Effect of MMA on the Physical Properties of Urethane–Methacrylate

P. SANTHANA GOPALA KRISHNAN, VEENA CHOUDHARY, and I. K. VARMA*

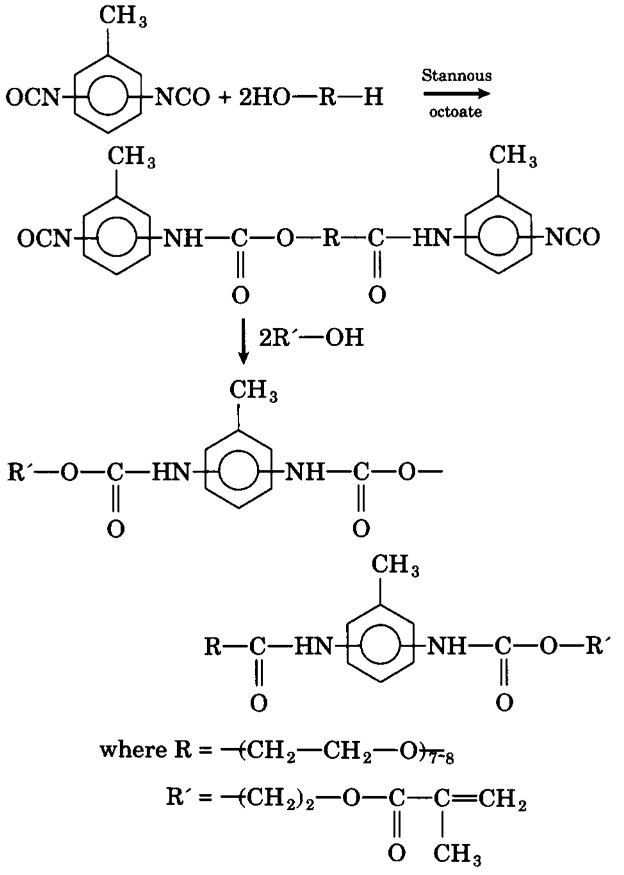
Centre for Materials Science and Technology, Indian Institute of Technology,
Delhi, Hauz Khas, New Delhi 110 016, India

SYNOPSIS

Urethane prepolymer was prepared by reacting two moles of tolylene diisocyanate with one mole of poly(ethylene glycol) (mol wt 400), followed by end-capping with two moles of 2-hydroxyethyl methacrylate at room temperature (30 ± 1°C) in the presence of stannous octoate as catalyst. Different proportions of methyl methacrylate (MMA) were added to the urethane prepolymer in order to study the effect of composition on mechanical properties. Sheets were fabricated by adding 1% azobis(isobutyronitrile) (w/w) to this solution. All the copolymer sheets had a transmittance similar to the PMMA sheet, in the wavelength range of 400–800 nm. Tensile strength and modulus decreased with decreasing MMA content, whereas percent elongation at break increased. All the samples showed 2–3 stages of degradation. Initial decomposition temperature increased with increasing carbamate content.

INTRODUCTION

Linear polyurethanes have good impact strength and mechanical properties and excellent processability, but, due to their thermoplasticity, thermal stability is limited. Thermoset polymers, on the other hand, have higher thermal stability but lower impact strength.[1] Therefore, one can tailor the properties by copolymerizing varying amounts of urethane prepolymer (having soft and hard segments and functionality greater than two) with MMA. Lai and Baccei[2] have studied the effects of various diisocyanates and polyols and the mol wt of poly(propylene glycol) (PPG) on the physical properties of UV-curable urethane acrylates. Oxygen permeability was found to increase with the mol wt of PPG. In the present work, poly(ethylene glycol) (PEG, mol wt 400), along with tolylene diisocyanate (TDI) and 2-hydroxyethyl methacrylate (HEMA), was used to prepare urethane–methacrylates. The reaction scheme of prepolymer synthesis can be depicted as follows:



where $R = -(CH_2-CH_2-O)_{7-8}$

$R' = -(CH_2)_2-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}=CH_2$

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* To whom correspondence should be addressed.

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Isocyanate terminated prepolymer was prepared by reacting two moles of TDI with one mole of PEG-400, followed by end-capping with two moles of HEMA. MMA was used as a diluent. The reaction was monitored using the volumetric method.[3]

Several sheets of 180 × 240 × 2 mm^3 were prepared by adding 30, 40, 50, 60, 70, and 75% (w/w) of MMA in the initial feed. These copolymer sheets have been designated as CS-30, CS-40, CS-50, CS-60, CS-70, and CS-75, respectively.

EXPERIMENTAL

Materials

An 80/20 mixture of 2,4-/2,6-tolylene diisocyanate (TDI, E. Merck), MMA (Fluka), stannous octoate (Sigma), and HEMA (Fluka) were used as received. The PEG-400 was dried by keeping it over activated 4A molecular seives. Azobis(isobutyronitrile) (AIBN) was recrystallized from chloroform.

Prepolymer Preparation

The reaction was carried out in the presence of the requisite quantities of MMA, which was added in two installments. The MMA, added in both installments, depicts the MMA taken in the fabrication of sheets. Whereas the quantity of MMA taken in the second installment was fixed (i.e., 10 mL containing 1% AIBN), the quantity of MMA in the first step depended on the ratio of carbamate–MMA content in the prepolymer syrup.

