SHORT COMMUNICATIONS

Unusual Thermal Degradation Behavior of PEGMA in Air at Different Heating Rates

Jiann-Wen HUANG[†] and Chiun-Chia KANG*

*Department of Styling and Cosmetology, Tainan Woman's College of Arts and Technology,
529 Chung Cheng Rd., Yung Kang City, 710, Taiwan, R.O.C.*

**R&D Center, Taroko International Co., Ltd., 473 Jong Shan South. Rd., Yung Kang City 710, Taiwan, R.O.C.*

(Received February 27, 2004; Accepted April 27, 2004; Published July 15, 2004)

KEY WORDS Crosslinking / Poly(ethylene-co-glycidyl methacrylate) / Thermal Degradation / Thermogravimetric Analysis (TGA) / [DOI 10.1295/polymj.36.574]

Poly(ethylene-co-glycidyl methacrylate) (PEGMA) is a copolymer of ethylene and glycidyl methacrylate with epoxy groups. The epoxy groups can react with functional groups such as carboxyl, hydroxyl, or amines. PEGMA has been extensively used as an impact modifier for engineering plastic such as poly(butylenes terephthalate) (PBT),¹ poly(ethylene terephthalate) (PET),² poly(phenylene sulfide) (PPS)³ and polyamides⁴ because of its elastomeric nature and impact absorbing properties. PEGMA has been also used as compatibilizer for polymer blends such as PBT/polypropylene,⁵ PET/polyethylene^{6–9} and Nylon-6/PP.¹⁰

The thermal stability of polyethylene has been studied extensively under both air¹¹ and nitrogen.^{12–17} Degradation behaviors of poly(glycidyl methacrylate) (PGMA) and its copolymers have also been studied under nitrogen atmosphere.¹⁸ There are very few studies, however, on thermal stability of PEGMA under air atmosphere. Because PEGMA is often blended with engineering plastics and applied at a high temperature under air atmosphere, it is worthy to study the thermal stability of PEGMA under air atmosphere.

EXPERIMENTAL

Materials

Low density polyethylene (LDPE) and poly(ethylene-co-glycidyl methacrylate) (PEGMA) used in this study are all commercially available grades. LDPE was supplied by Formosa Plastics (TAISOX 6323F). PEGMA was supplied by Sumitomo Chemical Co., Ltd. (CG5004) and contains 81 wt % ethylene and 19 wt % glycidyl methacrylate.

Synthesis of PGMA

Glycidyl methacrylate (GMA) monomer, 2,2'-Azo-bis(isobutyronitrile) (AIBN) and methyl ethyl ketone (MEK) were purchased from Aldrich Co., Ltd. All chemicals were used without further purification.

Synthesis of Poly(glycidyl methacrylate) (PGMA)

PGMA was prepared by radical polymerization of 20 wt % GMA in MEK using 0.3 wt % AIBN as an initiator. The polymerization proceeded at 60 °C for 12 h under nitrogen. The PGMA was precipitated in ethanol and dried in a vacuum oven at 50 °C for 12 h.

Characterizations

Thermogravimetric analysis (TGA) was conducted with a PerkinElmer TGA-6 thermogravimetric analyzer under a nitrogen and air flow of 50 ml/min from 50 to 600 °C at different heating rates. In each scan 10–12 mg of the sample was used.

[†]To whom correspondence should be addressed (Fax: +886-6-2433812, E-mail: jw.huang@msa.hinet.net).

Figure 1. TGA curves of LDPE in Air. Black points (●) denote the T_0 estimated by bitangent method.

Figure 2. TGA curves of PGMA in Air. Black points (●) denote the T_0 estimated by bitangent method.

RESULTS AND DISCUSSION

Figures 1 and 2 show the thermal degradation TGA curves of LDPE and PGMA in air at several heating rates. The curves shift to higher temperature with heating rate for both LDPE and PGMA, in consistent with previous studies.^{11–18} In general, TGA curves for most polymers would shift to a higher temperature with heating rate and several explanations have been proposed to account for this phenomenon. Some consider that a change of mechanism of thermal degradation occurred when there is a change in heating rate, and others consider inefficient heat transfer from furnace to samples when increasing heating rate.

Figures 3 and 4 show TGA curves of PEGMA in nitrogen and air respectively. The curves under nitrogen atmosphere shifted to high temperature when heating rate was increased. The curves in air, however, showed a complicated shifting pattern as can be seen from its initial weight loss temperature (T_0) variation with heating rate. The initial weight loss tem-

Figure 3. TGA curves of PEGMA in Nitrogen. Black points (●) denote the T_0 estimated by bitangent method.

Figure 4. TGA curves of PEGMA in Air.

Table I. The initial temperature of weight loss (T_0), °C

Heating rate	LDPE		PGMA		PEGMA
	Nitrogen	Air	Nitrogen	Air	Nitrogen
5 °C/min	—	353	—	256	—
10 °C/min	432	362	280	267	421
20 °C/min	453	366	283	271	432
30 °C/min	468	370	285	276	442
40 °C/min	474	377	291	279	456
60 °C/min	487	385	295	284	461

peratures (T_0) were determined by bitangent method from TGA curves for LDPE, PGMA, and PEGMA and were summarized in Table I.

