S0032-3861(96)00501-0

Polymer Vol. 38 No. 2, pp. 317–323, 1997

0032-3861/97/$17.00 + 0.00

Thermal/oxidative degradation and stabilization of polyethylene glycol

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(Received 12 December 1995; revised 10 April 1996)

Thermal degradation and stabilization of polyethylene glycol (PEG) with a molecular weight of 6000 have been investigated in order to develop PEG as a thermal energy storage material. Low molecular weight esters including formic esters were produced as the main products of the thermal degradation of PEG at 80°C in air. No degradation was observed for PEG aged in a vacuum. The mechanism of thermal degradation is found to be the random chain scission of the main chain. Thermal degradation could be suppressed by adding 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) (MBMTBP) as an antioxidant. In the stabilizing process, MBMTBP itself is transformed to dimers or trimers. Copyright © 1996 Elsevier Science Ltd.

(Keywords: PEG 6000; phase change material; degradation mechanism)

INTRODUCTION

Polyethylene glycol (PEG) is a white, free flowing powder, or creamy white flakes and is used as a water soluble lubricant for rubber moulds, textile fibres and metal forming operations[1]. It is also used in water paints, paper coatings, polishes and in the ceramic industry, as well as for chromatographic stationary phases[2]. PEG has been considered a promising thermal energy storage material, because of its relatively large heat of fusion, congruent melting behaviour, non-corrosiveness and wide melting point range as a phase change material (PCM)[3–8].

In order to utilize PEG as a thermal energy storage material, it should not be degraded during the period of application. But PEG is susceptible to free radical oxidative attack because the high strains at the chain folds of the lamellar structure lower the activation energy of hydrogen abstraction[9]. Thermal degradation of PEG produces low molecular weight products, which cause a lowering of the melting point and the heat of fusion[10–12]. As thermal degradation proceeds, the amount of low molecular weight products become larger, and hence the performance of the thermal energy storage system declines.

Bortel *et al.*[13] have reported that significant oxidation of PEG occurs if it is stored in bulk for 2 years, and the free radical oxidative degradation of PEG leads to the formation of many oxygenated products. Han *et al.*[14] reported that PEG was severely degraded in air; the melting point and heat of fusion were reduced by as much as 13°C and 32 kJ kg^{-1}, respectively. Han *et al.* also investigated the mechanism of thermal degradation of PEG with an average molecular weight of 4000. They reported that the thermal degradation of PEG in air followed a random chain scission oxidation mechanism, and that the thermal degradation of PEG could be suppressed by addition of an antioxidant, 2,2'-methylene-bis(4-methyl-6-tert-butylphenol) (MBMTBP).

Many researchers[15–17] have found that during the inhibition of the thermal degradation of polymers by phenolic antioxidants (InH) such as MBMTBP, termination of the kinetic chain of oxidative degradation occurs due to the reaction with InH and ROO• radicals formed in the propagation step. Such inhibition is formulated by the following scheme:

$$\mathrm{InH} + \mathrm{ROO}\bullet \longrightarrow \mathrm{In}\bullet + \mathrm{ROOH}$$

Aryloxy radical In• and hydroperoxide are formed in the system, and the amount of the antioxidant (InH) in its original form decreases and the products of transformation of InH increase with time. The products of transformation of InH are usually dimers and trimers of In• which terminate the inhibition process of the thermal degradation of polymers. Pospil and co-workers[18–21] investigated the reaction between MBMTBP and *tert*-butoxy or *tert*-butylperoxy radicals.

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They found that the products of the reaction were dimers, trimers and cyclohexanone derivatives. They reported that these products were also formed in stabilizing the oxidation reaction of tetralin and isotactic polypropylene. Gömöry[22] studies the induction period of oxidation of polymers stabilized by phenolic and amino antioxidants. He reported that during the induction period, non-volatile active compounds were produced by the oxidation of the original antioxidant and the products of oxidative transformation of aromatic amines and hindered phenols acted as antioxidants, too. He also reported that the products could participate in mutual interactions and interactions with the unconsumed antioxidant, which produced dimers and trimers of the antioxidant.

In this work we have studied the thermal degradation of PEG in air and in a vacuum. The effect of MBMTBP on thermal degradation is investigated, and the transformed products of MBMTBP formed in the stabilization process of thermal degradation are identified. The results show that the thermal degradation could be effectively suppressed by adding MBMTBP as an antioxidant. The results also imply that MBMTBP stabilizes the oxidative degradation by capturing the peroxide radical of PEG. In this process, MBMTBP is itself transformed to dimers or trimers.

