of PLA/zeolite composites plasticized by TEC, TBC, and PEG400, and the results of tensile strength and elongation at break were shown in Figure 2. PLA/zeolite composites fractures without yielding behavior, exhibiting as a typical

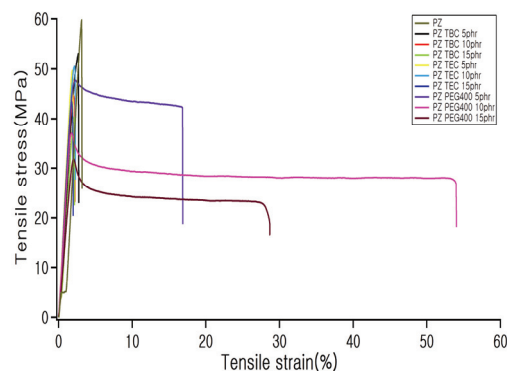
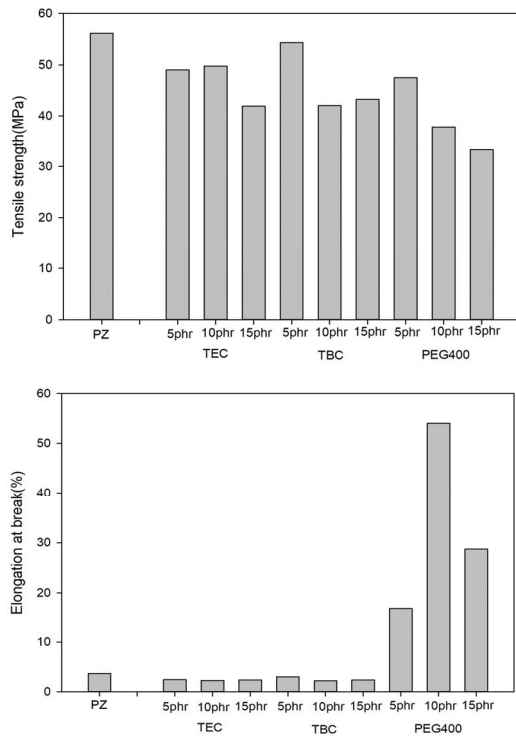


Fig 1. Tensile stress-strain curves of PLA/zeolite plasticized by TEC, TBC, and PEG400



**Fig 2. Tensile strength and elongation at break of PLA/zeolite plasticized by TEC, TBC, and PEG400**

brittle material with a high tensile strength of 56.1 MPa and a low elongation at break of 3.7%. For PLA/zeolite composites plasticized with TEC, the tensile strength dropped to 49.0 MPa, even elongation at break decreased to 2%. The increase of TEC content to 15 phr further decreases the tensile strength to about 41.9MPa. PLA/zeolite composites plasticized with TBC also showed the same phenomenon. When the addition amount of TBC was 15 phr, the tensile strength decreased to 43.3 MPa and the elongation at break was just only 2.4%. The plasticization of TEC and TBC led to lower decrease in tensile strength and almost no change in the elongation at break

compared with PEG400. Related reports pointed out that TBC containing hydroxyl group has the properties of hydrogen bonding donor and acceptor, and could form strong hydrogen bonds with the ester group of PLA, which is not conducive to the movement of the PLA segment. [18] Besides, although the addition of plasticizers increases the fluidity of the PLA molecular chain, it also makes the zeolite uniformly dispersed in the PLA matrix, resulting in the overall composite material still appear brittle. This could be seen from the fact that the tensile strength of the TEC and TBC plasticized PLA/zeolite composites were not significantly reduced.

Relatively, the tensile strength of PLA/zeolite composites plasticized by PEG400 decreased, whereas the elongation at break improved dramatically. The addition of plasticizers has been known to be resulted in reduced tensile strength because the plasticizers permeate the polymer chain and reduce the intermolecular forces that cause lower polymer cohesion.[23]

On the other hand, the PLA/zeolite composites plasticized by PEG400 at 10phr had the highest elongation at break value, namely, 54.04%, which was almost 25 times that of PLA/zeolite composites plasticized by TEC and TBC.

