

Thermal and Mechanical Properties of Copolymers of Methyl Methacrylate with *N*-Phenyl Maleimide

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SYNOPSIS

Structural modification of PMMA was done by copolymerizing it with low mole fraction (≤ 0.1) of *N*-phenyl maleimide (NPM) using benzoyl peroxide as an initiator. Four copolymers were prepared by changing the mole fraction of NPM in the monomer feed from 0.025 to 0.1. The copolymer composition was determined by $^1\text{H-NMR}$. An increase in NPM content resulted in an increase in T_g of copolymers. Tensile stress and % elongation decreased, whereas modulus increased with an increase in NPM content. The flexural strength was not affected by the NPM content. The dynamic mechanical properties were also evaluated in the temperature range of -20 to 100°C . © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(methyl methacrylate) sheets have been used as a substitute for glass in solar collector covers. This is primarily because of their light weight, excellent weather resistance,¹ light transmittance, and good insulating properties. Thermal losses to the environment are much higher in glass than in PMMA. However, one of the limitations of PMMA is its low softening point. It tends to soften above 90°C and thus undergoes distortion when used as an inner glazing material.² At high collection temperatures, the inner glazing, made of PMMA, reportedly loses its flatness.³ Hence, there is a need to modify the structure of PMMA so that its T_g increases without losing its useful properties.

The introduction of aryl maleimide moieties in PMMA backbone is expected to increase the rigidity of the polymer, thereby affecting its softening temperature. The copolymerization of alkyl(meth)acrylates with *N*-aryl maleimides, using free radical initiators, is well documented in the literature.⁴⁻⁷ Considerable work has been performed in order to understand polymerization behavior and substituent effects in copolymerization and determination of monomer reactivity ratios of *N*-aryl maleimide-vinyl

monomer pairs. Some studies have also been carried out for evaluating the effect of the structure of these copolymers on thermal behavior.^{6,7} However, no studies have been reported on the physico-mechanical properties of these copolymers. Hence, it was considered of interest to examine the thermal behavior and mechanical properties of copolymers of MMA and *N*-phenyl maleimide. In order to retain the transparency and useful properties of PMMA, only low mole fraction of NPM was introduced in the PMMA backbone.

EXPERIMENTAL

Materials

Aniline (BDH) was freshly distilled in nitrogen atmosphere before use. Acetone (Qualigens) was dried over Na_2SO_4 , was refluxed for $\frac{1}{2}$ h, and was then distilled. Anhydrous sodium acetate was obtained by fusion. Methyl methacrylate (Fluka) was passed through a column of alumina to remove hydroquinone. Benzoyl peroxide was recrystallized from chloroform.

Preparation

N-Phenyl maleimide was synthesized according to the procedure reported in literature,⁸ using acetone as a solvent. Freshly distilled aniline (0.66 mol) was

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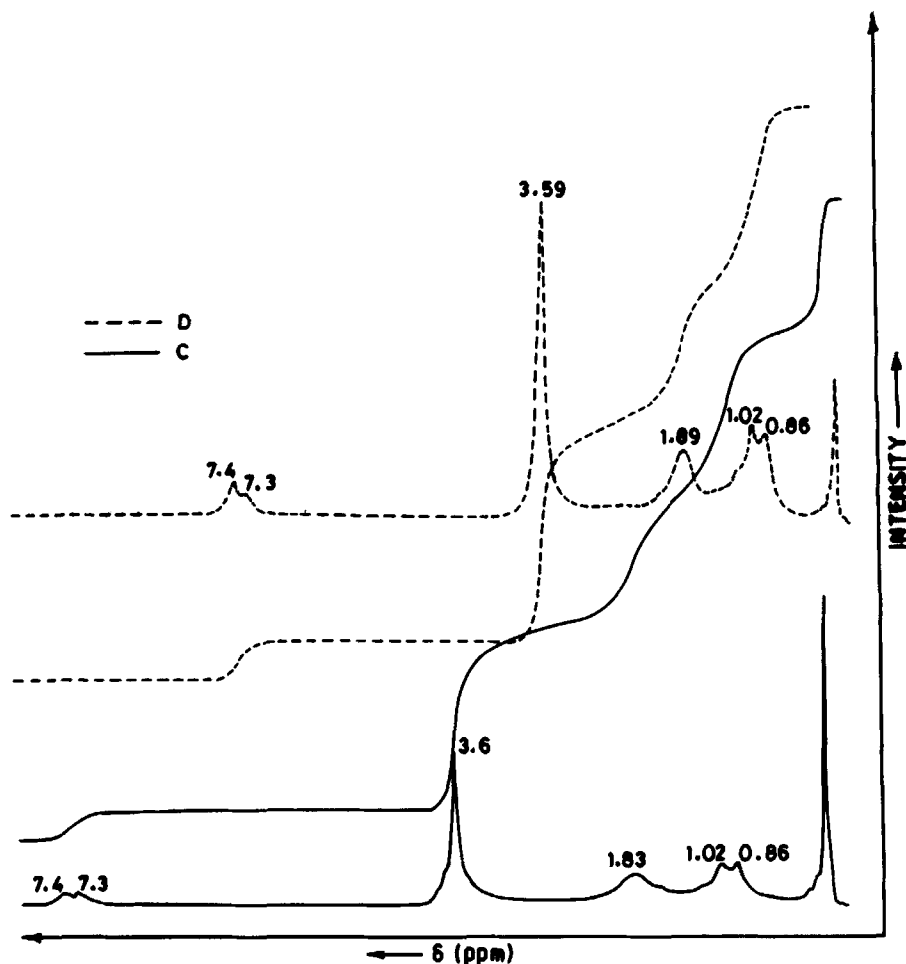