EXPERIMENTAL

Reagent grade PEG with an average molecular weight of 6000 (Fluka Chem. Co.) was used as received. For thermal degradation studies, PEG samples were placed in a thermostatted air circulating oven at 80°C for 1000 h. The PEG samples were maintained either under a vacuum or in air. For the stabilization experiment, PEG doped with 0.1 mol kg^{-1} of MBMTBP was maintained under the same condition.

The melting point and heat of fusion were determined using a differential scanning calorimeter (d.s.c., Perkin-Elmer DSC-4). The heating rate was $10°C\,min^{-1}$. Thermal decomposition of PEG was examined using thermogravimetry (t.g., Cahn TG 121 system thermobalance). About 10 mg of PEG were heated at $10°C\,min^{-1}$ under a dynamic nitrogen atmosphere. The molecular weight distribution was determined by gel permeation chromatography (g.p.c., Waters R401 ALC/GPC) using a series of columns for 10^4, 10^3 and 500 Å. A polystyrene standard was used for the universal calibration curve.

The degraded products were identified using Fourier transform infra-red (*FT*i.r.), and ^1H and ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopic methods. To exclude the effect of water absorption, the reference method was applied in operating the Perkin Elmer transition mode *FT*i.r. *FT*i.r. spectra were obtained by averaging 20 scans for a given sample. ^1H and ^{13}C n.m.r. spectra were recorded on a Bruker WM 400 operating at 300 MHz. Chemical shifts were recorded in ppm units with reference to the internal TMS.

The oxidatively transformed products of MBMTBP were separated from the mixture of PEG and MBMTBP by thin layer chromatography (t.l.c.: silica gel $60F_{254}$, solvent: acetone + methanol). The increase in the oxidatively transformed products was confirmed by measuring ultraviolet (u.v.) absorbance with time. The identification of the products was performed by the electrospray ionization method using a triple quadrupole mass spectrometer. The solvent was methanol.

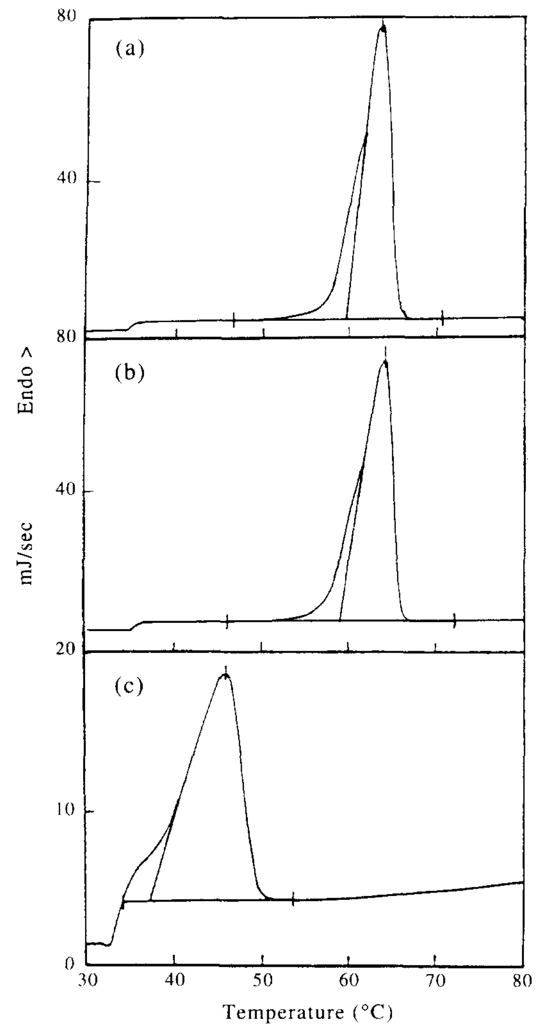


Figure 1 D.s.c. diagrams of PEG 6000: (a) fresh; (b) aged in a vacuum at 80°C for 1000 h; (c) aged in air at 80°C for 1000 h

RESULTS AND DISCUSSION

Thermal degradation of PEG

Thermal degradation of PEG at 80°C in air causes a considerable change in its shape. After 100 h of thermal oxidation, PEG is transformed from a free flowing powder to a soft waxy solid.

