



# Thermo-oxidative degradation of poly(ethylene glycol)/poly(L-lactic acid) blends

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## Abstract

The thermo-oxidative degradation of poly(ethylene glycol)/poly(L-lactic acid) (PEG/PLLA) blends was studied by infra-red spectroscopy (IR), differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and thermogravimetry (TGA). The thermo-oxidative degradation of PEG occurred after a period time of aging in air at 80 °C. The mechanism of thermo-oxidative degradation of PEG was found to be the random chain scission of the main chain. As PEG blending with PLLA, the existence of PLLA appeared to enhance the thermo-oxidative degradation of PEG. The enhancement of thermo-oxidative degradation increased first and then decreased with the increase of PLLA. The results could be attributed to the ease of abstraction of the carboxylic hydrogen (–COOH) of PLLA, which enhanced the thermo-oxidative degradation of PEG. Also, the dilution effect of PLLA on the concentration of free radicals was an important factor of the thermo-oxidative degradation.

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**Keywords:** Blends; Free radical; Thermo-oxidative degradation

## 1. Introduction

Both polyethylene glycol (PEG) and poly(L-lactic acid) (PLLA) are very interesting and important polymers. PEG is soluble in water and many organic solvents. Meanwhile, PEG shows hydrophilicity and biocompatibility. Poly(L-lactic acid) (PLLA) is a biodegradable thermoplastic polyester and has attracted increasing attention due to their potential applications as biomedical and environment-friendly materials. PLLA and its random or block copolymers have been used for biomedical applications such as drug delivery systems, implant materials, and bioabsorbable surgical sutures. Blending PEG with PLLA could change the mechanical properties and biodegradation of PLLA [1–5]. It was reported that PEG/PLLA blend systems were miscible in the melt and the crystallization behavior of PLLA could be influenced by the addition of PEG [6–10].

The thermo-oxidative degradation of PEG has been

studied for a while [11–17]. They found that PEG undergoes marked thermo-oxidative degradation. Thus, thermo-oxidative degradation is the major problem in the development of polyethylene glycol (PEG) as a thermal energy storage material. PEG is susceptible to free-radical oxidative attack, so it could cause the reduction of molecular weight and the formation of low molecular weight oxygenated products [13–17]. However, there are very few reports about the thermo-oxidative degradation of PEG/PLLA blend. It is well known that the free radicals should influence the normal body chemistry and make some toxins [18]. Thus, the purpose of the present study is to study the thermo-oxidative degradation of PEG and the PEG/PLLA blends by IR, DSC and GPC instruments.

## 2. Experimental

### 2.1. Materials and preparing method of sample

The PLLA sample used in this study was obtained from polysciences Co., and its weight-average molecular weight

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was 200,000 g/mol. The PEG polymer with weight-average molecular weight of 2000 g/mol obtained from Aldrich Co.

All samples used in this study were prepared by solution-casting method. Certain amount of PEG and PLLA were dissolved in chloroform yielding a 2% (0.4 g polymer blends/20 ml solvent) solution according to the desired composition. The solution was subsequently poured onto a glass dish. A film was obtained after evaporating most chloroform solvent very slowly under ambient condition at room temperature. The film was then further dried in vacuum at 80 °C for 24 h. In this stage, no significant thermo-oxidative degradation was found. Also, TGA was used to check the residual solvent in the final films. The results showed no measurable residual solvent in the films.

For the study of thermo-oxidative degradation, dried films with same geometry and size were aged either under vacuum (virtually no air present) or in air at 80 °C for several hours.

## 2.2. Measurements

Thermal transitions of films were measured using a differential scanning calorimeter (DSC, TA instruments DSC 2010). All samples (with or without aging) were first heated up to 180 °C, hold for 3 min, and then were cooled down to -100 °C. At a heating rate of 10 °C/min, the samples were heated from -100 to 200 °C, thus the melting temperature ( $T_m$ ) and enthalpy of melting ( $\Delta H$ ) would be determined. All the measurement was under the nitrogen atmosphere.

The chemical structures of films (with or without aging) were determined using Fourier transform infra-red (FTIR, Jasco FT/IR-300E Infra-red spectroscopy). The samples were dissolved in chloroform yielding a 5% (w/v) chloroform solution and cast onto NaCl plates. Then the IR spectra were obtained.

The molecular weight ( $M_n$ ) and molecular weight distribution (PDI) of films (with or without aging) were measured using gel permeation chromatography (GPC, Showa Denko K-K Shodex RI-71). All samples were dissolved in THF yielding a 4% solution.