Figure 1 ^1H -NMR spectra of samples *C* and *D* (cast sheets).

added to dry acetone (200 mL). The solution of maleic anhydride (0.66 mol) in acetone (135 mL) was added dropwise to the aniline solution with stirring. The reaction was carried out in nitrogen atmosphere at 60°C for 4 h. Anhydrous sodium acetate (0.66 mol) and freshly distilled acetic anhydride (270 mL) were added and the solution was refluxed for 3 h. The contents were cooled and added to crushed ice with stirring. The precipitates, thus obtained, were washed with diluted HCl and then by sodium bicarbonate solution until neutral. The precipitate was recrystallized from ethanol to produce needle-shaped crystals, with m.p. = 91°C , % yield = 78.6.

Copolymer Sheet Fabrication

Preparation of Polymer Syrup

In a round-bottomed flask, requisite quantities of MMA and NPM and 1% by weight benzoyl peroxide were taken, and the temperature was raised to 80°C .

When the % conversion was around 15%, the flask was removed from the thermostat and was cooled in ice. The syrup, thus obtained, was poured into the glass mold, which was prepared as described below.

Preparation of Mold

Two toughened glass plates, $215 \times 290 \text{ mm}^2$ in size, were cleaned with chromic acid, water, and acetone, followed by drying. A PVC gasket, with a diameter of 3 mm, was placed between the plates, which were held together by steel clamps. The glass mold was kept open on one side for pouring the prepolymer syrup. A small strip of mylar sheet was folded and used as a funnel for pouring the prepolymer syrup.

Casting of Sheets

Approximately 100 mL of prepolymer syrup was poured into the mold. The opening of the mold was closed, using a metal plate, and then was clamped.