In *Figure 1* typical d.s.c. diagrams are shown for PEG before and after degradation. The sample degraded under a vacuum has almost the same melting point after 1000 h as the fresh PEG. But the samples degraded in air have a lower melting point. These results are consistent with those obtained by Scheirs *et al.*[23]. In the case of linear polymers, the polymer degradation process leads to a reduction in molecular weight and to diminution of chain length, resulting from the bond scission in the backbone of the macromolecules. It appears that the degradation of PEG also follows the same process. *Figure 2* shows the changes in the melting point and heat of fusion of the aged samples in air and in a vacuum at 80°C with time. The melting point and heat of fusion of thermally degraded PEG in air decline linearly with time. Therefore, PEG cannot be used eventually as a PCM in

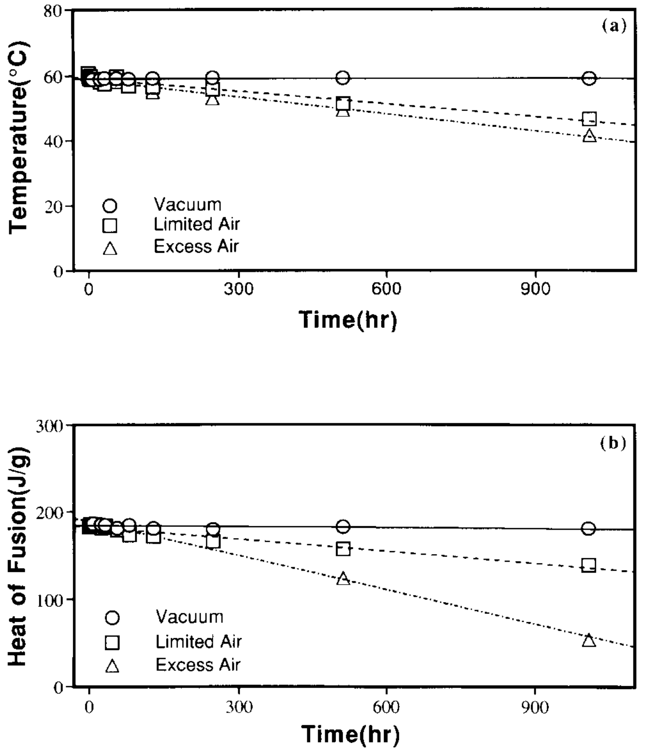


Figure 2 Changes of the thermal properties of PEG 6000 aged in a vacuum or air with time: (a) melting point; (b) heat of fusion

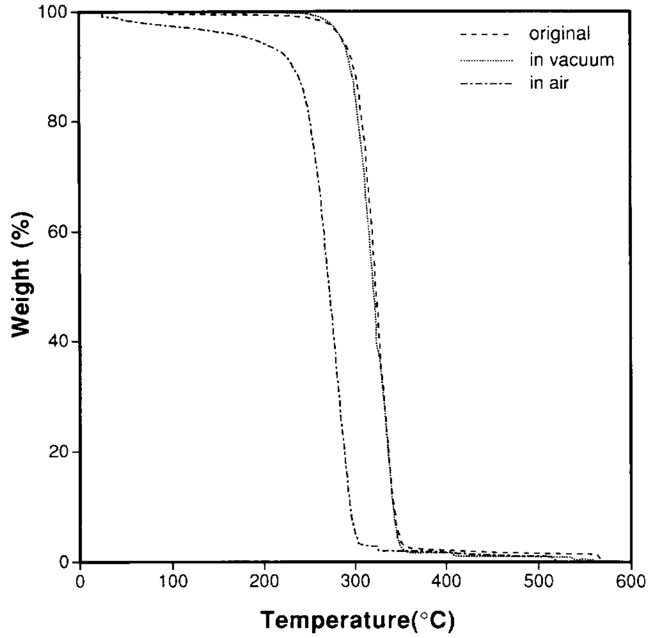


Figure 3 T.g. curves of PEG 6000

thermal energy storage. PEG degrades more severely in the presence of excess air. It is shown in the following that this is because PEG and oxygen can easily react to form PEG peroxide in excess air, which produces low molecular weight oxygenated products by the random chain scission process. Since the quantitative relationships between the melting point or heat of fusion and the degree of degradation are not known, it is not possible to determine the kinetic model for the degradation of PEG using only the experimental data obtained here. *Figure 3* shows t.g. curves of PEG. Fresh PEG and PEG degraded in a vacuum lose weight in one step at almost the same temperature, but the aged PEG in air loses a significant portion at the lower temperature. This means that lower molecular weight species were produced during the thermal degradation process.