The thermal weight decomposition of PEG (with or without aging) was examined using a thermogravimetry (TGA, TA instruments TA-90). About 8–10 mg of samples were heated to 80 °C for 12 h.

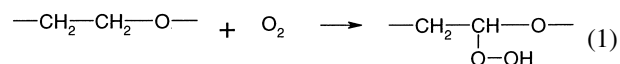
## 3. Results and discussion

It is noticed that both PEG and PLLA are crystalline polymers. However, the aging temperature (80 °C) is between the melting points of PEG and PLLA. Also, the aging temperature is higher than the glass transition of samples. Thus, the polymer blends consist of the PLLA crystal phase and the miscible PEG-PLLA amorphous phase during the aging. It is assumed that the crystallinity of PLLA

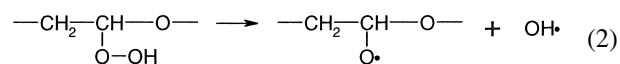
would not change significantly during the aging. Thus, the crystallinity of PLLA during the aging is estimated from the heat of fusion of PLLA ( $\Delta H = 93.7$  J/g [19] for 100% PLLA crystalline was used) as it cast before the aging. The DSC results are shown in Fig. 1. The compositions of samples during aging are estimated as Table 1. It is expected that the PLLA crystals would not involve the thermo-oxidative degradation.

IR instrument is direct and useful to examine the thermal oxidative degradation of PEG and PEG/PLLA blends. Fig. 2 shows the IR spectra of neat PEG before and after the aging at 80 °C for 12 h. The PEG aged in vacuum has almost the same spectrum as the cast PEG without the aging. However, the PEG aged in air has a new band at 1600–1750  $\text{cm}^{-1}$ . The result is consistent with that obtained by other researchers [14,15]. According to them, the mechanism of oxidation of PEG could be summarized as follows [11,16]:

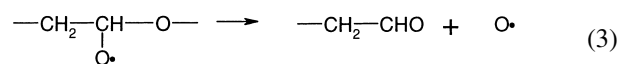
1. PEG reacts with oxygen to form  $\alpha$ -hydroperoxide.



2. This peroxide is expected to be thermally labile. Therefore it decomposes according to a radical mechanism.



3. Formic esters (carbonyl group) are produced as the thermal degradation products in air.



The new band at 1600–1750  $\text{cm}^{-1}$  is assigned to the carbonyl stretching vibration and confirms that new products could be produced during the thermal oxidation process. However, the band at 1600–1750  $\text{cm}^{-1}$  for the

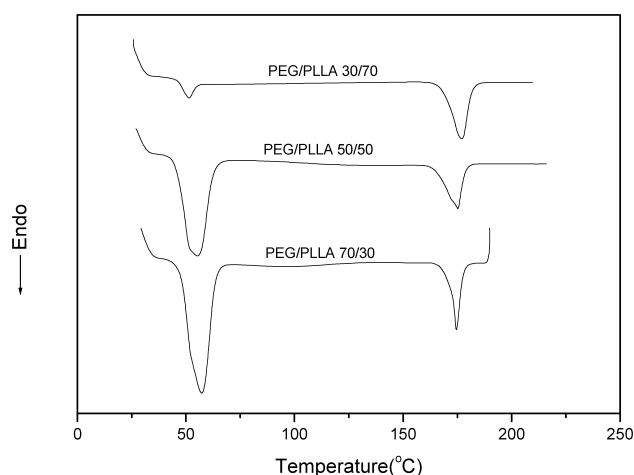


Fig. 1. DSC traces of PEG/PLLA blends as it cast without aging.

Table 1  
The composition of samples during aging

	Amorphous PEG (%)	Amorphous PLLA (%)	Crystalline PLLA (%)
PEG/PLLA 30/70	30	36.2	33.8
PEG/PLLA 50/50	50	21.4	28.6
PEG/PLLA 70/30	70	6.8	23.2