Figure 5 shows T_0 of PEGMA under air atmosphere. Three regions can be identified in the figure: region 1, T_0 increased with heating rate; region 2, T_0 decreased when heating rate was increased from 8 °C/min to 30 °C/min.; and region 3, T_0 increased again with heating rate. T_0 of PEGMA fell between that of LDPE and PGMA at same heating rate when heated in nitrogen. However, T_0 of PEGMA heated in air is higher than that of LDPE and PGMA indicating supe-

Figure 5. The relation of T_0 and heating rate for PEGMA.

rior thermo-oxidative stability of PEGMA to LDPE and PGMA.

Lee *et al.*¹⁹ studied the thermal decomposition of poly(3-hydroxyl-butyrate) (PHB)/PGMA blends under nitrogen atmosphere by TGA. The degradation of PHB/PGMA blends shows higher thermal stability than neat PHB due to crosslinking reactions of the epoxy groups in the PGMA component with the carboxyl chain ends of PHB fragments during the degradation process. The higher thermal stability of PEGMA copolymer under air atmosphere in this study was believed to be caused by the thermal crosslinking reaction during the thermal oxidation process.

Two competitive factors are proposed to influence T_0 of PEGMA in this study: heating rate^{11–18} and crosslinking reaction. At a higher heating rate, T_0 of PEGMA will shift to a higher temperature; but since not enough time is allowed for extensive crosslinking reactions to take place before decomposition, a lower T_0 for PEGMA will be obtained. T_0 increased in region 1 of Figure 5 because extensive crosslinking reaction was believed to have occurred due to very low heating rate. T_0 decreased when heating rate was raised further in region 2 since only limited degrees of crosslinking reaction had occurred before PEGMA degraded. T_0 will increase again when heating rate is very high in region 3.

Antioxidants are commonly added in commercial products and may be a influential factor at TGA out-

come. Similar TGA graphs were obtained in the present study after PEGMA being purified by dissolving it in THF solvent and precipitating it in ethyl alcohol. Detailed mechanisms of PEGMA decomposition in air have not been fully understood and are the subject of ongoing research in our laboratory.

REFERENCES

1. A. Aróostegui and J. Nazábal, *J. Polym. Sci., Part B: Polym. Phys.*, **41**, 2236 (2003).
2. M. Penco, M. A. Pastorino, E. Occhiello, F. Garbassi, R. Braglia, and G. Giannotta, *J. Appl. Polym. Sci.*, **57**, 329 (1995).
3. S. I. Lee and B. C. Chun, *Polymer*, **39**, 6441 (1998).
4. E. G. Koulouri, A. X. Georgaki, and J. K. Kallitsis, *Polymer*, **38**, 4185 (1997).
5. C. H. Tsai and F. C. Chang, *J. Appl. Polym. Sci.*, **61**, 321 (1996).
6. Y. Pietrasanta, J. J. Robin, N. Torres, and B. Boutevin, *Macromol. Chem. Phys.*, **200**, 142 (1999).
7. N. Torres, J. J. Robin, and B. Boutevin, *J. Appl. Polym. Sci.*, **81**, 2377 (2001).
8. N. K. Kalfoglou, D. S. Skafidas, J. K. Kallitsis, J. C. Lambert, and L. Van der Stappen, *Polymer*, **36**, 4453 (1995).
9. S. S. Dagli and K. M. Kamdar, *Polym. Eng. Sci.*, **34**, 1709 (1994).
10. J. Y. Wu, W. C. Lee, W. F. Kuo, H. C. Kao, M. S. Lee, and L. L. Lin, *Adv. Polym. Technol.*, **14**, 47 (1995).
11. C. Vasile, E. Costea, and L. Odochian, *Thermochim. Acta*, **184**, 305 (1991).
12. Y. Cho, M. Shim, and S. Kim, *Mater. Chem. Phys.*, **52**, 94 (1998).
13. R. W. J. Westerhout, R. H. P. Balk, R. Meijer, J. A. M. Kuipers, and W. P. M. van Swaaij, *Ind. Eng. Chem. Res.*, **36**, 3360 (1997).
14. R. W. J. Westerhout, J. Waanders, J. A. M. Kuipers, and W. P. M. V. Swaaij, *Ind. Eng. Chem. Res.*, **36**, 1955 (1997).
15. P. L. Beltrame, P. Carniti, G. Audisio, and F. Bertini, *Polym. Degrad. Stabil.*, **26**, 209 (1989).
16. J. A. Conesa, A. Marcilla, R. Font, and J. A. Caballero, *J. Anal. Appl. Pyrolysis*, **36**, 1 (1996).
17. B. Dickens, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1065 (1982).
18. S. Zulfiqar, M. Zulfiqar, and M. Nawaz, *Polym. Degrad. Stabil.*, **30**, 195 (1990).
19. S. N. Lee, M. Y. Lee, and W. H. Park, *J. Appl. Polym. Sci.*, **83**, 2945 (2002).