

The Effect of Strain Rate and Temperature on the Mechanical Properties of Poly (Methyl Methacrylate-co-Styrene) Copolymers

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Abstract: The thermo mechanical properties of poly (methyl methacrylate-co-styrene) copolymers as a function of strain rate and temperature in the range 10^{-3} to 10^{-1} s^{-1} and 30-200°C respectively were investigated. Copolymers of three different Methyl Methacrylate (MMA) and STyrene (ST) ratios with various percentages of cross-linking agents were prepared and tested. By measurement of the stress versus strain at various strain rates and temperatures, plots of flow stress/temperature (σ_f/T) versus strain rate ($\dot{\epsilon}$) and log Young's Modulus (log E) versus Temperature (T) were obtained. Plot of σ_f/T versus $\dot{\epsilon}$ observed the Eyring equation. Increasing the amount of cross-linking agent improved the copolymer strength. The graph for log E versus T plot at constant strain rate indicates that a transition temperature exist at ~ 110°C. This is attributed to the glass transition i.e. the zones are interpreted in terms of visco-elastic transition.

Keyword: Young's Modulus, Yield Stress, Cross-Linking Agent, Strain Rate and Temperature

Introduction

Several useful medical applications of copolymers require favorable elastic and mechanical properties. Useful copolymers both have a moderate mechanical strength and compatible with high water content. Small amount of cross-linking agent yields soft, elastic and low melting point polymer. The addition of concentrated cross-linking agent increases the Young's Modulus (E)¹. (Davis and Huglin, 1990). However, excessive amount of cross-linking agent causes the copolymer to become brittle and thus decreasing the tensile strength². (Nagaoka, 1989).

The stress-strain curve is very important to determine the mechanical characteristics of a material such as the elastic properties i.e. E, yield strength (σ_y) and plastic behavior. In this work, Methyl Methacrylate (MMA) and STyrene (ST) monomers were used to produce three different compositions of copolymers. The copolymers were loaded with various percentages of cross-linker Ethylene Glycol Dimethacrylate (EGDMA). The mechanical properties were investigated with regard to different strain rates and temperature.

Eyring theory stated that stress increase slowly with the logarithm of strain rate. An Eyring equation relating stress with the strain rate used to model a constitutive

relationship is given by: $\frac{\sigma}{T} = \frac{\Delta H}{V_A T} + \frac{R}{V_A} \ln \frac{2\dot{\epsilon}}{\dot{\epsilon}_0}$ where σ

is the flow stress, T temperature in Kelvin, ΔH activation energy, V_A activation volume, R gas constant, $\dot{\epsilon}$ strain rate and $\dot{\epsilon}_0$ is a constant pre-exponential factor.

The aim of this work is to examine the behavior of the copolymer, in order to obtain some information about the effect of strain rate and temperature. It is expected that different composition of monomers and cross-linker help to improve the comprehension of thermomechanical properties in the strain rate and temperature range studied. The compressive properties

were studied over the temperature range 30-200°C at strain rates ranging from 10^{-3} to 10^{-1} s^{-1} . This study clearly showed that the sample strength increase with strain rate as reported earlier by several workers³⁻⁸. (Ward, 1979; Andrews and Ward, 1970; Dietz and McGarry, 1971; Nielsen, 1971; Walley *et al.*, 1989 and Hamdan and Swallowe, 1996)

Materials and Methods

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 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%). A sample code 111 then indicate an experiment using MMA:ST:EGDMA ratio of 1:1:1 (wt:wt:wt%). The copolymer rods were cut into specimens of 8mm diameter and approximately 4mm in length.

A universal Instron Testing Machine Series IX was used to measure the thermomechanical properties of the copolymers. The compression anvils and the cylindrical sample were placed inside an Instron oven chamber series 3119-005 capable of heating between -70 to 250°C. At room temperature (30°C) the test was done with anvil cross head speed of 0.5, 5, 50 and 100 mm/min up to ~70% strain. At elevated temperature testing between 60 to 250°C, the sample was heated for half an hour to achieve stable and equilibrium temperature before compression was carried out at 5mm/min. A total of five compressions were carried out at each strain rate and temperatures. Stress was calculated based on the force

Measured by the load cell divided by the original area of the sample. Strain was computed from anvil cross head movement divided by the original height. The average flow stress at 30% strain ($\sigma_{30\%}$) and E was calculated from the mean of the best three curves.