PEG/PLLA polymer blend is more complex because the PLLA also contains the carbonyl group. The band at  $1600\text{--}1750\text{ cm}^{-1}$  due to the thermal oxidation of PEG overlaps with it due to the carbonyl group of PLLA. However, it is possible to find the solvent that is able to extract the PEG from the PEG/PLLA blend. Thus the thermo-oxidative degradation of extracted PEG from PEG/PLLA blend is able to estimate separately. In this study, the ethanol is chosen as the solvent to extract the PEG from PEG/PLLA blend. Fig. 3 shows the IR spectra of neat PEG and extracted PEG from PEG/PLLA blends aged in air at  $80\text{ }^{\circ}\text{C}$  for 12 h. The degree of thermo-oxidative degradation of the air-aged PEG is determined by measuring the carbonyl index. The carbonyl index of air-aged PEG used in this study is the ratio of the  $1720\text{ cm}^{-1}$  carbonyl peak to the  $2880\text{ cm}^{-1}$  reference peak [13]. The reference peak at  $2880\text{ cm}^{-1}$  is assigned to the symmetry stretching ( $\text{CH}_2$ ). The intensity of the  $2880\text{ cm}^{-1}$  peak remains constant with increasing oxidation. The carbonyl index is larger, which means the higher degree of thermo-oxidative degradation of PEG [13]. The carbonyl indices of PEG/PLLA 100/0, 70/30, 50/50 and 30/70 aged in air for 12 h are 0.0648, 0.0695, 0.1726 and 0.0681 respectively. From the carbonyl indices estimated from IR results, it shows that the degree of thermo-oxidative degradation of PEG increases first and then decreases with the increase of PLLA. The PEG/PLLA 50/50 has the largest carbonyl index.

Fig. 4 shows the isothermal TGA curves of the neat PEG without the aging in air at  $80\text{ }^{\circ}\text{C}$  for 12 h. There are no weight losses during 12 h at  $80\text{ }^{\circ}\text{C}$ . This implies that the

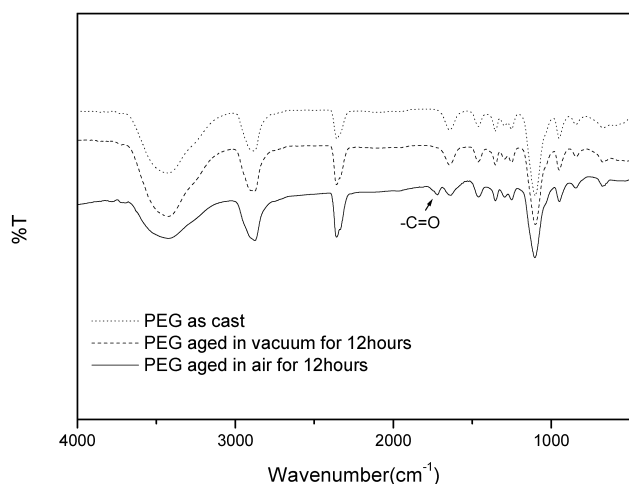


Fig. 2. IR spectra of PEG as cast, PEG aged in vacuum and in air at  $80\text{ }^{\circ}\text{C}$  for 12 h.

chain scission procedure of PEG during thermo-oxidative degradation would not start from the chain end of PEG. If the chain scission procedure starts from the chain end of PEG, it is expected that the TGA results show larger weight losses in the initial stage. Besides, from the following GPC results, it shows the molecular weight distributions of PEG are broadened for the air-aged samples. It indicates the mechanism of thermal oxidative degradation of PEG would be the random chain scission mechanism [16].

From GPC results, the changes in the molecular weight ( $M_n$ ) and molecular weight distribution (PDI) of samples before and after the aging are shown in Figs. 5 and 6. It is consistent with the IR results that no significant thermo-oxidative degradation of PEG is found for all samples aged in vacuum. The  $M_n$  and PDI of PEG aged in vacuum are about the same as the samples without aging. However, from Fig. 5, it shows that the  $M_n$  of PEG decreases with time, meanwhile the PDI of PEG increases for air-aged samples. Also, it shows the decrement of  $M_n$  of PEG increases first and then decreases with the increase of PLLA. Again, the PEG/PLLA 50/50 blend shows the largest decrement of  $M_n$  and largest increment of PDI. It is consistent with the IR results that the PEG/PLLA 50/50 blend shows the largest degree of thermo-oxidative degradation. Fig. 7(a)–(d) show the GPC curves of air-aged samples. The extra peaks at short retention times in Fig. 7(b)–(d) belong to the PLLA. The vertical line indicates the retention time for the largest molecule of the PEG without aging. If one exams the GPC curves of