The random chain scission mechanism of the thermal degradation of PEG was confirmed by examining the molecular weight distribution of PEG before and after degradation. G.p.c. examination of the molecular weight distribution of PEG before and after degradation (*Figure 4*) shows that there is no significant change for the sample heated in vacuum, but the distribution is broadened for the sample heated in air. The distribution curve of the latter shows some structure, which may indicate the scissions are not totally random. Fresh PEG has a narrow distribution of molecular weight, with $M_w/M_n = 1.10$. PEG degraded in a vacuum has almost the same distribution. But PEG degraded in air has a broader distribution with $M_w/M_n = 1.89$. The broad distribution is due to the low molecular weight species produced by oxidative degradation[24].

The degraded products of PEG in air were identified using *FT*i.r. and ^{1}H and ^{13}C n.m.r. spectroscopy. In the *FT*i.r. diagrams, characteristic changes in wave number, 3000–3600 and 1600–1750 cm^{-1} are shown for fresh PEG and the aged sample in air for 1000 h. The aged PEG in air has a broader peak at 3000–3600 cm^{-1}. This appears to be due to –OH groups of the lower molecular weight species produced by degradation. The new band at 1600–1750 cm^{-1} indicates that new products with carbonyl groups are produced by thermal degradation in air. But the aged PEG in a vacuum shows little changes in the absorption peaks compared with those of the fresh PEG. In the ^{1}H and ^{13}C n.m.r. spectra, new peaks

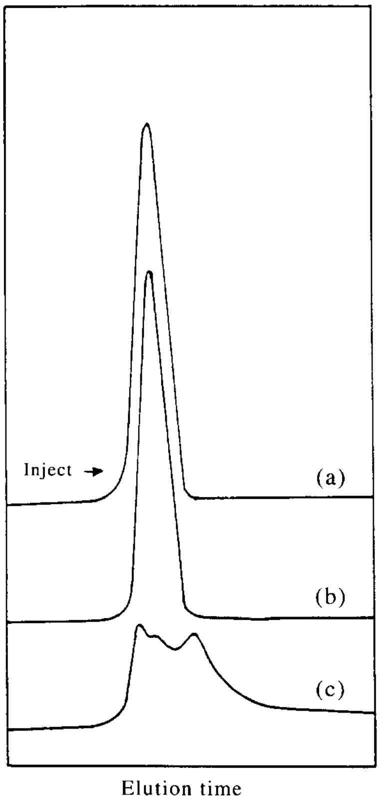


Figure 4 G.p.c. diagrams of PEG 6000: (a) fresh; (b) aged in a vacuum at 80°C for 1000 h; (c) aged in air at 80°C for 1000 h

appear for the PEG degraded in air. In ^{1}H n.m.r., a singlet at 8.0 ppm, a triplet at 4.2 ppm and some peaks at 3.9–4.1 ppm can be identified. In ^{13}C n.m.r., two peaks near 160 ppm and many new peaks at 60–80 ppm can be identified. These changes indicate that esters were produced in the process of thermal degradation in air. Especially, the singlet at 8.0 ppm in ^{1}H n.m.r. and the two peaks at 160 ppm in ^{13}C n.m.r. can be assigned to the formic ester proton and the carbon of the formate, respectively. The peaks at 3.1–4.1 ppm in the ^{1}H n.m.r. spectrum may be assigned to the methylene of ester. The many peaks at 60–80 ppm in the ^{13}C n.m.r. spectrum may be assigned to the carbon of the esters produced by the degradation reaction. But no other signals corresponding to the aldehyde or the carboxylic groups are observed in either the ^{1}H or the ^{13}C n.m.r. spectra. Therefore, it may be confirmed that low molecular weight esters including formic esters were produced as the main products of the thermal degradation of PEG. The mechanism of formic ester formation can be summarized as follows:

1. PEG reacts with oxygen to form α-hydroperoxide.

$$\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-} + \text{O}_2 \longrightarrow \text{-O-CH}_2\ \text{-(COOH)H-O-CH}_2\text{-}$$

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

$$\text{-O-CH}_2\text{-(COOH)H-O-CH}_2\text{-} \longrightarrow \text{-O-CH}_2\text{-(CH)}\ \text{O}\bullet\text{-O-CH}_2\text{-} + \bullet\,\text{OH}$$