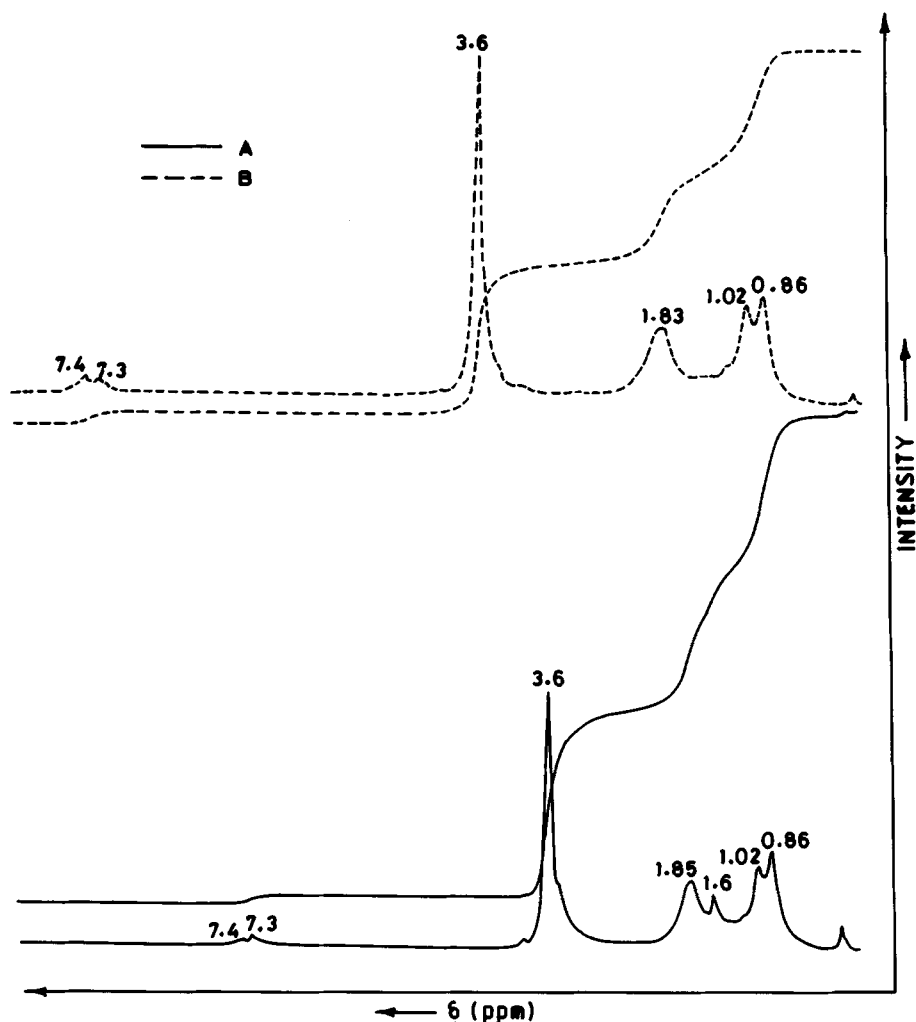


Figure 2 ^1H -NMR spectra of precipitated copolymer samples A and B.

The filled mold was placed in a preheated water bath at 75°C for 3 h. It was then removed and was placed in an air oven at 90 – 110°C for 3 h. Later, it was allowed to cool. The clamps were removed and the copolymer sheet was taken out. The sheet was washed with water, followed by wiping off the excess water with tissue paper. The thickness of sheets obtained was in the range of 1.6 ± 0.3 mm.

A small portion of copolymer sheet, thus obtained, was dissolved in CHCl_3 ; the solution was filtered and the polymer was precipitated with an excess of methanol. The precipitated polymer was washed with methanol and was dried. This precipitated polymer was used for structural characterization.

CHARACTERIZATION

The structural characterization of the copolymer was determined by recording ^1H -NMR spectra in CDCl_3 ,

using a Jeol-JNM-FX 100 FT NMR spectrometer and tetramethyl silane as an internal standard. For this purpose, polymer sheets, as well as precipitated polymer, were used.

Intrinsic viscosities were determined in chloroform at $30.0 \pm 0.1^\circ\text{C}$, using an Ubbelohde suspension level viscometer. Glass transition temperatures were determined by DSC, using a Dupont 9900 thermal analyzer having a 910 DSC module. The sample size of 5.9 ± 0.9 mg, and the heating rate of $10^\circ\text{C}/\text{min}$, were used.

Dynamic mechanical properties were measured using Polymer Laboratories' Dynamic Mechanical Thermal Analyzer (model MK II), in a bending mode, in the temperature range of -20°C to 150°C . A heating rate of $5^\circ\text{C}/\text{min}$, frequencies of 1 and 10 Hz, and a sample size of 30×10 mm² were used.

The mechanical properties were measured using an Instron tensile tester, model 1121. Tensile testing

Table I Copolymers of MMA and NPM—Copolymer Composition (Determined by $^1\text{H-NMR}$), and Intrinsic Viscosity in CHCl_3 at 30.0°C

Sample Designation	Mole Fraction of NPM		$[\eta]$ dL/g
	In Feed	Copolymer ^a	
PMMA	0.0	0.0	1.775
A	0.027	0.0291	1.865
B	0.053	0.0480	1.865
C	0.0765	0.0761	1.94
D	0.0996	0.0992	2.51

^a Obtained by precipitation of the cast sheets using the $\text{CHCl}_3/\text{CH}_3\text{OH}$ system.

was done according to ASTM D-638, using dumbbell shaped specimens (length, 165 mm; width of narrow section, 13 mm). These specimens were made from the cast sheets by cutting pieces that were 165 mm long and 20 mm wide and shaping them using a metal mold. The edges of the specimens were pol-

ished using fine sand paper. The specimens were conditioned, as per the standard, before testing.