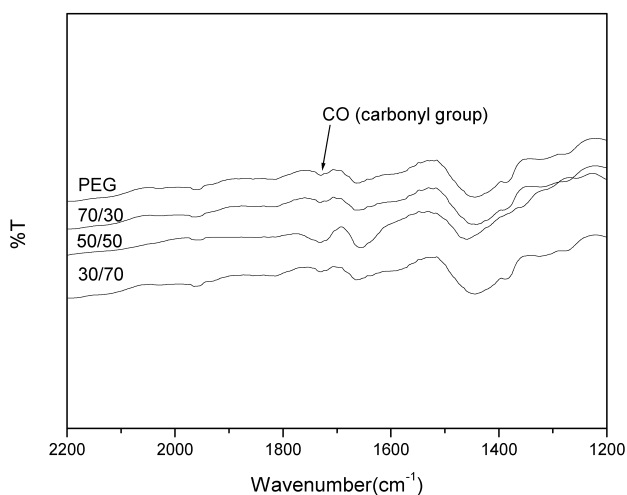


Fig. 3. IR spectra of neat PEG and extracted PEG from PEG/PLLA blends aged in air at  $80\text{ }^{\circ}\text{C}$  for 12 h.

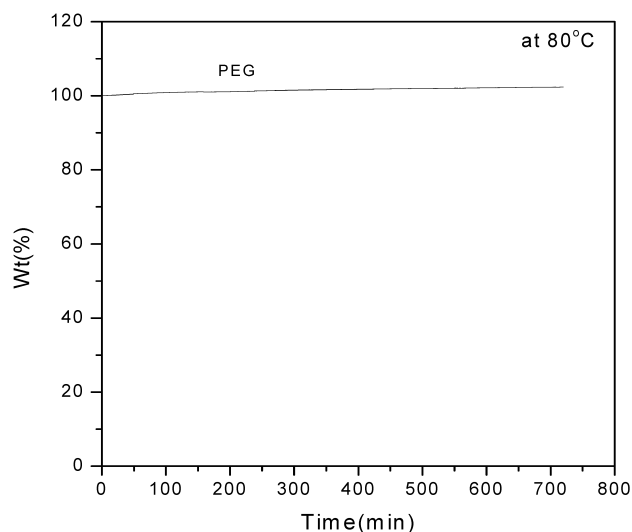


Fig. 4. Isothermal TGA curves of the neat PEG without aging in air at 80 °C for 12 h.

air-aged neat PEG, it is found that the molecular weight distribution is broadened and extended to both lower and higher molecular weight regions after the aging. It is consistent with the report by Taoda et al. [17]. The extension to the lower molecular weight regions is due to the bond scission in the backbone, resulting in a reduction of molecular weight and a diminution of PEG chain length. The extension to the higher molecular weight regions is due to the recombination of chains with free radicals [15,17]. For neat PEG, it also shows that the appearance of extension to the higher molecular weight regions is later than it to the lower molecular weight regions. Obviously, it is necessary to reach a certain concentration of free radicals to have the recombination. Thus, the occurrence of chain scission is earlier than it of recombination. However, the degree of extension to the higher molecular weight regions is not so significant for the air-aged PEG/PLLA blends. Even there is no extension to the higher molecular weight regions for the air-aged PEG/PLLA 30/70 blend. It shows the recombination of free radicals for the air-aged PEG/PLLA blends is

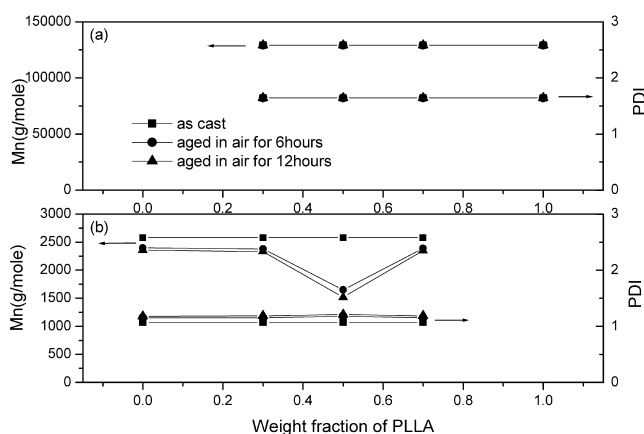


Fig. 5. Molecular weight and molecular weight distribution for PEG/PLLA blends aged in air (a) PLLA (b) PEG.

