

Differential Scanning Calorimetric Studies of Poly (Methyl Methacrylate -Co- Styrene) (MMA-co-ST) Copolymers

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Abstract: Copolymers of methyl methacrylate (MMA) and styrene (ST) at different ratios (1:1, 2:1 and 1:2) were prepared with various percentage of ethylene glycol dimethacrylate (EGDMA) as cross-linking agent. The percentage of cold crystallization was estimated on the basis of exothermal energy. Copolymers with higher ratios of MMA produce higher percentage of crystallization, but surprisingly yield lower melting temperature. Although the percentage of crystallization increases with EGDMA content, the melting temperature decreases with higher content of EGDMA.

Keyword: Cross-linking, Cold Crystallization, Melting Temperature

Introduction

In order to achieve high mechanical strength while maintaining high percentage of water, copolymers are usually used. The hydrophilic component absorbs large amount of water and the hydrophobic component gives high mechanical strength. At the same time, high cross-linking density due to the cross-linking agent increase the resistance toward water absorption for dried gel. Nevertheless excessive amount of cross-linking agent produces brittle gel which will reduced the tensile strength.

A copolymer with a hydrophobic monomer methyl methacrylate (MMA) as the main component can easily control the equilibrium water content (EWC). Compared with styrene (ST), MMA is more hydrophilic and thus copolymers with higher ratio of MMA have higher EWC. As the ratio of ST increases, EWC decreases and the copolymer become stiffer (Corkhill *et al.*, 1766).

Hydrophobic monomer absorbs more organic solvent than water. Davis and Huglin (1990) found that the increase of cross linker in a hydrogel increases the Young modulus and decreases the EWC. The mechanical properties of hydrogel decrease with water contents, as water does not enhance the mechanical properties. This is due to the macroscopic phase separation between water and polymer (Nagaoka, 1989).

The increase of heat capacity that occur at the glass transition temperature (T_g) during a temperature scan indicate structural changes that occur from glass state to viscous liquid (Richardson *et al.*, 1979). T_g is very obvious in amorphous polymer whereas in semi-crystalline polymer T_g is less significant. T_g only occur in the amorphous portion of the polymer, while in the crystal portion only small vibration at the equilibrium position of the lattice occur until melting temperature is reached.

Amorphous polymer can be crystallized with heating above the T_g (Holdsworth and Turner, 1971). According to Hsu *et al.* (1989), polymer become crystallized at temperature above T_g since at this temperature the molecule which is originally in the form of random coil changes to three dimensions crystal. This is because at elevated temperature, the polymer chains gain high energy and thus move and arranged easily to form crystal.

The degree of crystallinity and crystal perfection depends

greatly on the thermal history imparted during processing. This study examines the effect of cross-linking agent and the ratio of monomers (MMA and ST) namely 1:1, 2:1 and 1:2 on the crystallinity and melting over the range of temperature studied. Major effect on cold crystallization was noted with an increase in cross-linking agent.

Methodology

Materials and sample preparation: The monomers, MMA and ST and the cross-linking agent, EGDMA were obtained from Fluka Chemika. To remove inhibitors, these starting materials were passed through columns filled with chromatographic grade activated alumina. The initiator α , α' -azobisisobutyronitrile (AIBN) were of Sigma, U.S.A. and other chemicals used were of analytical reagent grades.

The reaction mixtures, of 5g each were polymerized in cylindrical ampoules with 8 mm inner diameter, using 0.016g, (1×10^{-4} mole) AIBN at 60°C for 2 hours. Three monomer compositions, MMA:ST, 1:1, 1:2, 2:1 were used with varying amounts of EGDMA (1, 2, 4, 8, 10% by weight relative to the total weight of MMA+ST+EGDMA).