3. Formic esters are produced as the thermal degradation products in air.

$$\text{-O-CH}_2\text{-(CH)O}\bullet\text{-O-CH}_2\text{-} \longrightarrow \text{-O-CH}_2\text{-CHO}\ + \bullet\ \text{O-CH}_2\text{-}$$

Stabilization of PEG with MBMTBP

Figure 5 shows the changes in the melting point and heat of fusion when MBMTBP is added to PEG. The melting point depression is linear in concentration when the concentration is less than 0.3 mol kg^{-1} of PEG. The decrease in heat of fusion is also linear in concentration. As an antioxidant, the amount of MBMTBP to be added

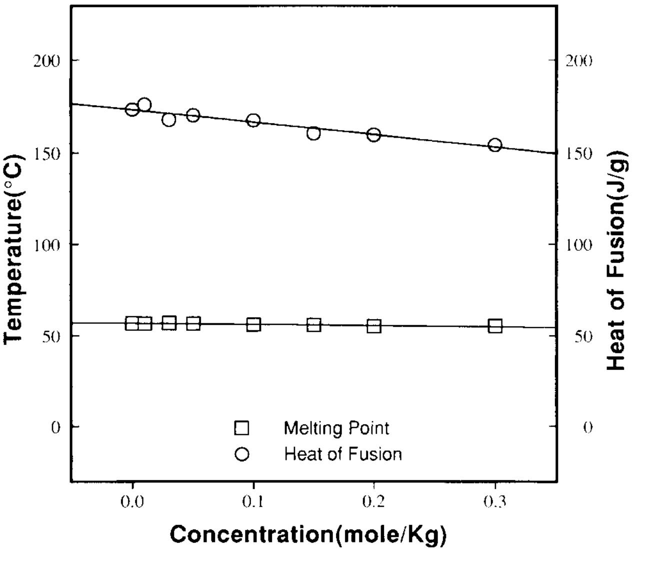


Figure 5 The effect of MBMTBP on the melting point and heat of fusion of PEG 6000

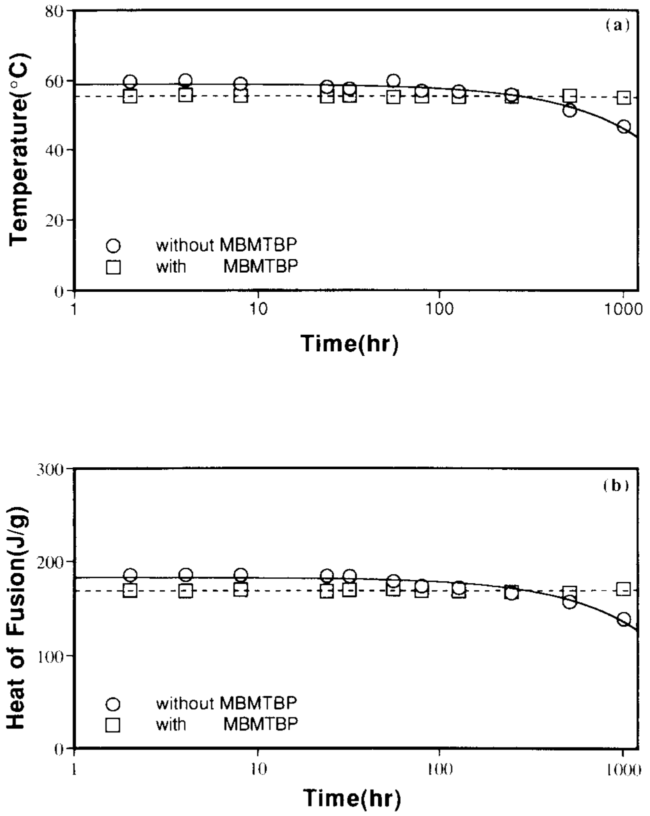


Figure 6 Changes of the thermal properties of PEG 6000 aged in air with time when 0.1 mol kg^{-1} of MBMTBP is added: (a) melting point; (b) heat of fusion