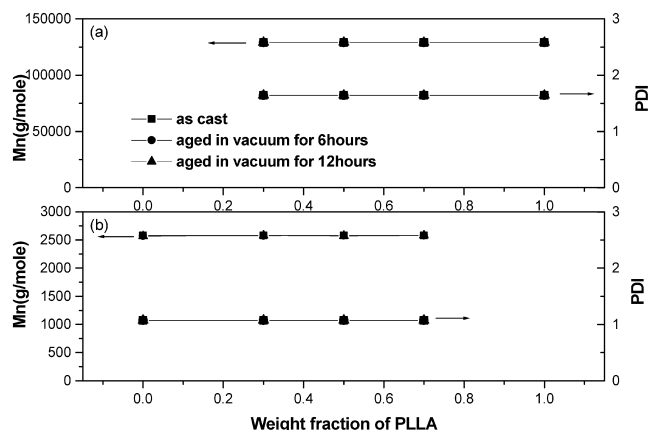


Fig. 6. Molecular weight and molecular weight distribution for PEG/PLLA blends aged in vacuum (a) PLLA (b) PEG.

less than it for the air-aged neat PEG. Therefore, the concentration of free radicals of the air-aged PEG/PLLA blends is less than it of the air-aged neat PEG. However, from IR and  $M_n$ , the degrees of thermo-oxidative degradation of PEG in polymer blends are greater than it of neat PEG. Obviously, it is not due to the decrease of thermo-oxidative degradation. It is due to the dilution effect of PLLA. The concentration of free radicals is diluted.

From Figs. 5 and 6, it is found the  $M_n$  and PDI of PLLA for all aged samples are about the same as they without aging no matter what aging-environment and what composition. There is no significant thermo-oxidation degradation in PLLA. However, it is noted that the molecular weight of PEG is very smaller than it of PLLA. Thus, the increase of molecular weight of PLLA due to the combination of PLLA and PEG chains is not so sure. To check it, a PEG/PLLA 50/50 blend, which the weight average molecular weight of PEG is 19,000 g/mol is prepared as before. The GPC results of such air-aged sample are shown in Fig. 8. Again, it shows that there is no significant change on  $M_n$  and PDI of PLLA. Therefore, it is expected that there is no recombination between PEG and PLLA.

From DSC results, the decrement of melting point ( $\Delta T_m = T_{m, \text{aged}} - T_{m, \text{as cast}}$ , respectively) and decrement of heat of fusion ( $\Delta H_m = \Delta H_{\text{aged}} - \Delta H_{\text{as cast}}$ , respectively) of samples before and after the aging are shown in Figs. 9–12.

From Figs. 9 and 10, it shows that the melting points and heats of fusion of PLLA and PEG for vacuum-aged samples are about the same as the samples without aging. Again, it reconfirms that there is no significant thermo-oxidative degradation in vacuum-aged samples.

For the neat PEG sample, it is found the melting point and heat of fusion of PEG decrease with time for the air-aged PEG. These results are consistent with those obtained by Han et al. [16]. The reason could be the degradation process leads to the bond scission in the backbone of PEG polymer chains, resulting in a reduction of molecular weight and a diminution of PEG chain length. Another reason could be the chemical-structure modification of PEG due to the