The following conditions were used for testing: gage length, 50 mm; full scale load, 200 Kg; chart speed, 50 mm/min; crosshead speed, 1 mm/min. A minimum of 5 samples were tested for each composition and an average value was determined.

Flexural strength was determined according to the ASTM D 790-81, using specimens that were $50 \times 25 \text{ mm}^2$ in size, cut from the cast sheets; the edges were polished. Span length was kept at 30 mm and the full scale load was 50 kg. A chart speed of 50 mm/min and a crosshead speed of 1 mm/min was used.

RESULTS AND DISCUSSION

A yellow tinge was observed in the cast sheets by introduction of an even low mole fraction of NPM. The color deepened by an increase in NPM content in the MMA backbone. However, the precipitated polymer powder was devoid of any color, even at high NPM content (i.e., 0.1 mole fraction).

The NMR spectra of precipitated copolymers are

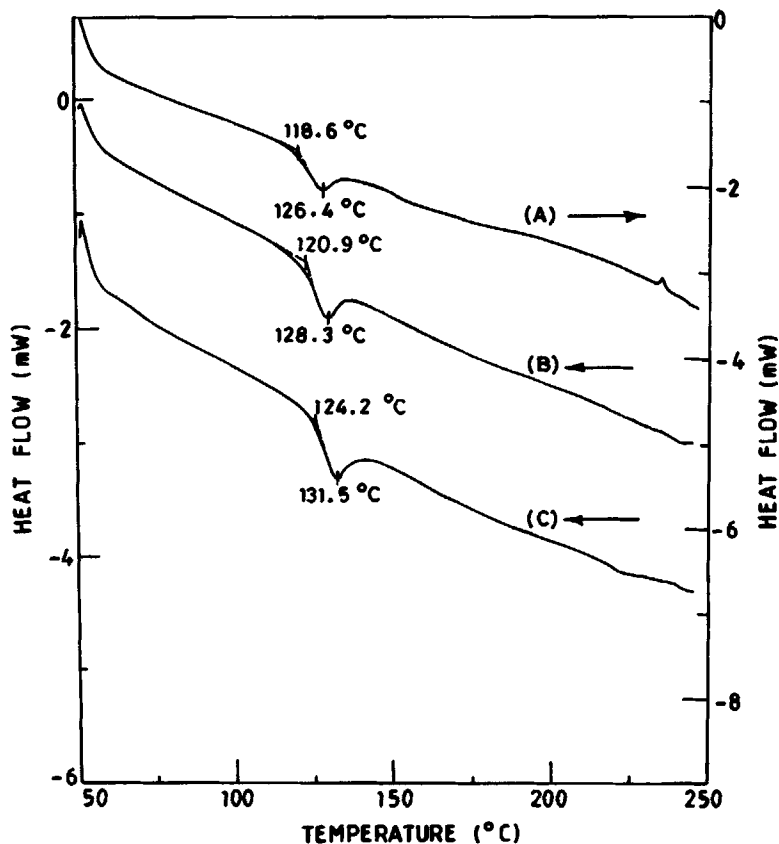


Figure 3 DSC scans of copolymer sheets A, B, and C.