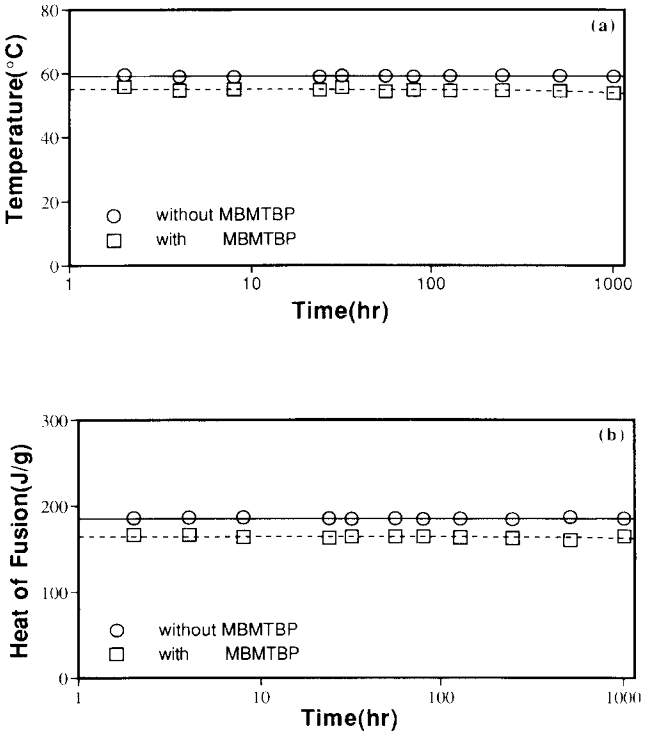


Figure 7 Changes of the thermal properties of PEG 6000 aged in a vacuum with time when 0.1 mol kg^{-1} of MBMTBP is added: (a) melting point; (b) heat of fusion

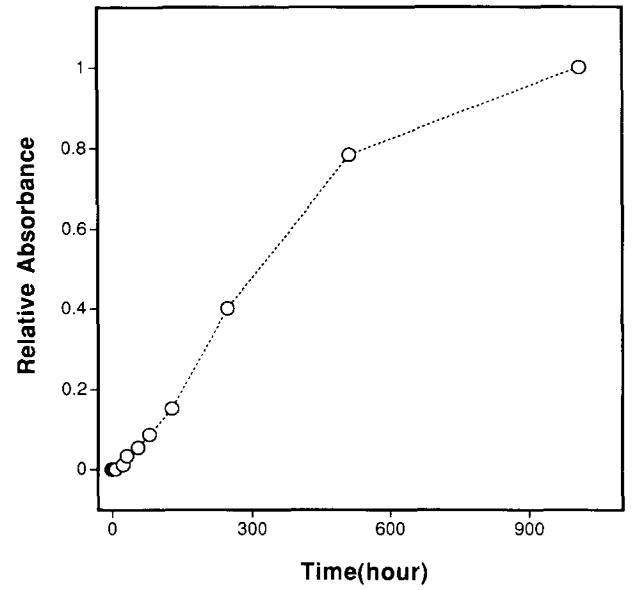


Figure 8 Relative absorbance of u.v. ($\lambda = 590\,\mathrm{nm}$) of PEG 6000 aged in air at 80°C with time when 0.1 mol kg^{-1} of MBMTBP is added

should be as small as possible while maintaining the sufficient stabilizing effect. Even though this research is aimed at the development of PEG as a PCM in thermal energy storage, we have not pursued determination of the optimum amount of MBMTBP, since the major objective was to examine the degradation and stabilizing mechanism. In this research, therefore, we set the amount of MBMTBP to 0.1 mol kg^{-1} as used in the previous report[14].

In *Figures 6* and *7*, the melting point and heat of fusion with and without MBMTBP are plotted against time for PEG degraded in air and in a vacuum, respectively. It is noted that, when the antioxidant is added, the melting point and heat of fusion remain the same after degradation even in the presence of air. This is in contrast to the case of degradation in the presence of air without adding the antioxidant. For PEG degraded in a vacuum no visible changes are noted except for the slight depression of melting point and reduction of heat of fusion due to the addition of the antioxidant. This is another evidence of the oxidative degradation of PEG.

In stabilizing the thermal degradation of PEG in air with MBMTBP, it was confirmed that stably transformed products of MBMTBP were produced and that the amount of transformed products increased with time. In the case of PEG with MBMTBP degraded in a vacuum, no such product was produced. They could be distinguished by the colour change from white to violet. This criterion is due to Pospil[18] and Taimr and Pospil[21] who showed that the change of colour resulted from the formation of oxidatively transformed products of the reaction of MBMTBP with *tert*-butylperoxide. Therefore the extent of colour change can be considered as the degree of transformation of MBMTBP, which is actually the degree of stabilization of thermal degradation of PEG by MBMTBP.