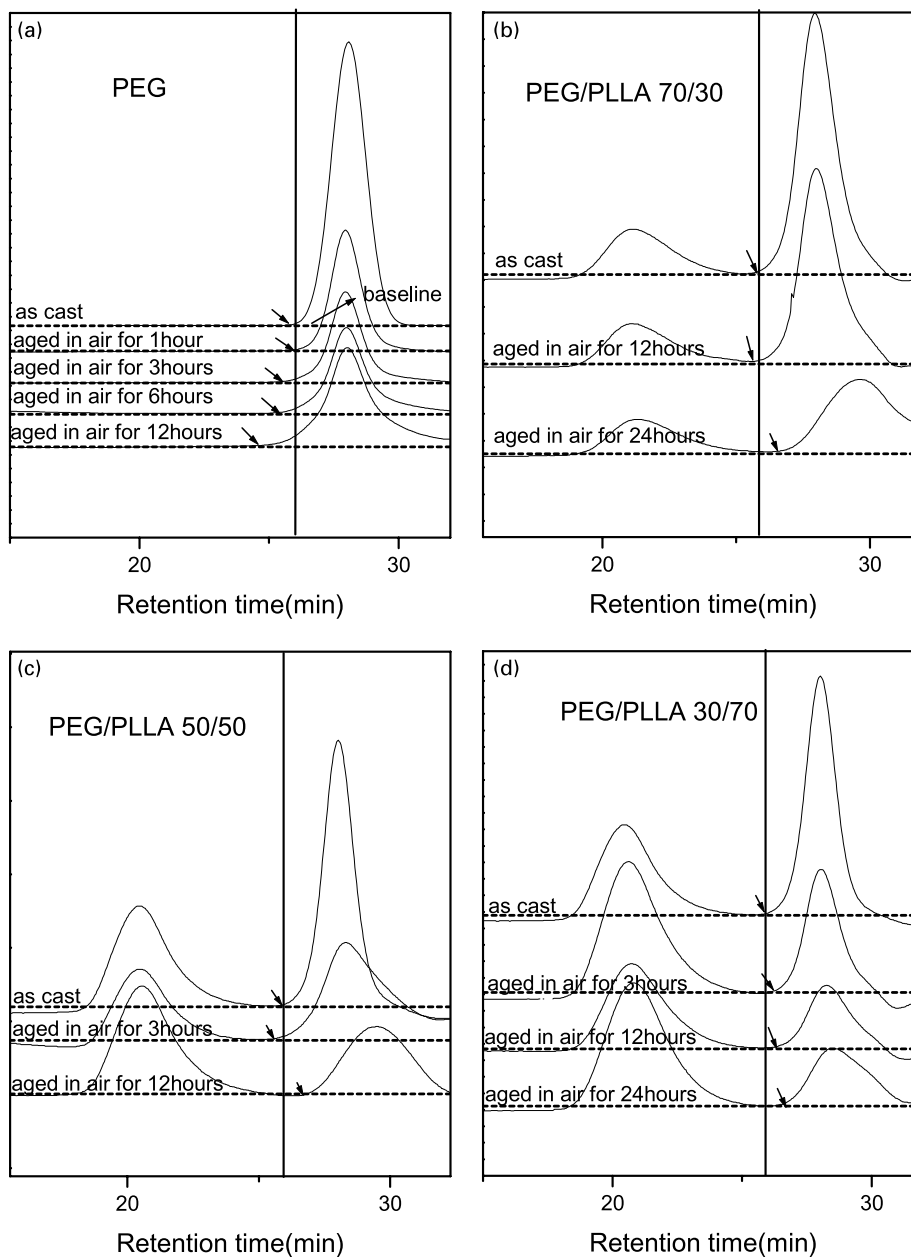


Fig. 7. (a) GPC curves of PEG aged in air for several hours. The vertical line indicates the retention time for the largest molecule of the PEG without aging. (b) GPC curves of PEG/PLLA 70/30 aged in air for several hours. The vertical line indicates the retention time for the largest molecule of the PEG without aging. (c) GPC curves of PEG/PLLA 50/50 aged in air for several hours. The vertical line indicates the retention time for the largest molecule of the PEG without aging. (d) GPC curves of PEG/PLLA 30/70 aged in air for several hours. The vertical line indicates the retention time for the largest molecule of the PEG without aging.

thermo-oxidation. Such change in chemical structure could decrease the melting point and heat of fusion [20].

For polymer blends of PEG/PLLA, the PEG/PLLA 70/30, 50/50 and 30/70, aged in air also shows decrease in melting point and heat of fusion of PEG with time as neat PEG. Moreover, the decrement of melting point and heat of fusion of PEG in air-aged polymer blends increases first and then decreases with the increase of PLLA. However, the decrement of melting point and heat of fusion of PEG in aged 30/70 samples in air is still slightly larger than it in neat PEG.

Also, it is found from Figs. 11 and 12 that the melting point and heat of fusion of air-aged neat PLLA are the same as them without aging. However, the decrement of melting point and heat of fusion of PLLA for the air-aged PEG/PLLA increase slightly with time. Again, the PEG/PLLA 50/50 has the largest decrement.

The melting point depressing of blend is more complex. It is well known that the melting point will be depressed by blending with a miscible polymer. However, the decrement is based on the respective polymer blends as cast. Thus it is

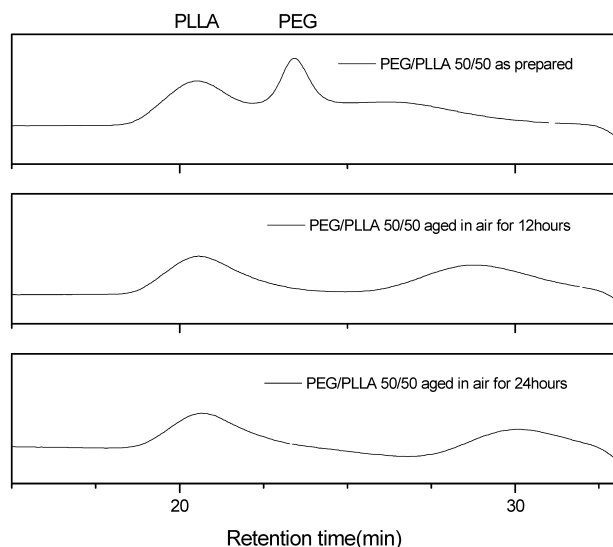


Fig. 8. GPC curves of PEG( $M_w = 19,000$ )/PLLA 50/50 aged in air for several hours.