Differential Scanning Calorimetry (DSC): A Polymer Laboratory Differential Scanning Calorimeter (PL-DSC) was used to measure the enthalpy changes in the copolymer. After each copolymer was surface dried with filter paper, a small piece of about 5 mg was cut off and crush to powder form before weighing accurately in a sealed aluminum pan using an electronic balance. The DSC curves were obtained by heating from 30 to 600°C at a rate of 10°C/min with nitrogen gas flow at 20 ml/min. The DSC was calibrated with indium.

The exothermic 'cold' crystallization enthalpy was determined from direct integration of the exothermic peak and was checked by cutting traces of the curves and weighing the area under the peak. The heat of fusion obtained is directly proportional to the degree of crystallinity. Since MMA:ST:EGDMA (1:1:10%) sample yield the maximum heat of fusion in this work the degree of crystallinity was calculated as the area relative to the area obtained from MMA:ST:EGDMA (1:1:10%) sample (the percentage of crystallization is set as 100%). The authors were unable to ascertain the heat of fusion of 100% crystalline MMA:ST copolymers from the open literature. Although not an ideal procedure for e.g. the

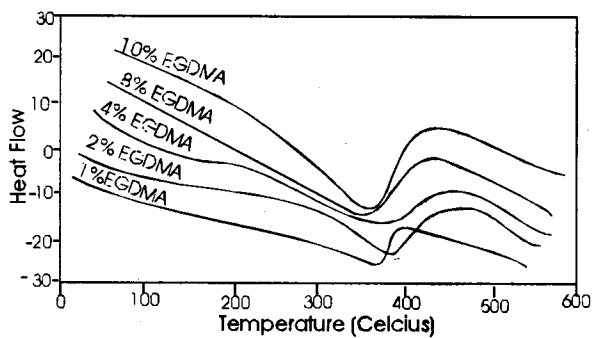


Fig. 1: Thermogram of MMA:ST(1:1) with Various Percentage of EGDMA

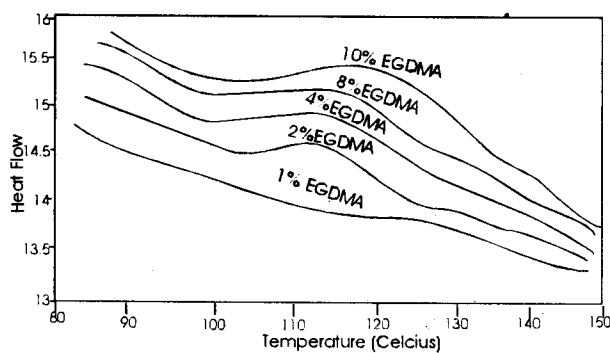


Fig. 4: Thermogram of Cold Crystallization MMA:ST(1:1) with Various Percentage of EGDMA

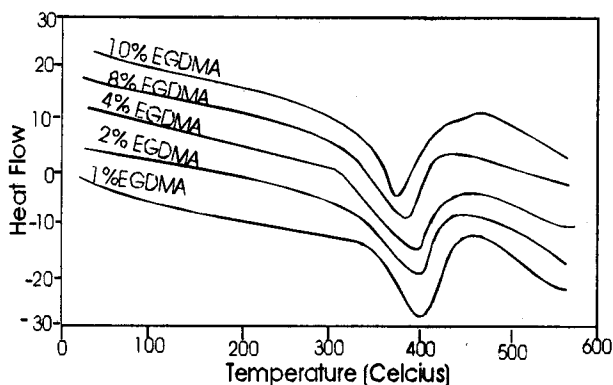


Fig. 2: Thermogram of MMA:ST(2:1) with Various Percentage of EGDMA

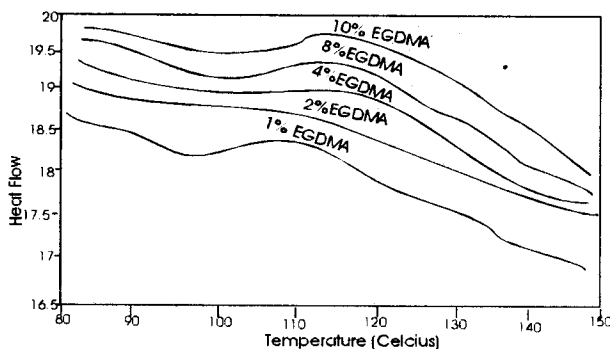


Fig. 5: Thermogram of Cold Crystallization MA:ST(2:1) with Various Percentage of EGDMA

