

Poly(methyl methacrylate-g-propylene oxide)

2. Thermal and mechanical behavior

Clara Marize F. Oliveira* and Ailton S. Gomes

Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, C.P. 68525,
Rio de Janeiro, Brazil

Summary

Graft copolymers of poly(methyl methacrylate) with grafted branches of poly(propylene oxide) showed a single glass transition temperature and significant lowering of T_g when the percentage of grafted branches increased. Thermogravimetric analysis of graft copolymers showed a marked improvement in thermal stability when compared with poly(methyl methacrylate) homopolymer. Tensile properties of graft copolymers showed a decrease in tensile modulus and tensile strength but an increase in ultimate elongation with increase in grafted branches.

Introduction

Thermal behavior has been used to verify segment compatibility in graft copolymers. The glass transition temperature of graft copolymer lies between the T_g 's of the corresponding homopolymers when the segments are compatible (1). Mechanical properties, such as tensile strength, modulus and extensibility of polymers can be affected by grafting (2).

Physical mixtures of poly(methyl methacrylate) (PMMA) and poly(propylene oxide) showed a plasticizing effect up to 0.2 weight fraction of poly(propylene oxide) (3).

In this paper we investigate the plasticizing effect of grafted poly(propylene oxide) branches on poly(methyl methacrylate) backbone and the thermal stability of the graft copolymers.

Experimental

Materials

Poly(methyl methacrylate-g-propylene oxide) samples were prepared as reported (4). Chloroform was used as received.

*To whom correspondence should be addressed

Characterization techniques

The glass transition temperatures of all samples were determined with a Perkin Elmer DSC-2 differential scanning calorimeter. Polymer samples were heated at 10°C/min under a constant stream of nitrogen.

The thermogravimetric analysis of PMMA, poly(propylene oxide) and graft copolymers were carried out by means of a Du Pont 951 termobalance attached a Du Pont 990 module. The nitrogen flow was kept constant at 30 mL/min and a heating rate of 10°C/min was used. The sample weights were about 11-13 mg.

Films of PMMA and graft copolymers were cast from chloroform solutions (10% w/v) on to a glass surface at room temperature and the solvent was allowed to evaporate at room temperature very slowly for 2 days. The resulting films were subjected to further drying under vacuum for 20 days.

Stress-strain measurements were conducted on film strips of PMMA and graft copolymers by an Instron tester (crosshead speed of 0.05 cm/min) at $27 \pm 1^\circ\text{C}$. Averages of five specimens are reported.

Results and discussion

The glass transition temperatures were determined to see the effect of grafted poly(propylene oxide) branches on the backbone of poly(methyl methacrylate). DSC thermograms were recorded from -100°C to 150°C ; they showed only one transition between -66°C , T_g of poly(propylene oxide) and 110°C , T_g of PMMA. These results are presented in Table 1. When the percentage of grafted branches in the copolymer increases, the T_g decreases; this suggests a plasticizing effect by poly(propylene oxide) on poly(methyl methacrylate).

Studies of thermal degradation of the homopolymers, poly(propylene oxide) and PMMA, as well the graft copolymers of these polymers, were carried out using thermogravimetry. The thermogravimetric trace shown in Fig. 1 for poly(propylene oxide) shows that the homopolymer decomposes in a single stage while PMMA (Fig. 2) decomposes in three stages. The thermal degradation of PMMA has been studied extensively (5-8). When the polymer is obtained by radical initiation, it has unsaturated chain ends. Then the first and the second stages of decomposition can be due to depolymerization initiated at those ends (8) or head-to-head linkages (7) which occur at lower temperatures, while the third stage is due to depolymerization initiated by random chain scission. Poly(propylene oxide) decomposes by random scission without chain-end-initiated depolymerization. In the thermogravimetric trace of poly(methyl