expected that the blending effect on the change of decrement with composition will be excluded. Also, Gallardo et al. [21] reported that the transesterification could occur in PEG/PLLA blends at 200 °C. If it occurs, the melting point will be depressed. However, it is shown from the above GPC results that no significant change in the molecular weight of PLLA. Thus, the aging temperature is too low to have significant transesterification. Another factor that could have influence on the melting point temperature is the miscibility of polymer blend. It was reported [9] that the miscibility of PEG/PLLA blends increased with decrease molecular weight of PEG. In this study, the above GPC results do show the decrease of molecular weight of PEG due to the thermal oxidative degradation. Thus, the miscibility would be better. Therefore, the melting point of PEG in blend decreases. Also, the miscibility effect on the melting point depressing can observe from the decrease of melting points of PLLA for air-aged samples. For neat

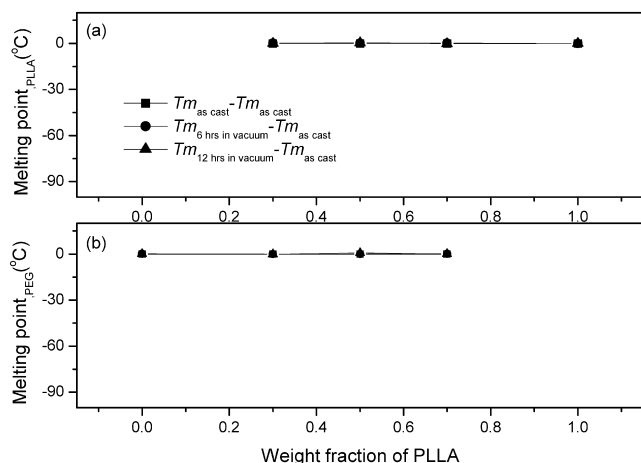


Fig. 9. The decrement of the melting point of PEG/PLLA blends in vacuum at 80 °C (a) PLLA (b) PEG.

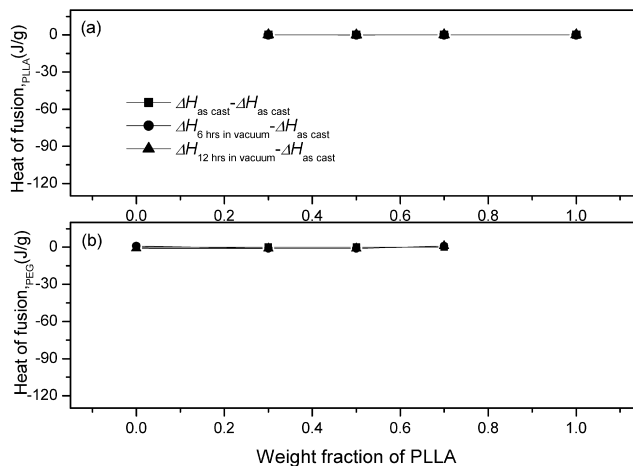


Fig. 10. The decrement of heat of fusion of PEG/PLLA blends in vacuum at 80 °C (a) PLLA (b) PEG.

PLLA, which does not have miscibility effect, the melting point dose not change with aging time. However, the melting points of PLLA for air-aged blends decrease with time, although the IR and GPC results show no significant thermo-oxidative degradation for PLLA. Certainly, the enhancement of miscibility due to the decrease of molecular weight of PEG depresses the melting points of PEG for air-aged samples. It was reported [20] that the chemical structures of chain ends of low molecular weight PEG have influence on the miscibility of PEG/PLLA blends. Therefore, the changes of chemical structures due to thermo-oxidative degradation of PEG could have influence on the miscibility of PEG/PLLA and the decrement of melting point and heat of fusion of PEG. However, it is not clear that it will increase or decrease the melting point of PEG. As the neat PEG sample, the chemical structure modification of PEG due to the thermo-oxidation decrease the melting point and heat of fusion of PEG in blend. Certainly, the melting point and heat of fusion decrease with the decrease of molecular weight of PEG too. Obviously, the decrease of