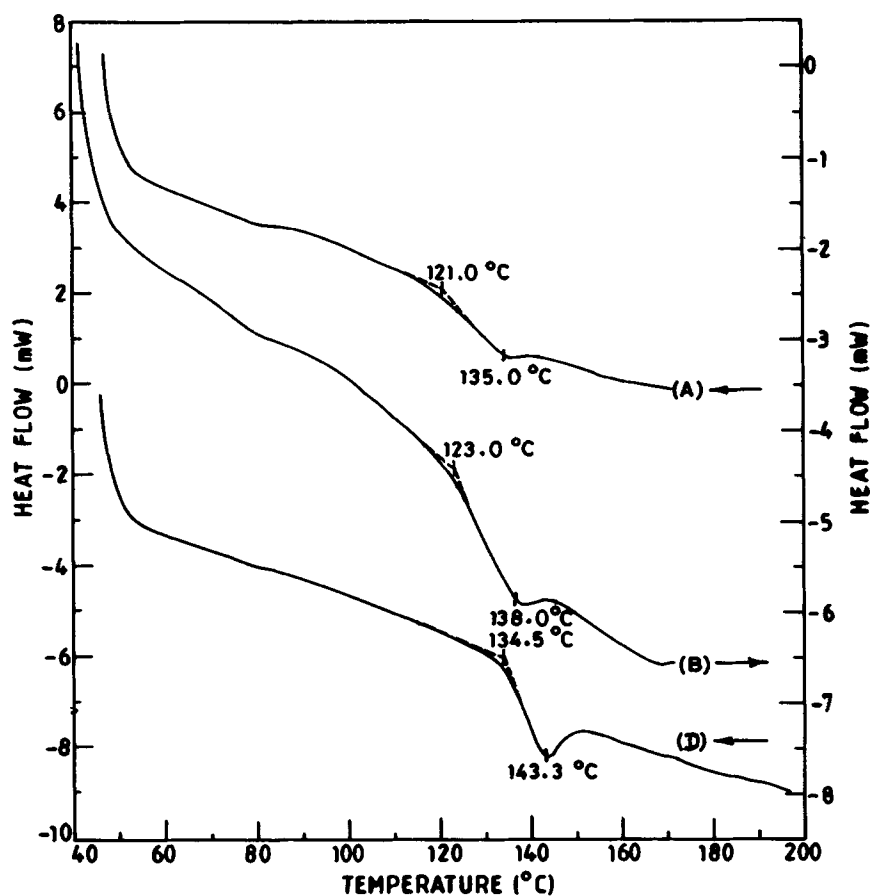


Figure 4 DSC scans of precipitated copolymer sheets A, B, and D.

shown in Figure 2. The NMR spectra of copolymer sheets were also recorded (Fig. 1). No residual monomer was observed in the copolymer sheets either. In order to determine the copolymer composition, the ratio of aromatic proton resonance signals (present in NPM) and methoxy protons (present in MMA), at 7.3–7.4 ppm and 3.58 ppm, respectively, was taken (Table I). The other characteristic proton resonance signal, observed in $^1\text{H-NMR}$, due to the PMMA segment, was at 0.85–1.05 ppm (CH_3 group) and 1.82–1.89 ppm (CH_2 group).

A marginal increase in the intrinsic viscosity of copolymers was obtained by incorporation of up to 0.076 mole fraction of NPM in the backbone. However, a further increase in NPM content, up to 0.1 mole fraction, resulted in approximately a 25% increase in intrinsic viscosity. This may be attributed to the increase in rigidity of side chain in these copolymers.

The DSC scans of various copolymers are shown in Figures 3 and 4. In the temperature range of 100 to 150°C, an endothermic transition with the dis-

Table II Results of DSC Scans of MMA–NPM Copolymers

Sample Designation	Copolymer Sheets		Precipitated Copolymer	
	T_1 (°C)	T_2 (°C)	T_1 (°C)	T_2 (°C)
A	118.6	126.4	121.0	135.0
B	120.9	128.3	123.0	138.0
C	124.2	131.5	133.5	140.4
D	123.1	130.9	134.5	143.3