This may be because the addition of PEG would aggravate the reduction of PLA molecular weight, thereby broadening the PLA molecular weight distribution. Due to the lubricating effect of low molecular weight molecules, large molecular chains have better deformability. [24, 25]

### 3.2 Thermal properties

Figure 3. shows the DSC thermograms of PLA/zeolite composites plasticized by three different plasticizers during the second heating scan. Meanwhile, the details of thermograms on the phenomena of  $T_g$ ,  $T_{cc}$ , and  $T_m$ , as well as the degree of crystallinity of PLA/zeolite composites with different plasticizers are recorded in Table 2. As shown in Figure 2, the addition of plasticizers could significantly decrease  $T_g$ ,  $T_{cc}$ , and  $T_m$  of PLA/zeolite composites. Initially, the value of  $T_g$  of PLA/zeolite composite without plasticizer was 60.19°C. It could be seen from Table 2 that the  $T_g$  value of PLA/zeolite composites decreased by nearly 5°C when compounded with 5 phr plasticizers. And with the increase of the plasticizer content, the  $T_g$  value of PLA/zeolite composites decreased significantly. This is because the introduction of plasticizers increases the free volume between PLA chains, resulting in a significant decrease

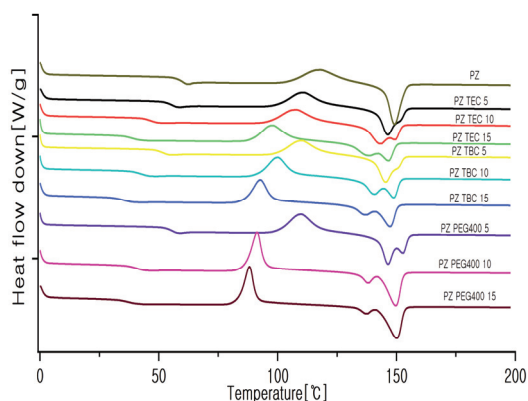


Fig 3. DSC curves of PLA/zeolite composites plasticized by different plasticizers

in the  $T_g$  value of the mixed materials. Due to the increase in chain mobility, the increase in plasticizer contents enhances the decrease in the  $T_g$  value.[26]

Such obvious change was also reflected in the cold crystallization temperature. From the DSC curves, PLA/zeolite without adding plasticizer exhibits  $T_{cc}$  of 117.97°C, and as the content of plasticizers increased, the  $T_{cc}$  value of PLA/zeolite composites decreased significantly.  $T_{cc}$  of PLA/zeolite composites plasticized by TEC decreased from 110.80°C to 97.9°C respectively with the increased content of TEC from 5 to 15 phr, and when adding TBC and PEG400,  $T_{cc}$  decreased from 110.21°C to 92.67°C and 109.91°C to 88.09°C. Besides, the degree of crystallinity of PLA/zeolite composites plasticized by TEC and TBC decreased compared with PLA/zeolite composites without adding plasticizer. Relatively, the degree of crystallinity of PLA/zeolite composites plasticized by PEG400 increased with the content of PEG400 increase. When the content of PEG400 increased to 15phr, the degree of crystallinity increased to 5.56%. This could be related to the fact that the added PEG gradually reduces the content of disordered  $\alpha'$  crystals generated when PLA is crystallized, while the content of ordered  $\alpha$  crystals gradually increases, making the crystal form of PLA more complete.[27]

Moreover, after the flexible PEG molecular chain is inserted into the PLA molecular chain, it acts as a lubricant, weakening the interaction force between the PLA molecular



chains, increasing the mobility of the PLA molecular chain, enhancing the mobility of the chain segment. It could reduce the  $T_g$  and  $T_{cc}$  of the composites, and  $T_c$ , resulting in the increase of the crystallization rate.

Meanwhile, double melting peaks were observed in the PLA/zeolite composites plasticized by plasticizers. This may be related to the formation of a crystal structure with different integrity and thermodynamic stability during the crystallization of PLA.[28]

The thermal stability of PLA/zeolite composites plasticized by three different plasticizers is given in Figure 4. The main thermal properties obtained from TGA and DTG curves are presented in Figure 4. It could be observed from the DTG curve that the peak corresponding to the plasticizer vaporization was observed before the main degradation peak(s), which has also been reported in other studies.[29] Meanwhile, PLA/zeolite composites plasticized by PEG400 showed a higher T5% value than PLA/zeolite composites plasticized by TEC and TBC suggesting the PLA/zeolite composite plasticized by PEG400 had higher initial degradation temperature and better thermal stability.

### 3.3 Migration behavior

The incorporation of low molecular weight compounds improves the functional properties of PLA/zeolite composites. However, low-molecular-weight plasticizers are also easy to migrate from the material, which