Figure 8 shows the relative u.v. absorbance of PEG containing MBMTBP aged in air. The wavelength was chosen to be 590 nm where the sample showed the maximum absorbance. The maximum absorbance was set to be the value of the sample degraded in air for

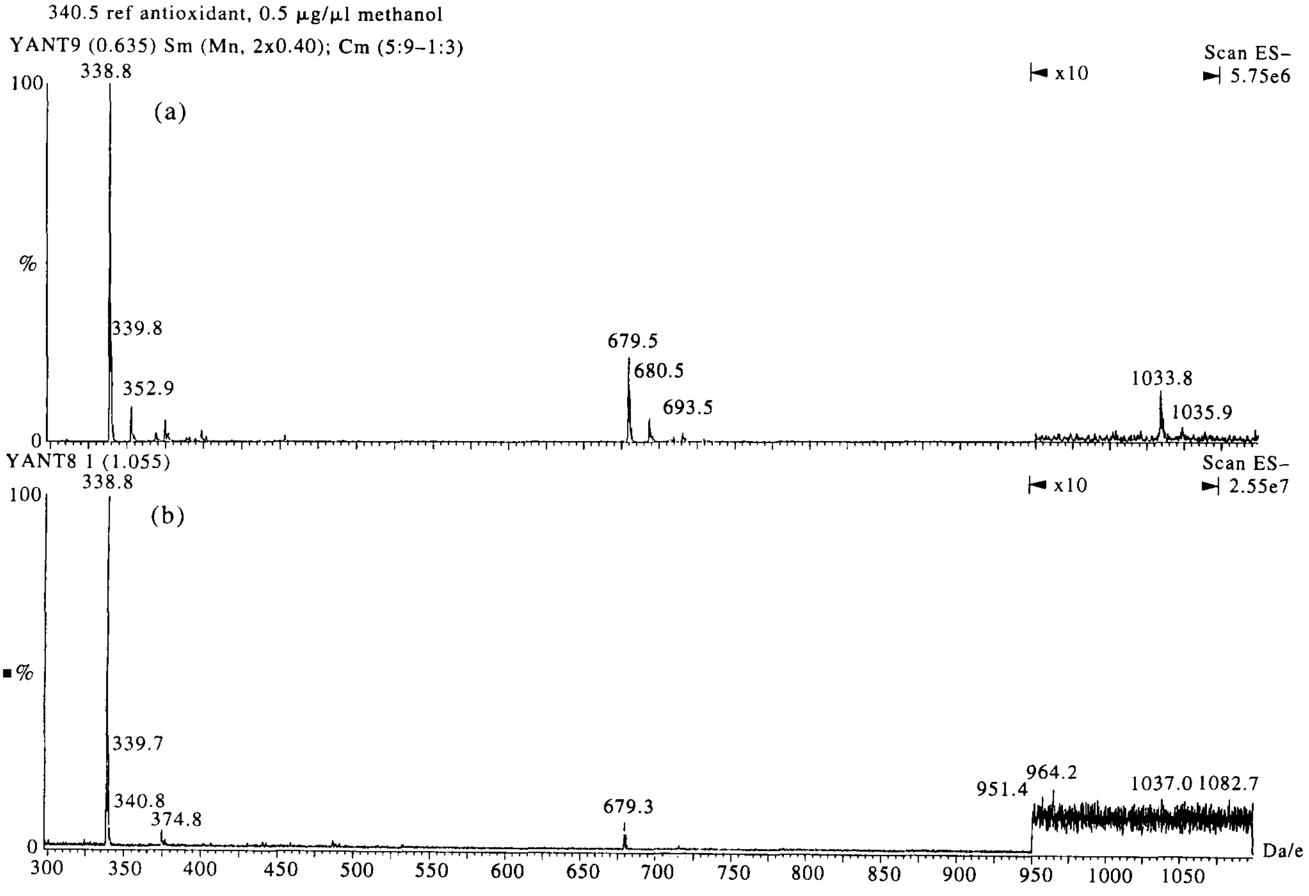
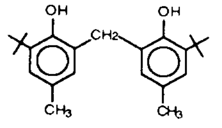
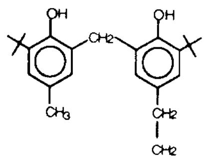
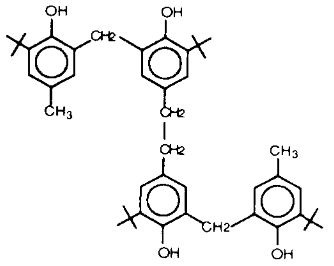
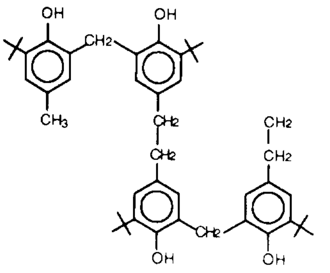
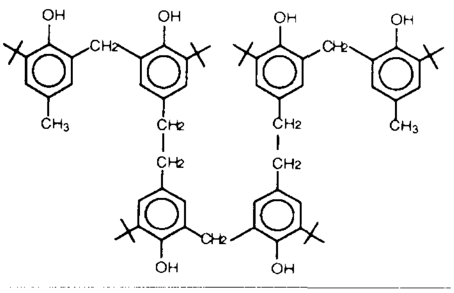