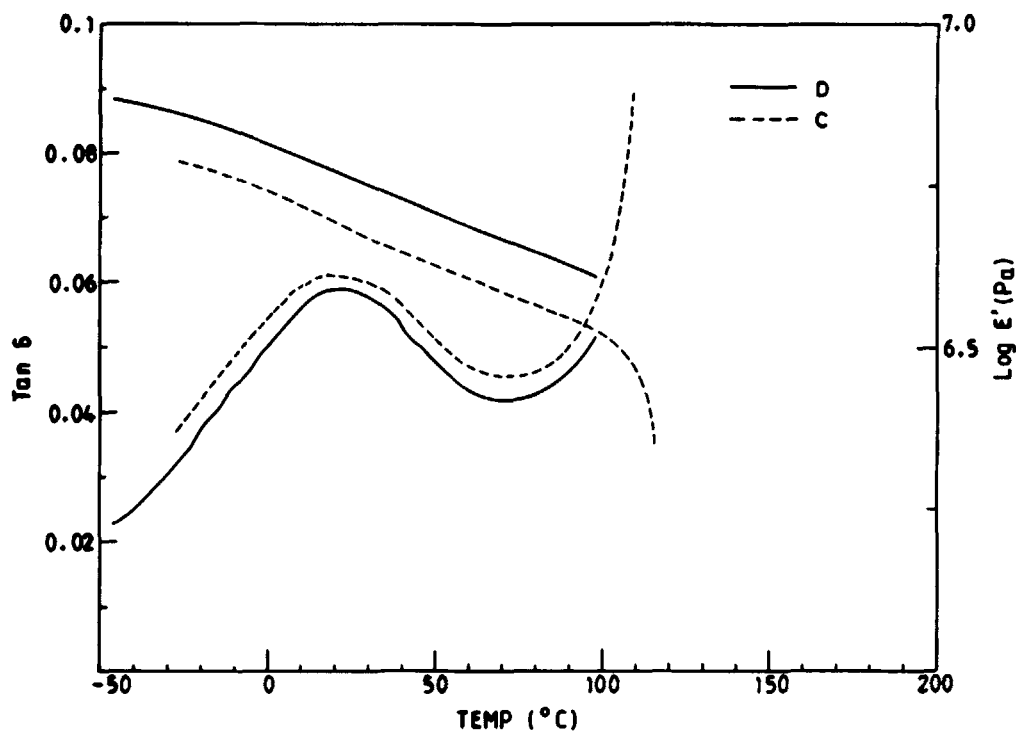


Figure 5 DMTA traces of copolymer sheets *C* and *D*, recorded at 1 Hz.

tinct peak minimum was observed in the copolymers. In order to characterize this transition, which can be attributed to T_g , two characteristic temperatures were noted.

T_1 Corresponds to the deviation in the base line and was obtained by extrapolation of steep portion of the endotherm.

T_2 The peak temperature of the endothermic transition.

Table III β -Relaxation Temperature and Activation Energy of β -Relaxation of the Copolymers

Sample Designation	β -Relaxation Temperature (°C)		ΔH^* of β -Relaxation (J/mol)
	1 Hz	10 Hz	
PMMA	18.9	37.8	721.2
A	21.6	47.3	761.2
B	20.3	42.5	739.5
C	19.6	40.5	724.5
D	18.2	35.8	710.5

The results of DSC of various copolymers are given in Table II. The T_g of PMMA sheets fabricated in the laboratory was found to be 109.6°C. The value reported for heterotactic PMMA is 105°C.^{9,10} In copolymer sheets, the incorporation of even 0.025 mole fraction of NPM in the backbone results in $\sim 9^\circ\text{C}$ increase in T_1 and T_2 , which was at 126.4°C. However, further increase in NPM resulted only in a marginal change in T_2 . In the case of precipitated copolymers, the T_1 and T_2 values were found to be higher, as compared to those obtained by the DSC of copolymer sheets. The lower T_1 and T_2 values, observed in the case of copolymer sheets, may be due to the presence of oligomers, which may act as internal plasticizers.

The dynamic mechanical thermal analysis (DMTA) traces of samples *A* and *D* are shown in Figure 5. The storage moduli ($\text{Log } E'$) at -20°C were found to be independent of the NPM content in the PMMA backbone.

A broad transition, which has been attributed to β -relaxation (due to the torsional libration of ester group of MMA), was observed in all the copolymer sheets. The temperature of relaxations was obtained by extrapolation at two frequencies, that is, 1 Hz and 10 Hz (Table III). β -relaxation temperature was found to decrease with an increase in NPM content

Table IV Mechanical Properties of Copolymer Sheets

Sample Designation	Tensile Stress ($\text{kg}/\text{m}^2 \times 10^{-4}$)	% Elongation	Modulus ($\text{kg}/\text{m}^2 \times 10^{-6}$)	Flexural Strength ($\text{kg}/\text{m}^2 \times 10^{-6}$)
PMMA	610.0	7.15	120.0	9.83
A	601.2	5.56	152.1	11.20
B	590.6	4.94	155.4	11.62
C	540.6	4.26	157.1	11.56
D	489.2	4.23	170.4	11.19