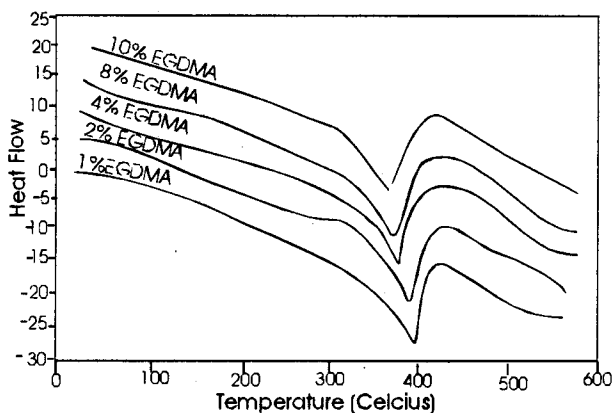


Fig. 3: Thermogram of MMA:ST(1:2) with Various Percentage of EGDMA

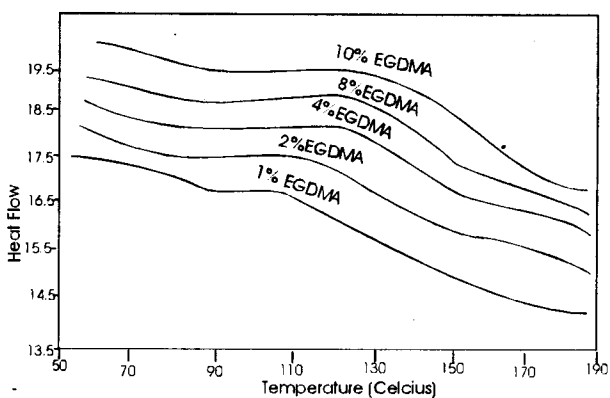


Fig. 6: Thermogram of Cold Crystallization MA:ST(1:2) with Various Percentage of EGDMA