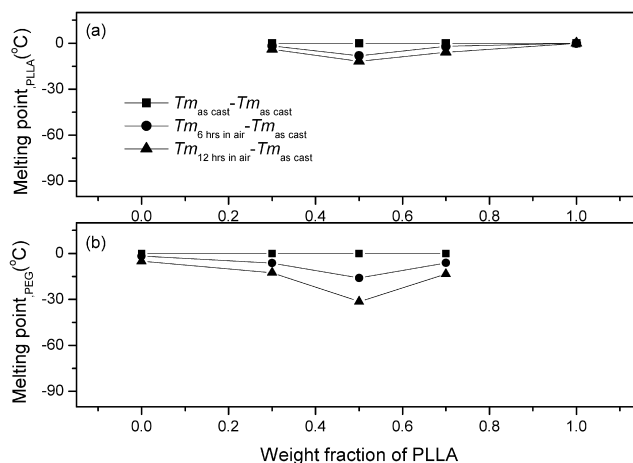


Fig. 11. The decrement of the melting point of PEG/PLLA blends in air at 80 °C (a) PLLA (b) PEG.

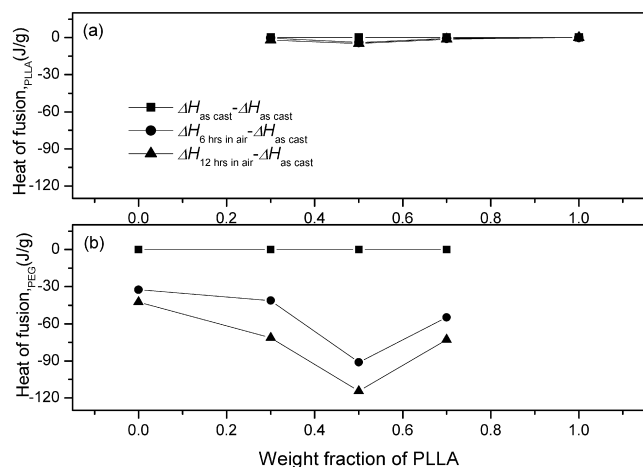


Fig. 12. The decrement of heat of fusion of PLLA/PEG blends aged in air at 80 °C (a) PLLA (b) PEG.

melting and heat of fusion of PEG is due to the decrease of molecular weight of PEG, change of miscibility and change of chemical structure. It is difficult to separate the contribution to corresponding factors. However, all contributions result from the thermo-oxidative degradation of PEG. On the other hand, the decrease of melting point of PLLA is due to the change of miscibility of polymer blends resulted from the thermo-oxidative degradation of PEG components.

From the above results, it indicates that the enhancement of thermo-oxidative degradation of PEG by blending with PLLA and the greatest enhancement occurs in the PEG/PLLA 50/50 blend. It was proposed [22,23] that EAA accelerated LDPE thermo-oxidative degradation. This enhancement of thermo-oxidative degradation could be attributed to the ease of abstraction of the carboxylic hydrogen ( $-\text{COOH } H$ ) of acrylic acid, which was highly acidic [24]. In this study, the end group of PLLA also is carboxylic hydrogen, which might enhance the thermo-oxidative degradation of PEG. Although the proportion of carboxylic hydrogen in PLLA is very little, the concentration of carboxylic hydrogen in this study is comparable to it in Ref. [22] and [23]. Table 2 lists these results.

The enhancement of thermo-oxidative degradation due to the carboxylic hydrogen should increase with the increase of PLLA. However, from the DSC, GPC and IR results it is found PEG/PLLA 50/50 blend exhibits the greatest enhancement of thermo-oxidative degradation of PEG. This could be explained by the dilution effect. The concentration of free radicals is diluted by the PLLA.

Table 2  
The concentration of COOH group

Samples	The concentration of COOH group (%)
PEG/PLLA 50/50	$1.125 \times 10^{-2}$
0.5 wt% EAA (20 wt% acrylic acid) [22,23]	$6.250 \times 10^{-2}$

Then the recombination of free radicals decreases with the increase of PLLA. It will decrease the molecular weight. However, the dilution of free radicals will also decrease the chain scission due to the decrease of chain attacking by free radicals. Hence the decrease of molecular weight of PEG is inhibited.

Because of these factors, the molecular weight of PEG would decrease first and then increase with the increase of PLLA. Thus, the air-aged PEG/PLLA 50/50 shows the lowest molecular weight of PEG.

#### 4. Conclusion

PEG was oxidized easily at moderate temperature. The mechanism of thermo-oxidative degradation of PEG followed a random chain scission mechanism by DSC, GPC and TGA instruments.

As PLLA adding to PEG, it was found PLLA promoted the thermo-oxidative degradation of PEG. Also, the dilution effect of PLLA was found. Thus the degree of thermo-oxidative degradation of PEG increased first with the increase of PLLA then decreased as further adding of PLLA. However, no significant thermo-oxidation degradation or transesterification were found in PLLA.

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