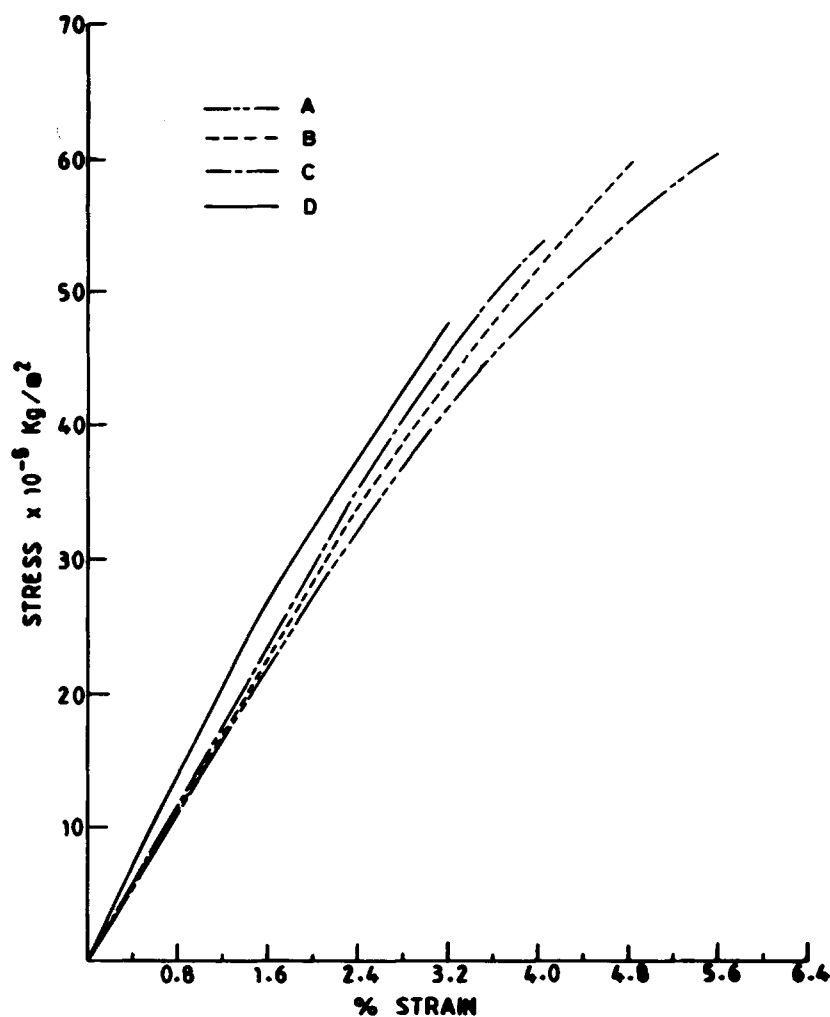
in the copolymers. This difference is more obvious at 10 Hz than at 1 Hz.

Activation energy of the β -relaxation process (diffusional motion) was calculated using the relationship,¹¹

$$\Delta H^* = [R \ln(F_2/F_1)] / (1/T_1 - 1/T_2)$$

where ΔH^* is the activation energy (enthalpy) for the relaxation, T_1 and T_2 are the temperatures of β -relaxation at frequency F_1 (1 Hz), and F_2 (10 Hz), respectively. A decrease in ΔH^* , with an increase in NPM content, was observed (Table III).

The stress-strain curves of various copolymer sheets are given in Figure 6. Tensile stress decreased


Figure 6 Stress-strain curves of copolymer sheets (A-D).

only marginally with an increase in NPM content, below 0.05 mole fractions of NPM. However, at higher mole fractions of NPM (0.05–0.1 mole fractions), the decrease in tensile strength was more significant. With an increase in NPM content, % elongation also decreased. Modulus increased with the increase in NPM mole fraction in the copolymer. Flexural stress did not change with NPM content; it remained almost constant (Table IV).

CONCLUSIONS

Incorporation of NPM in the backbone of PMMA results in an increase in the softening temperature of PMMA sheets. With the introduction of 0.1 mole fraction of NPM, the decrease in the tensile strength was 20% and elongation 41%. However, a 42% increase in modulus was observed. The softening temperature increased by 35°C. These sheets, therefore, are potential material for application in solar energy collectors (inner glazings). Further studies on long term performance of these sheets and their optical characteristics are in progress.

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