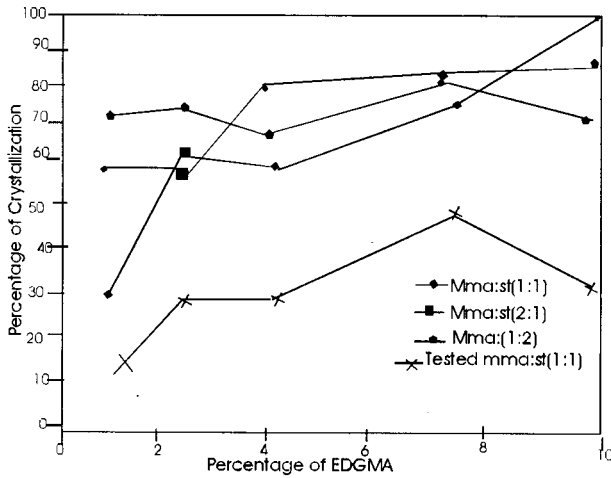


Fig. 7: Percentage of Crystallization Various Percentage of EDGMA

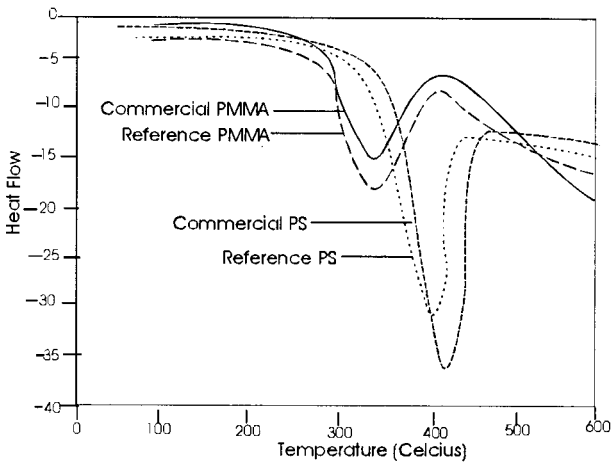


Fig. 8: Thermogram of Commercial and Reference PMMA and PS

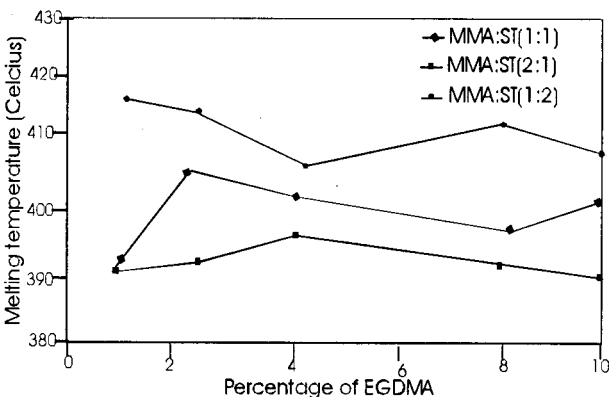
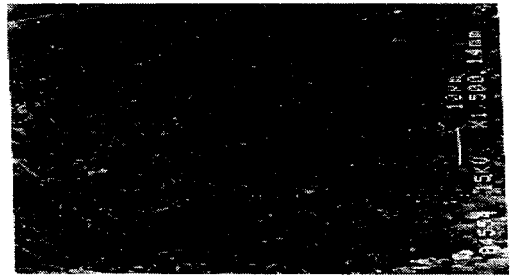


Fig. 9: Melting Temperature Versus Percentage of EDGMA

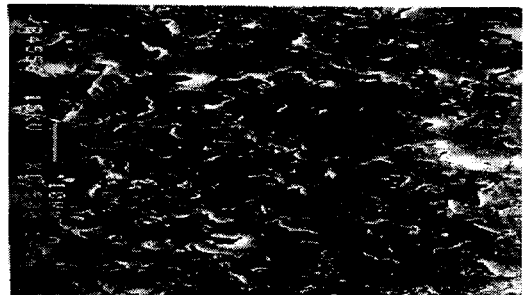
Plate 1: SEM of MMA:ST (1:1) with Various Percentage of EDGMA



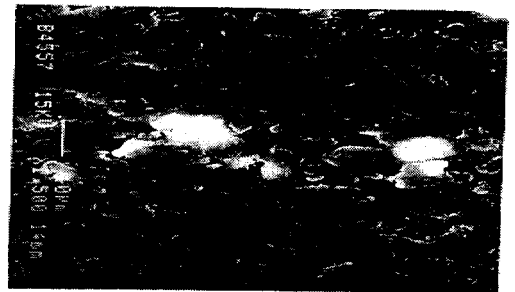
MMA:ST:EGDMA(1:1:1%)



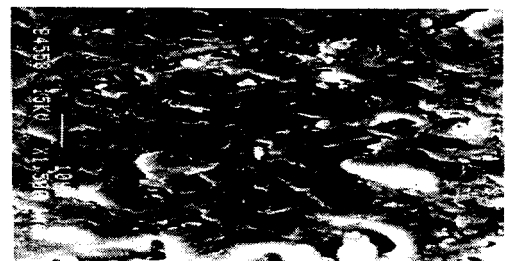
MMA:ST:EGDMA(1:1:2%)



MMA:ST:EGDMA(1:1:4%)

