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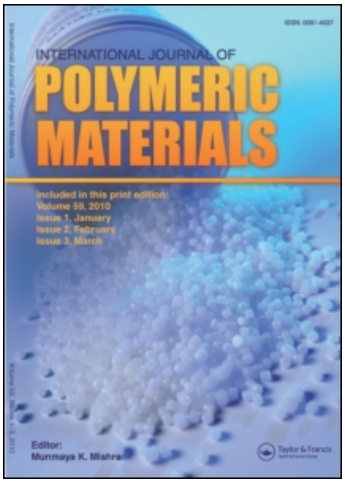

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Crosslinking Density, Thermal and Mechanical Behavior in PMMA Networks

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To cite this Article Zawadzki, Snia Faria , Sereda, Luciane and Akcelrud, Leni(1996) 'Crosslinking Density, Thermal and Mechanical Behavior in PMMA Networks', International Journal of Polymeric Materials, 33: 1, 31 — 36
To link to this Article: DOI: 10.1080/00914039608028604
URL: http://dx.doi.org/10.1080/00914039608028604

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Intern. J. Polymeric Mater., 1996, Vol. 33, pp. 31–36
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Crosslinking Density, Thermal and Mechanical Behavior in PMMA Networks

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(Received August 15, 1995; in final form August 21, 1995)

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Poly(methyl methacrylate-co-ethyleneglycol dimethacrylate) networks were synthesized with systematic variation in crosslinking density. The molecular weight between crosslinks ($\bar{M}_c$) was determined by equilibrium swelling measurements. The glass transition temperature was used to evaluate the effect of curing time and the degree of crosslinking on the networks. Flexural strength and impact resistance decreased with increasing $\bar{M}_c$.

KEY WORDS Networks, PMMA, crosslink, mechanical properties and thermal properties.

INTRODUCTION

Free radical processes for the production of linear and crosslinked polymethacrylates have long been subject of intense study, due to the great applicability of these materials.[1,2] Poly(methylmethacrylate) (PMMA) networks in particular are widely used products, but a systematic study showing the influence of crosslinking density on thermal and mechanical behavior cannot be found in the literature. In this work methylmethacrylate (MMA) was copolymerized with ethyleneglycol dimethacrylate (EGDMA) and the relationships between the level of crosslinking, glass transition temperature and mechanical properties are presented.

EXPERIMENTAL

Syntheses

The poly(methyl methacrylate-co-ethyleneglycol dimethacrylate) networks, P(MMA-co-EGDMA), were prepared by heating the inhibitor-free monomer mixture with

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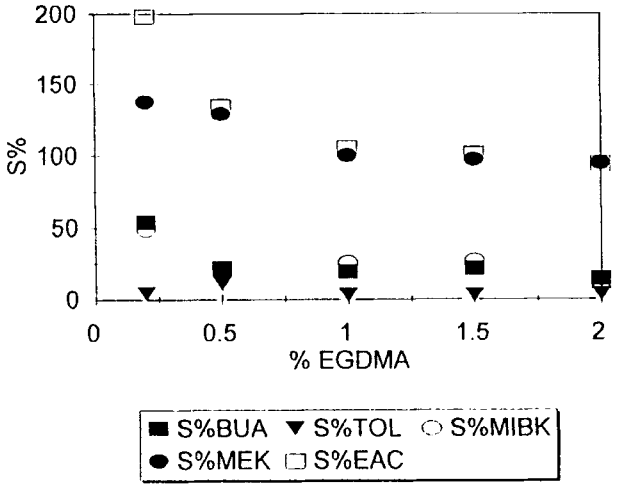

FIGURE 1 Effect of EGDMA concentration on swelling at equilibrium ($S\%$).

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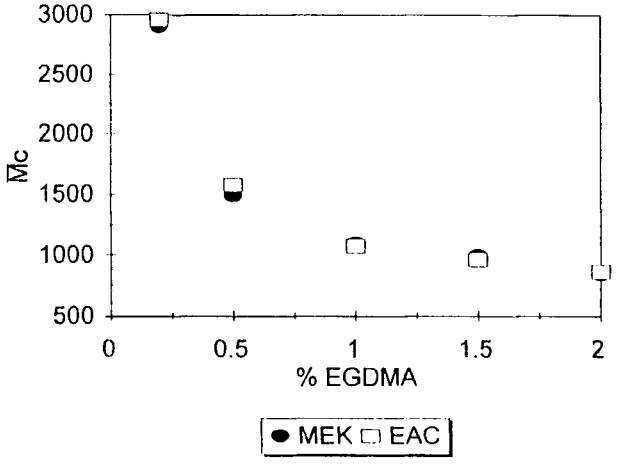

FIGURE 2 Effect of EGDMA concentration on average molecular weight between crosslinkings ($\bar{M}_c$).