Results and Discussion

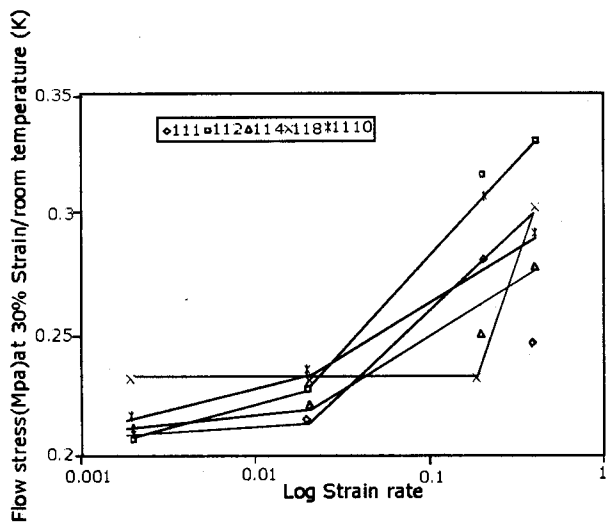


Fig. 1: Flow Stress (MPa) at 30% Strain/room Temperature (K) Versus Logarithm Strain Rate

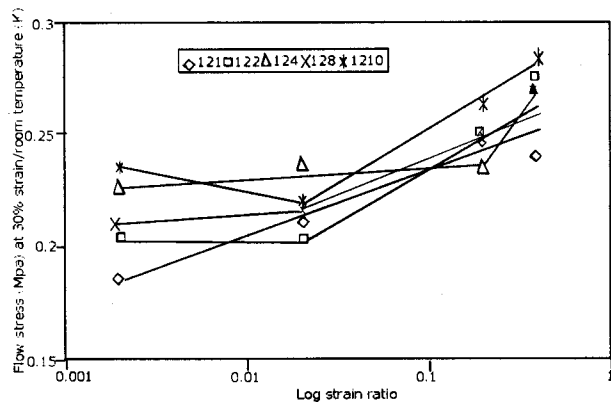


Fig. 2: Flow Stress (MPa) at 30% Strain/room Temperature (K) Versus Logarithm Strain Rate

Fig. 1-3 shows the plot for stress at 30% strain/temperature ($\sigma_{30\%/T}$) as a function log strain rate ($\log \dot{\epsilon}$) for all the three groups of MMA:ST samples with ratios 1:1, 1:2, 2:1 respectively. A straight line can reasonably be fitted through the data points for strain rate up to $0.2s^{-1}$. (Davis and Huglin, 1990). A much steeper line is obtained as the strain rate increased to $0.4s^{-1}$. With increasing strain rate, the Eyring theory becomes less likely to fit⁸. (Hamdan and Swallowe, 1996) Simultaneously as more cross-linker are introduced, the strain rate and cross-linker effects multiply to give the steeper rise of the $\sigma_{30\%/T}$ observed. In general the Eyring equation is true except for sample with maximum cross-linker i.e. 1110, 1210 and 2110.

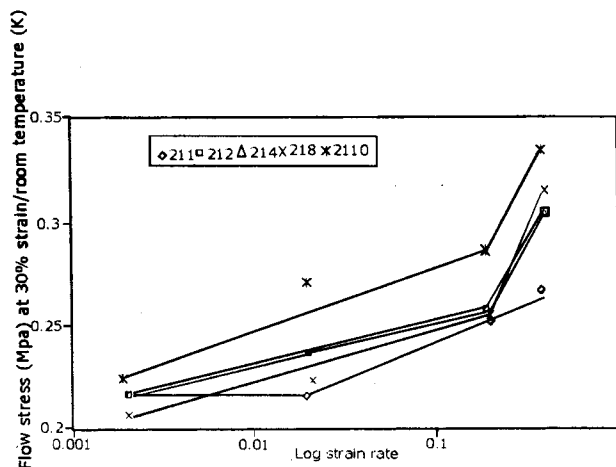


Fig. 3: Flow Stress (MPa) at 30% Strain/room Temperature (K) Versus Logarithm Strain Rate

According to Nagaoka (1989), the excessive amount of cross-linking agent will cause the polymer become brittle and reduce the tensile strength.

