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THERMAL BEHAVIOUR OF SOME NONPOROUS METHACRYLATE POLYMERS

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Abstract

Three nonporous methacrylate polymer samples were synthesized by suspension polymerization, and subsequently investigated. The surface area and the surface morphology of the spherical beads were examined by the BET method from the low-temperature adsorption isotherms and by scanning electron microscopy (SEM), respectively. Thermal behaviour of the two homopolymer samples, poly(glycidyl methacrylate) (PGMA) and poly(ethylene glycol dimethacrylate) (PEGDMA), and the copolymer sample poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) (PGME) was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All samples exhibit complex thermal degradation behavior. The copolymer is intermediate in stability between PGMA and PEGDMA.

Introduction

Homopolymers and copolymers of glycidyl methacrylate (GMA) have received considerable attention in recent years owing to their versatile applications and low cost [1-3]. The reported glass transition temperature values for PGMA, T_g , are as low as 74°C, which may be a limiting factor in commercial uses [4]. It is well known that the addition of a crosslinking comonomer, such as ethylene glycol dimethacrylate, (EGDMA), can substantially increase thermal stability of polymers. Also, at high crosslinking densities, an absence of the glass transition is observed. It has also been reported that the homopolymer of EGDMA undergoes self-crosslinking during free radical polymerization, which makes it suitable for comparison with its copolymers with GMA [5]. The purpose of this paper was to investigate the possibility of thermal stabilization of PGMA by crosslinking with EGDMA, and compare thermal properties of the copolymer with two homopolymers.

Experimental

Three polymer samples, PGME, PGMA and PEGDMA were synthesized by suspension polymerization, in the form of spherical beads. The monomer phase consisting of 39.0 g GMA and 26.0 g EGDMA for the copolymer, and 65.0 g of GMA for one homopolymer and 65.0 g of EGDMA for the other homopolymer, and containing the same amount of AIBN initiator (0.65 g), was suspended in the

aqueous phase containing 200.0 g of distilled water and 2.0 g of poly(vinylpyrrolidone). The polymerization reactions were carried out at 70 °C for 2 h and at 80 °C for 6 h with the stirring rate of 300 rpm. The resulting particles were washed with distilled water, followed by a 24 h Soxhlett extraction with ethanol, and dried at 50°C. The absence of porosity was ascertained by means of scanning electron microscopy (JEOL JSM-646 OLV scanning microscope) and specific area measurements by the BET method from the low-temperature nitrogen adsorption isotherms (77 K) (Sorptomatic 1990 Thermo Finnigen). Thermal stability of PGME, PGMA, and PEGDMA was investigated using a TG/DSC111 equipment with He as a carrier gas (30 ml/min), and the heating rate of 10°Cmin⁻¹.

Results and Discussion

The measured specific surface area of all samples was less than 1 m²/g, which indicated absence of any porosity, as was confirmed with SEM images.

The thermograms for all the samples are shown in Fig. 1. The characteristic temperatures obtained for mass losses of 5, 10 and 50% ($T_{5\%}$, $T_{10\%}$, $T_{50\%}$) are shown in Table 1., including the initial temperature of degradation (T_i), along with the mass percent char content at 450°C (m_{cc}). Table 1. also shows temperatures corresponding to the maximum degradation rates below 350°C (T_{max}). It is evident from these results that the PGME copolymer is intermediate in stability between the two homopolymers. Thermal degradation of these polymers is complex, with considerable overlap of multiple processes, which is apparent from the DTG curves. It was previously reported that thermal degradation of PGMA proceeds mainly through depolymerization to monomer, which is a major reaction, and through ester decomposition [6]. In the case of PEGDMA, it was found that its degradation involved chain reactions [7]. Below 400°C, depolymerization results in monomers evolved in proportion higher than 95 %, and at higher temperatures, other products due to cracking reactions are present. The

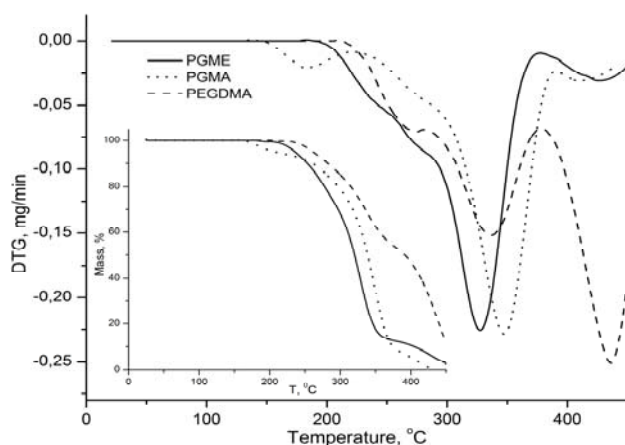


Fig.1. DTG and TGA thermograms of PGME, PGMA and PEGDMA.

DTG curve of PGME has similarities with the curves of both homopolymers, but even though the main degradation peak is at a lower temperature than for PGMA, the most important difference, from the practical point of view (threshold application temperature), is the shift of the 185°C peak to higher temperatures, or rather its absence.

Table 1. Characteristic temperatures of thermal degradation and char content of PGME, PGMA and PEGDMA

Sample	T _i , °C	T _{5%} , °C	T _{10%} , °C	T _{50%} , °C	m _{cc} , %	T _{max} , °C		
						240	284	327
PGME	180	235	253	320	2.3	240	284	327
PGMA	144	204	261	338	0.0	185	265	348
PEGDMA	204	261	281	390	8.1	-	270	336

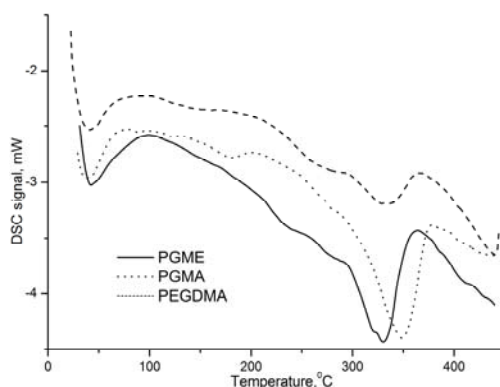


Fig.2. DSC curves for PGME, PGMA and PEGDMA.

Thermal degradation of all three polymers is dominantly endothermic. DSC curve for PGME does not show a discernible glass transition temperature, unlike PGMA curve, where we observe the glass transition at 86°C. The glass transition of PEGDMA is above 100°C, and it is spread out over a wide temperature interval, as is characteristic for crosslinked polymers. Even though the main degradation endotherm of PGMA is at a higher temperature than for PGME, the absence of thermal

transitions for PGME at temperatures lower than 200°C is of utmost importance.

Conclusion

In this study, it was shown that the thermal degradation profiles of the synthesized and investigated nonporous methacrylate polymers, PGME, PGMA and PEGDMA, are complex and composed of many overlapping processes. PGME copolymer is intermediate in stability between PGMA and PEGDMA homopolymers. It is evident that, in this case, crosslinking enhances thermal stability. There is no observable glass transition in the copolymer.

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