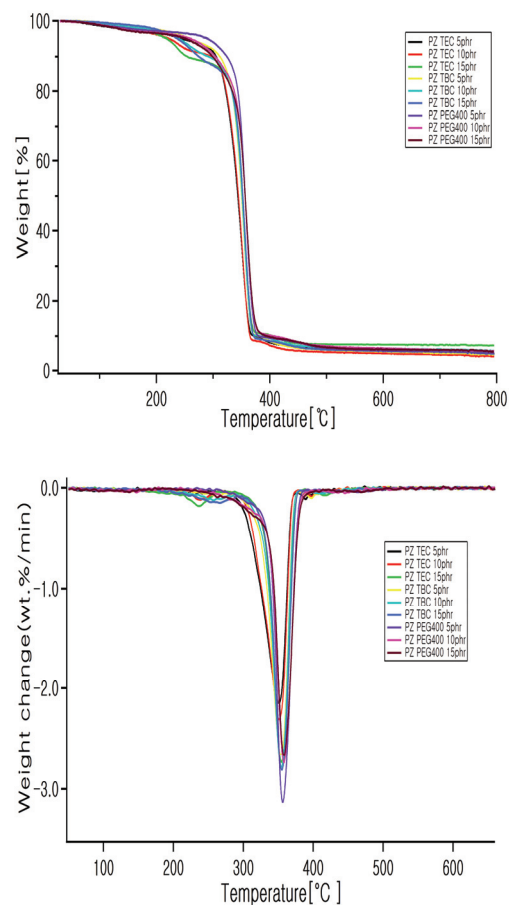
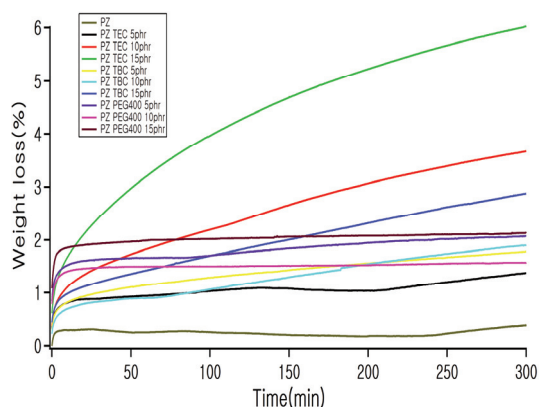


Fig. 4 TGA and derivative thermogravimetric (DTG) thermograms of PLA/zeolite composites plasticized by different plasticizers

reduces the performance of the material. In addition, in the application of food packaging, when the content of these migrating compounds in the food exceeds its prescribed limit, these substances have a potential impact on product safety and quality. [30] Figure 5 shows a comparison of the plasticizer weight loss of PLA/zeolite composites plasticized with three different plasticizers as a function of the time at 110°C. As shown in Figure 5, the migration of TEC





**Fig. 5 Weight loss percentage as function of the time for PLA/zeolite composites plasticized with different plasticizers**

and TBC increased with time. Among them, TEC has a higher migration rate than TBC at the same content, which may be related that TEC has a higher polarity and lower molecular weight. Moreover, with increasing the TEC content, the plasticizer has a relatively high migration rate toward the material surface at the same time. The migration of plasticizer depends on the molecular weight of plasticizers, the compatibility of the plasticizing system, the content of plasticizers, and the change of PLA crystallization. Plasticizers are mainly present in the amorphous fraction of PLA. [19] Relatively, PLA/zeolite composites plasticized with PEG400 showed a higher migration rate in the early stage and gradually stabilized later. The explanation of this phenomenon could be ascribed to the increase in the crystallization of PLA at 110°C, the amorphous area becomes smaller and leads to the plasticizer migrate to the surface of

the material. Furthermore, the existence of zeolite which acts as a nucleating agent in the PLA matrix also accelerates the crystallization rate of PLA. Also, as the content of PEG400 increases, the interaction between the two phases decreases, and PEG agglomerates, resulting in phase separation of PEG and PLA matrix. Similar behavior has been observed by other authors with PEG and other plasticizers. Indeed Pillin et al.[31] observed a macroscopic separation phase for PLA at 20 and 30 wt% of PEG 200(200 g/mol) and 30 wt% of PEG 400 (400 g/mol).

## 4. Conclusions

The PLA/zeolite composites plasticized with different content of TEC, TBC, and PEG400 were prepared by using a melt-mixing method. The tensile test results showed that PLA/zeolite plasticized with PEG400 at 10phr greatly elongation at break from 4% to 54%, significantly improved the ductility. DSC results showed that the addition of plasticizers drastically decreased the  $T_g$ ,  $T_{cc}$  of PLA/zeolite composites and improved the melt flow and processability. Among them, as the content of PEG400 increased, the degree of crystallinity of PLA/zeolite composites plasticized by PEG400 increased. From the TGA results, the PLA/zeolite composites plasticized with PEG has a higher initial thermal decomposition temperature and better thermal stability compared with TEC and

TBC. Nevertheless, the migration test results showed the PLA/zeolite composites plasticized with PEG400 has a relatively low migration rate compared with PLA/zeolite composites plasticized with TEC. Finally, it could be said that the PEG400 exhibited a greater plasticizing effect to the PLA/zeolite composites. However, when the content of PEG400 gradually increases, a macroscopic separation phase will occur. If the occurrence of phase separation could be overcome, PEG400 could be used as an excellent plasticizer for environmentally friendly packaging materials.

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