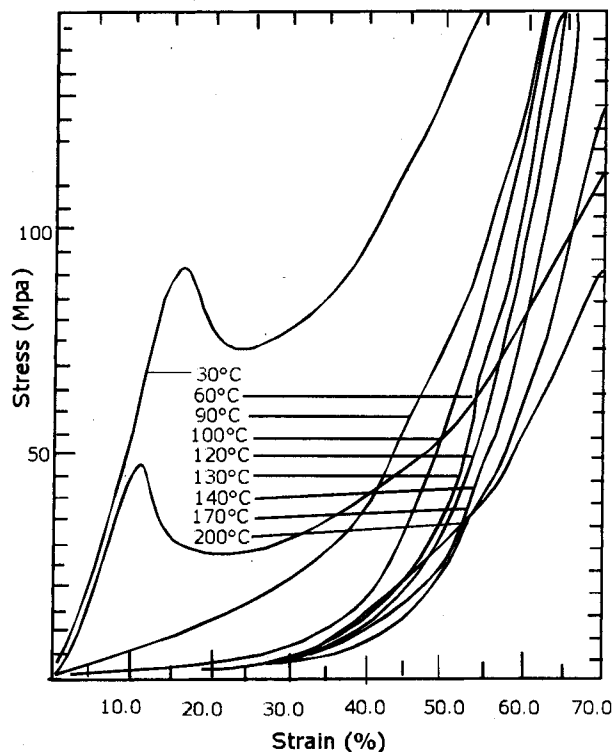


Fig. 4: Stress Strain Curve for MMA1: ST1 with 1% EGDMA at Various Temperature

The typical stress-strain curve of all the three groups of sample with the lowest content of EGDMA (1%) at $0.02s^{-1}$ (with cross head speed of 5mm/min tested at various temperature are shown in Fig. 4-6. The entire sample showed strain softening before strain hardening for temperatures up to $90^{\circ}C$ and above $90^{\circ}C$ only strain hardening occurred.

The temperature dependent of log E was measured in the range from 30 to 200°C. The plot of log E versus T is shown in Fig. 7-9. It is seen from the figs. that gradual temperature dependence was observed up to 90°C followed with a drastic drop of log E occurring at -90-110°C.

Based on the log E values a clear distinction between the elastic and viscous deformation occurs within this transition temperature. The log E values in the viscous region drop to more than one fold from the initial value at room temperature. This indicates that a phenomenon attributed to the glass transition temperature occur i.e. the zones are interpreted in terms of visco-elastic transition.

From the amount of cross-linker used to prepare the copolymer, the highest percentage of EGDMA (10%) clearly improved the strength of the different group of