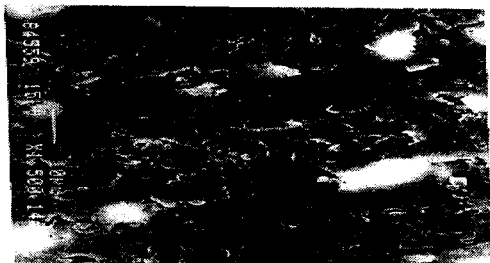


MMA:ST:EGDMA(1:1:8%)



MMA:ST:EGDMA(1:1:10%)

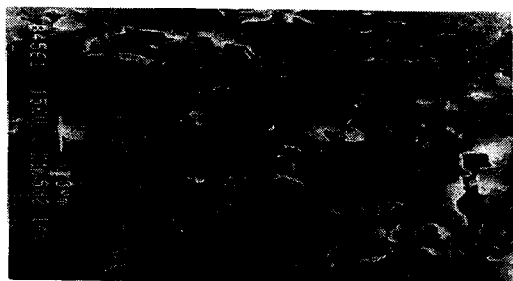
Plate 2: SEM of MMA:ST(1:2) with Various Percentage of EGDMA



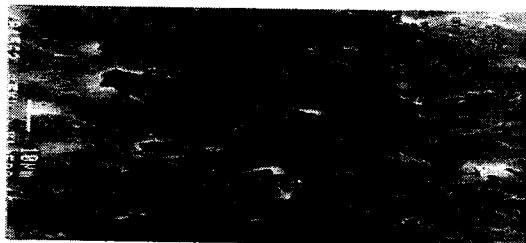
MMA:ST:EGDMA(1:2:1%)



MMA:ST:EGDMA(1:2:2%)



MMA:ST:EGDMA(1:2:4%)



MMA:ST:EGDMA(1:2:8%)

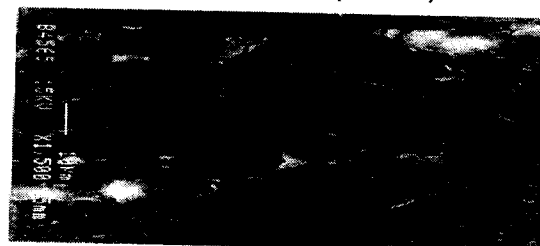


MMA:ST:EGDMA(1:2:10%)

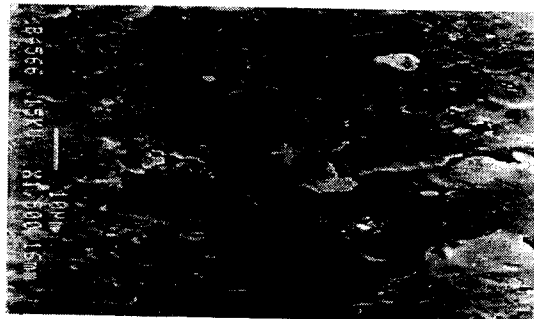
Plate 3: SEM of MMA:ST(2:1) with Various Percentage of EGDMA



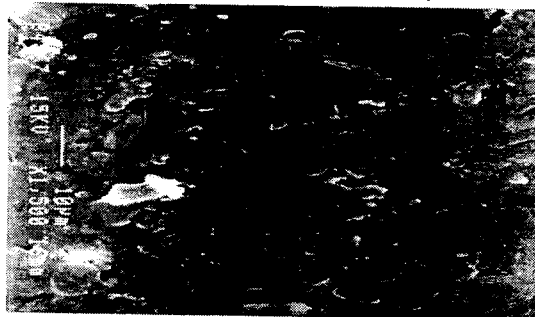
MMA:ST:EGDMA(2:1:1%)



MMA:ST:EGDMA(2:1:2%)



MMA:ST:EGDMA(2:1:4%)



MMA:ST:EGDMA(2:1:8%)



MMA:ST:EGDMA(2:1:10%)

area of MMA:ST:EGDMA (1:1:10%) sample are not necessary the same if the sample had been say MMA:ST:EGDMA (1:1:15%) the results will show the general trend for comparative studies, even if the accuracy of the absolute values can be questioned.