0.5% w/w benzoyl peroxide at 65°C until 30–40% conversion was reached. The polymer syrup was cast in a vertical glass mold, and was further polymerized during 24, 48, 72, 96, 190 or 240 hours at 45°C. Plates with dimensions of (20 × 10 × 0.2) cm were produced with EGDMA concentrations of 0.0, 0.2, 0.5, 1.0, 1.5 or 2.0%.

Swelling at Equilibrium

Polymer samples were cut into square pieces of 2.0 cm length, and immersed in the solvents, for 7 days in the dark. The solvents were: ethyl acetate (EAC), *n*-butyl acetate (BuAc), methyl ethyl ketone (MEK), methyl iso-butyl ketone (MIBK) and toluene (TOL). Swelling at equilibrium ($S\%$) was determined by the relationship:

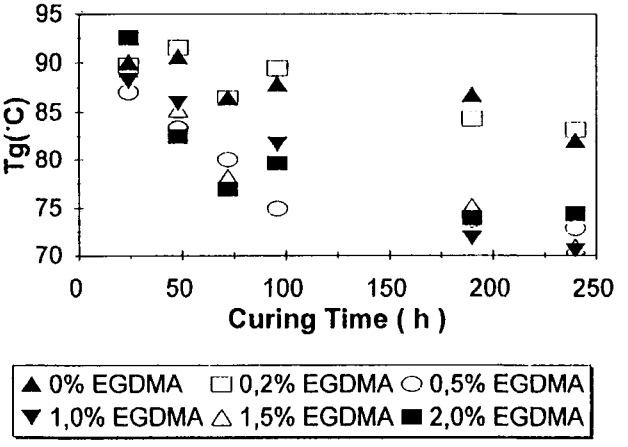

FIGURE 3 Variation of T_g with curing time.

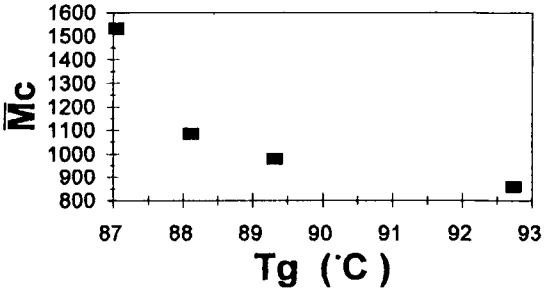

FIGURE 4 Effect of crosslinking density ($\bar{M}_c$) on T_g.

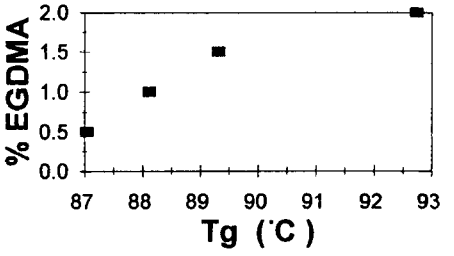

FIGURE 5 Effect of crosslinker concentration [EGDMA] on T_g.

$S\% = [(W - W_0)/W_0] \times 100$ where W and W_0 were the weight of dried and swollen samples respectively.

Thermal Analysis

The glass transition temperature were measured with a DuPont 9900 differential scanning calorimeter using a heating rate of 20°C/min. The reproducible value for T_g was usually taken from the second or third runs.

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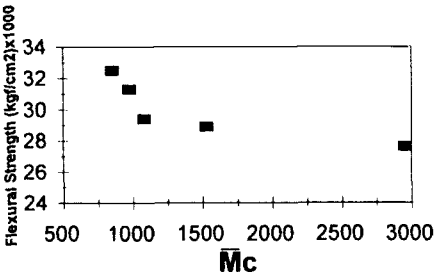

FIGURE 6 Effect of crosslinking density ($\bar{M}_c$) on flexural strength.

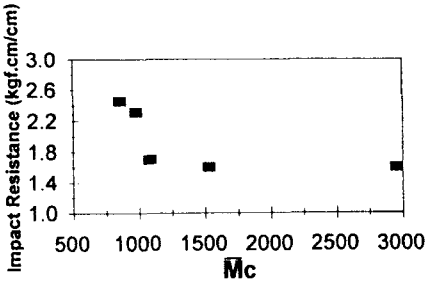

FIGURE 7 Effect of crosslinking density ($\bar{M}_c$) on impact resistance.