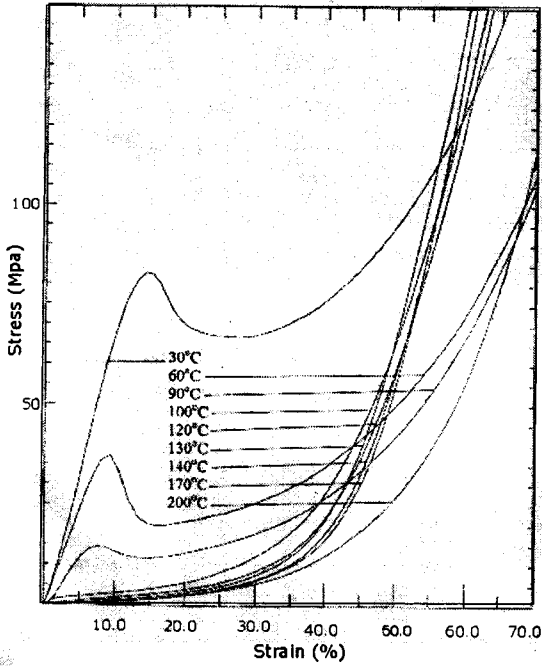


Fig. 5: Stress Strain Curve for MMA1: ST2 with 1% EGDMA at Various Temperature

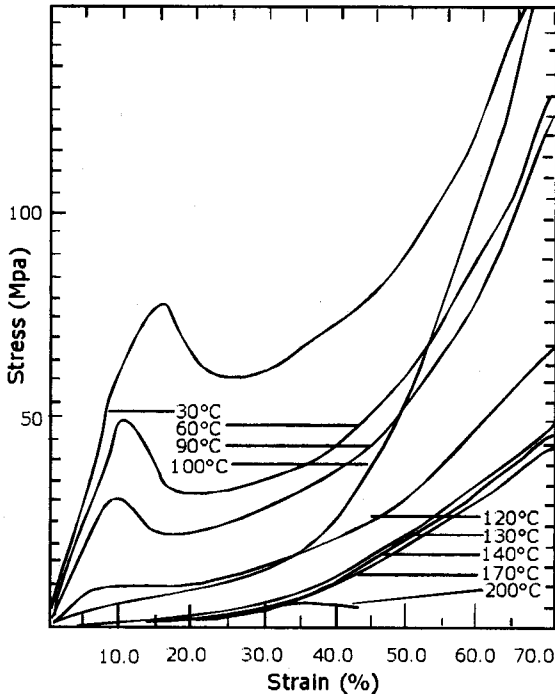


Fig. 6: Stress Strain Curve for MMA2: ST1 with 1% EGDMA at Various Temperature

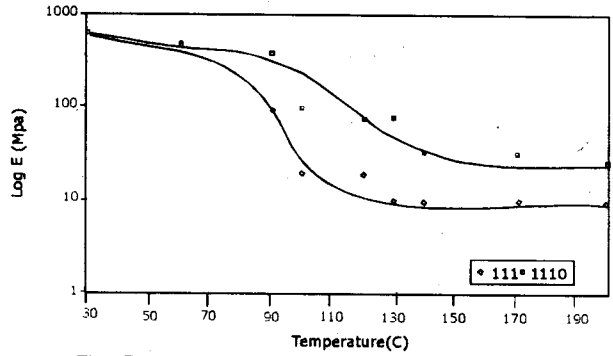


Fig. 7: Log E (MPa) Versus Temperature (c)

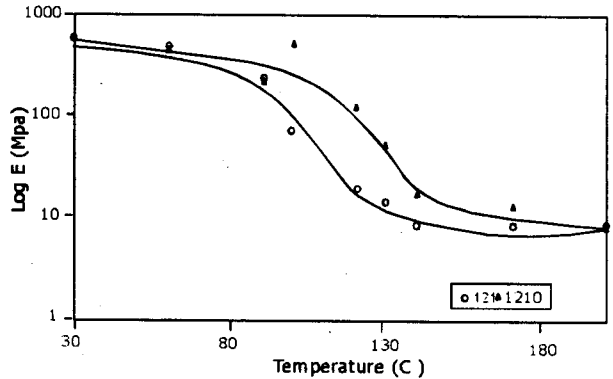


Fig. 8: Log E (MPa) Versus Temperature (c)

copolymers as compared to the lowest percentage of EGDMA (1%). This increase in strength corresponds to an ideal network where all the cross-linker molecules are incorporated in such a way that all chains are elastically effective⁹. (Oppermann *et al.*, 1985)

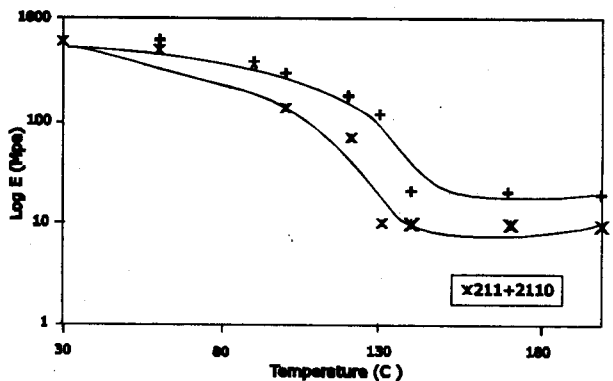


Fig. 9: Log E (MPa) Versus Temperature (c)

Conclusion

The flow stress/temperature versus strain rate plot clearly showed that the sample strength increase with strain rate as determined according to Eyring theory. The strain rate sensitivity of the copolymers also varies with EGDMA content. In general, the higher contents of EGDMA incorporate higher network cross-linking. This study also showed that the copolymers experienced glass transition temperature from the log E versus T plot. This obviously reflects the visco-elastic region of the sample in the temperature range tested.

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