Results and Discussion

Thermal Analysis: The heating curve showed an exothermic peak indicating cold crystallization and an endothermic peak i.e. melting phenomenon. The width of the exothermic peak in the thermogram indicates the formation of the crystal with different degree of perfection. Fig. 1-3 shows the DSC thermograms for MMA:ST with ratios of 1:1, 2:1 and 1:2 respectively. In Fig. 1 both 1% and 4 % EGDMA showed the onset of melting at lower temperature compared with 2%, 8% and 10% EGDMA. In Fig. 2 and 3 the whole series of sample showed similar onset of melting temperature. Fig. 4-6 shows the exothermal cold crystallization range for MMA:ST with ratios of 1:1, 2:1 and 1:2 respectively. In Fig. 4 except for 1% EGDMA sample, the heat of fusion of the other sample is almost similar. In Fig. 5. 1% and 10% EGDMA sample showed similar pattern while 2%, 4% and 8% showed less heat of fusion. The same trend of crystallization appears in Fig. 6.

Fig. 7 shows the degree of crystallinity versus the percentage of EGDMA. Samples with the same or higher ratio of MMA compared with ST showed a trend of increasing percentage of crystallization with percentage of EGDMA. The degree of crystallinity for samples with lower ratio of MMA i.e. MMA:ST (1:2) are hardly affected by the percentage of EGDMA although initially the values are slightly higher compared with the other group of samples. Also included in Fig. 7 is the percentage of crystallization of compressed MMA:ST:EGDMA (1:1:1%) sample (compressed with universal compression rig Instron series IX at 5 mm/min at ambient temperature $\sim 30^{\circ}\text{C}$). The lowest percentage of crystallization obtained from the compressed sample proves that cold crystallization is hindered due to the mechanical testing done earlier.

Commercial and reference (prepared without cross linker) PMMA and PS samples are shown in Fig. 8 Both commercial and reference samples show similar melting endotherms. T_m for commercial and reference PS are higher than PMMA. For this reason the T_m for the third group of samples i.e. MMA:ST (1:2) are higher than the first group MMA:ST (1:1) followed by the second group MMA:ST (2:1) as shown in Fig. 9 Copolymer with higher MMA content yields the lowest T_m .

Scanning Electron Microscope (SEM): Plate 1-3 shows the scanning electron microscope (SEM) photographs of the three groups of sample at 1,500x magnification. SEM of the various samples indicates that

samples with the same ratio of MMA and ST (Plate 1) yield an increase of particle size with percentage of EGDMA. This explained the increment of percentage of cold crystallization with percentage of EGDMA from the DSC thermogram. SEM photographs of MMA:ST (1:2) samples (plate 2) showed that the particle sizes are inconsistent although the percentage of EGDMA increases. Once again the particle sizes explained the constant percentage of crystallization in the DSC thermogram. SEM for MMA:ST (2:1) samples (plate 3) reveal significant changes in particle size which is in accordance with the increase of percentage of crystallization with EGDMA content.

Conclusion

The combination of two amorphous monomer namely MMA and ST produced a semicrystalline copolymer. Results in this study illustrate that higher ST i.e. MMA:ST (1:2) content yield the higher percentage of crystallization which eventually achieve the highest T_m among the three group of samples. Although the increase of EGDMA slightly increases the percentage of crystallization (as shown by Fig. 7, EGDMA yield an adverse effect on the melting temperature (as shown by Fig. 9). Higher MMA ratio i.e. MMA:ST (2:1) compared with MMA:ST (1:1) also yield higher percentage of crystallization as EGDMA increase. However, the high percentage of crystallization in MMA:ST (2:1) sample yield the lowest melting temperature. This adverse effect is due to higher amount of imperfect crystal that is produced.

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