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Mechanical Analysis

Hardness testing was performed according to ASTM D 2240-85 on a Rockwell durometer of R type. Notched specimens were impact tested (IZOD-Impact testing Machine), in accordance with ASTM D 256-78. Flexural testing was performed at room temperature using a Instron equipment, model n° 4202 according to ASTM D 791-70 at a cross-head speed of 11.5 mm/min.

RESULTS AND DISCUSSION

One of the most used methods for the determination of crosslinking density is based on the Flory-Rehner theory,[3-6] using equilibrium swelling measurements.[7,8] The average molecular weight between crosslinkings ($\bar{M}_c$) was determinated by means of the Flory-Rehner equation:

$$\nu = \rho/\bar{M}_c = -[\ln(1 - V_r) + \chi V_r^2]/\rho V_1(V_r - V_r/2) \quad (1)$$

where ν is the crosslinking density, which corresponds to the number of effective chains per volume unit and is equal to $\rho/\bar{M}_c$, where ρ is the polymer density. V_r is the reduced volume which is equal to the relation volume of dried sample/volume of swollen sample, χ is the Flory-Huggins polymer-solvent interaction parameter and V_1 is the molar volume of the pure solvent.

χ can be separated into an entropy term (χ_s) and an enthalpic term (χ_h)[9]

$$\chi = \chi_s + \chi_h \tag{2}$$

The relationships between χ_h, the solubility parameters of solvent (δ_1) and of the polymer (δ_2) for an endothermic mixture can be obtained from the Scatchard-Hildebrand theory for the heat of mixture of solutions[10]

$$\chi_h = \frac{V_1(\delta_1 - \delta_2)^2}{RT} \tag{3}$$

The reported values for χ_s are in the range 0.3–0.5.[11,12] An average value of 0.34 was found by Blanks and Prausnitz[13] for a series of polymers in a large number of solvents and that value has been adopted in several polar and non polar systems.[14] By making $\chi_s = 0.34$ and calculating χ_h by means of the reported values for PMMA solubility parameter (δ_2) and for the solvents (δ_1),[15,16] χ was obtained from Equation 2.

From Figure 1 where swelling at equilibrium (*S%*) is plotted against EGDMA concentrations it can be seen that toluene was the least effective solvent for swelling, *n*-butyl acetate and methyl iso-butyl ketone showed intermediate swelling capacity, whereas ethyl acetate and methyl ethyl ketone were the most effective swelling solvents. According to theory,[9,10] the smaller ($\delta_1 - \delta_2$), the better is the solvent. This was verified for all the oxygenated solvents, but not for toluene, and was attributed to the absence of oxygen atoms in this solvent, making it unable to present all the interactions with the polymer that occur with the oxygenated solvents, mostly hydrogen bonds.

The relationships between the degree of crosslinking and EGDMA concentration are shown in Figure 2. Methyl ethyl ketone and ethyl acetate were used as swelling solvents and it can be seen that for crosslinker concentration in the range 0.2% to 2.0% $\bar{M}_c$ varied form 3000 to 800. These results were obtained by means of Equation 1 and Equation 2 with the following values $\delta_2 = 9.5$ $(cal/cm^3)^{1/2}$, $\delta_1 = 9.22$ $(cal/cm^3)^{1/2}$; $\chi = 0.393$ for MEK and $\delta_1 = 9.10$ $(cal/cm^3)^{1/2}$, $\chi = 0.475$ for EAC.[17–20]

Figure 3 shows the influence of curing time on T_g for the five concentrations of crosslinker employed. It was found that T_g reached a maximum value for 24 hours of curing time, decreasing smoothly for EGDMA concentrations of 0.0 and 0.2% and quite sharply for EGDMA concentrations of 0.5, 1.0, 1.5 and 2.0% for periods of time between 48 and 240 hours, indicating that higher crosslinking densities corresponded to higher degradation rates. The correspondence of the highest T_g values with $\bar{M}_c$ and EGDMA concentration is seen in Figures 4 and 5.

Figures 6 and 7 show the influence of crosslinking density ($\bar{M}_c$) on flexural strength and impact resistance. It can be noticed that these mechanical properties showed increasing values with decreasing $\bar{M}_c$. Flexural strength had an increase of 22.2% and impact resistance of 71.4% in the range studied. Rockwell hardness did not show significant change with $\bar{M}_c$, remaining in the range of 116 to 124 for the samples tested.

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