Figure 9 Lc-ms spectra: (a) oxidatively transformed products; (b) MBMTBP

Table 1 Relationship between identified molecular weight and structure

Molecular weight $[(M-H)^{-1}]$	Related structure
339	
353	
680	
694	
1035	

1000 h. In the figure, a short induction period appears to exist. The rate of increase becomes larger after the induction period. But the absorbance appears to become saturated eventually, which indicates that the oxidatively transformed products are no longer produced. Since the relationship between the absorbance and amount of oxidatively transformed products was not known, using only the experimental data obtained in this research, it is not possible to determine the quantitative model for the kinetics of degradation and stabilization at the present time.

In this research, the oxidative transformed products of MBMTBP was identified to confirm the stabilizing effect of MBMTBP on thermal degradation. The oxidative transformed products were separated from the mixture of PEG and MBMTBP using t.l.c. The R_f value of the oxidative transformed products and MBMTBP were 0.4 and 0.7, respectively. The oxidative transformed products showed maximum u.v. absorbance at 460 nm. Taimr and co-workers[20,21] reported similar results of the R_f and absorbance for the reaction between MBMTBP and *tert*-butylperoxy or *tert*-butoxy radicals. Therefore the same mechanism is presumably operating in the stabilization of PEG degradation with MBMTBP.

The oxidative transformed products of MBMTBP were identified using l.c.-m.s. (liquid cromatograph-mass spectrometer) spectrometry. *Figure 9* shows the l.c.-m.s. spectra of MBMTBP and its oxidative transformed products. *Table 1* shows speculated structures of the oxidative transformed products, and their molecular weights. The dimer and trimer MBMTBP were identified in the oxidative transformed products of MBMTBP. Products with larger molecular weight than the trimer were not found.

From the present experimental results using u.v. and l.c.-m.s., it is expected that the stabilization of PEG thermal degradation by MBMTBP follows the mechanism:

1. MBMTBP captures a PEG peroxide radical or a PEG radical formed in the chain breaking cycle.
2. The formed phenoxy radicals of MBMTBP are stabilized by the combination of another MBMTBP.
3. The thermal degradation of PEG is terminated with the formation of the oxidative transformed products of MBMTBP in the above step.

CONCLUSION

In this research, the thermal degradation of polyethylene glycol with average molecular weight 6000 was investigated experimentally. From the point of view of developing PEG as a phase change material for thermal energy storage, PEG was maintained at 80°C for 1000 h in air and in a vacuum with or without adding MBMTBP as an antioxidant.

Without MBMTBP, PEG degraded severely in air so that the melting point and heat of fusion were reduced. In a vacuum, however, almost no degradation was observed. Both the fresh and degraded PEG samples were examined using d.s.c., t.g., g.p.c., *FT*i.r., and ^1H and ^{13}C n.m.r. All the results suggest that the thermal degradation of PEG in air at 80°C follows the chain scission mechanism for the oxidative degradation.

The degradation was successfully suppressed by adding MBMTBP as an antioxidant. The oxidatively transformed products of MBMTBP were isolated and identified to be the dimer and trimer of MBMTBP. The result implies that MBMTBP stabilizes the oxidative degradation by capturing the peroxide radical of PEG.

It is concluded that PEG can be effectively used as a phase change material if oxygen is excluded effectively and/or antioxidants are added properly, as far as thermal degradation is concerned.

ACKNOWLEGEMENTS

The authors gratefully acknowledge Dr J. Yoo of Korea Basic Science Center for l.c.-m.s. measurements. The authors also gratefully acknowledge Ms T. Kim of Korea Institute of Chemical Technology for t.l.c. work.

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