Table 1: Glass transition temperatures and mechanical properties of poly(methyl methacrylate-g-propylene oxide), PMMA and PPO^a

| Samples | Graft copolymer ^b | | T _g ^d °C | Tensile modulus MPa | Tensile strength MPa | Ultimate elongation % |
|---------|------------------------------|--|-----------------------------------|---------------------------|----------------------------|-----------------------------|
| | PPO ^c wt% | | | | | |
| PMMA | - | | 110 | 1070 | 30.3 | 3.5 |
| 1 | 20 | | 88 | 840 | 15.4 | 28.0 |
| 2 | 23 | | 83 | 820 | 14.6 | 36.0 |
| 3 | 32 | | 55 | 650 | 9.4 | 71.0 |
| 4 | 51 | | 44 | 10 | 1.3 | 438.0 |
| PPO | - | | -66 | - | - | - |

^a PPO - Poly(propylene oxide), $\overline{M}_n=2470$. ^b Obtained by reaction of methyl methacrylate and poly(propylene oxide) methacrylate macromonomer in benzene at 80°C with AIBN as initiator.

^c Obtained by ¹H NMR. ^d Obtained by DSC curves.

methacrylate-g-propylene oxide) shown in Fig. 3, the first stage of decomposition is not observed. This increase in stability may be due to the difficulty in depolymerization initiated at the chain ends and/or head-to-head linkages inhibited by the presence of bulky poly(propylene oxide) graft.

The mechanical properties of the graft copolymers were obtained by tensile analysis of polymers films. The introduction of grafted branches on poly(methyl methacrylate) shows variations in tensile properties of the samples. Films of the graft copolymers were transparent by visual observation up to 51% of grafted branches. Table 1 summarizes tensile strength, modulus and elongation of PMMA and the graft copolymers. When the grafted branches increase, the tensile modulus and strength decrease, while elongation increases. These results are characteristic due to the incorporation of flexible grafted branches on the rigid PMMA backbone.

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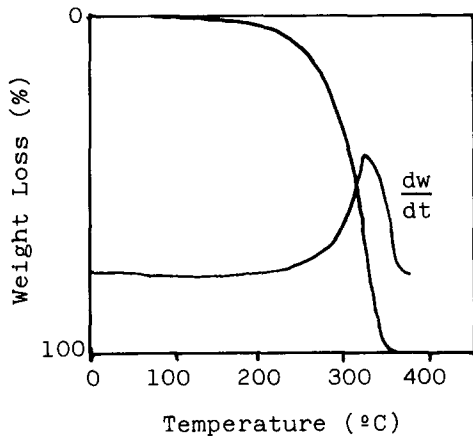


Fig. 1. Thermogravimetric curve of poly(propylene oxide)

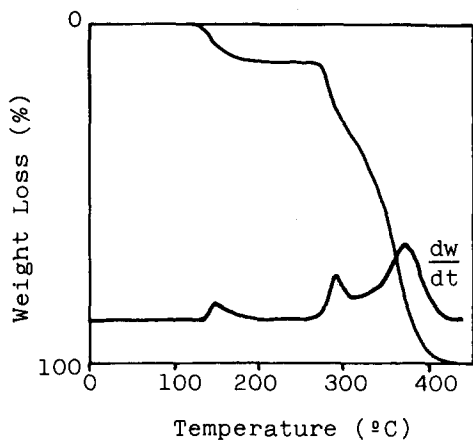


Fig. 2. Thermogravimetric curve of poly(methyl methacrylate)

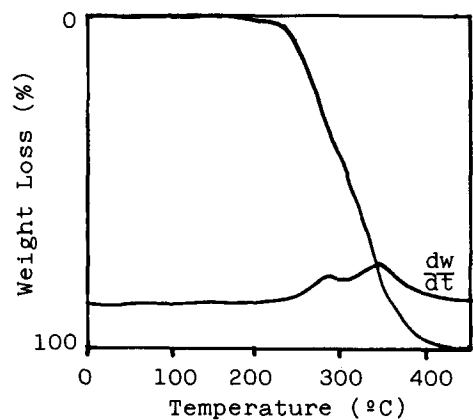


Fig. 3. Thermogravimetric curve of poly(methyl methacrylate-g-propylene oxide) with 20% of graft chains.

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