A typical procedure for the preparation of CS-40 is described. A mixture of 22 g of PEG-400 (0.055 mol), 30 mL (0.2775 mol) of MMA, and 13.4 mL of HEMA (0.11 mol), along with few drops of stannous octoate, was taken in a two necked flask fitted with a water condenser. The flask was kept in an ice bath and the solution was stirred using a magnetic stirrer. Then, 15.7 mL of TDI (0.11 mol) was added dropwise. The ice bath was removed after 10 min and the reaction was carried out at room temperature (30 ± 1°C). The reaction, as monitored by the volumetric method, was found to be complete in 26 h. To the above reaction mixture, 10 mL of MMA containing AIBN (1% w/w, 0.925 g) were added.

Monitoring the Cure Reaction of Urethane Methacrylate–MMA Using Viscosity Measurements

A Brookefield viscometer (RV TDV-II) was used for monitoring viscosity changes at 50 and 60°C. Prepolymer syrup and MMA, corresponding to composition CS-70, CS-80, and CS-90, were taken in the sample container and were kept for 2 min to attain the desired temperature. A shear rate of 10 rpm and a coaxial cylinder spindle (29BS) were used. The spindle was immersed up to the middle of the indentation in the shaft. The sample container was closed with cardboard that contained a small cleft for the insertion of the spindle. This apparatus minimized the loss of MMA during the curing reaction. The chart speed used was 1 or 3 cm/min. The percent viscosity was converted into viscosity in cps using a conversion table. Critical time (the minimum time after which viscosity increased drastically) was noted for each sample. This also gives an idea of how far the prepolymer syrup can be heated for making it viscous before pouring it into the glass mold. If the prepolymer syrup was heated for a longer period, then gelling took place.

Preparation of Mold

Two toughened glass plates, 215 × 290 mm^2 in size, were cleaned with chromic acid, water, and acetone, followed by drying. The glass plates were sprayed with the releasing agent (silicone spray) and then were wiped using tissue paper, to produce a thin uniform coating. A PVC gasket of 3 mm in diameter was placed between the plates, which were held together using steel clamps. One side of the glass plate was kept open for pouring the prepolymer syrup.

A small strip of mylar sheet was folded and used as a funnel for pouring the prepolymer syrup. Approximately 100 mL of prepolymer syrup was poured into the mold. The opening of the mold was then closed using a metal plate and clamps.

The filled mold was then placed in a preheated water bath at 60°C for 12 h. The mold was then removed and placed in an air oven at 80°C for 3 h. Later, it was allowed to cool. The clamps were then removed and the sheet was taken out by passing a stream of water. The sheet was washed with water followed by wiping the excess water with a filter paper.

CHARACTERIZATION AND TESTING

Optical Properties

Transmittance

Percent light transmittance of the sheet, in the wavelength range of 200–800 nm, was measured us-

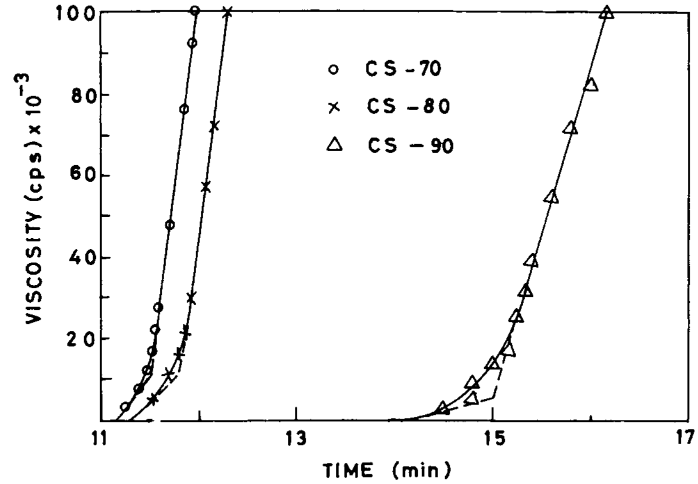

Figure 1 Plots of viscosity vs. time for copolymerization of CS-70, CS-80, and CS-90 samples containing 1% AIBN (w/w).

ing a Perkin–Elmer Lambda 3B UV-visible spectrophotometer. Two specimens, each 30 × 10 × 2 mm^3 in size, were used for testing and an average value was reported.

Refractive Index

Refractive indices of various copolymer sheets were measured using Abbe's refractometer (ASTM D542). A flat sample of copolymer sheet was placed in contact with the refractometer prism. The method determined the critical angle for total internal reflection of sodium light (*D* line). An immersion fluid, with a refractive index slightly higher than that of the sample, was used between the sample and the prism to avoid spurious refraction at the air–sample interface.[4]

Tensile Properties

Tensile properties were determined according to ASTM D 638, using an Instron Tensile tester model 1121 at ambient conditions, using dumbbell-shaped specimens (length 165 mm, width of narrow section 12.5 mm, and thickness 2 mm). These specimens were made from the cast sheets by cutting pieces, 165 mm long and 14 mm wide, and by shaping the pieces using a metal mold. The edges of the specimen were polished using fine sandpaper. The specimens were conditioned as per the standard before testing.

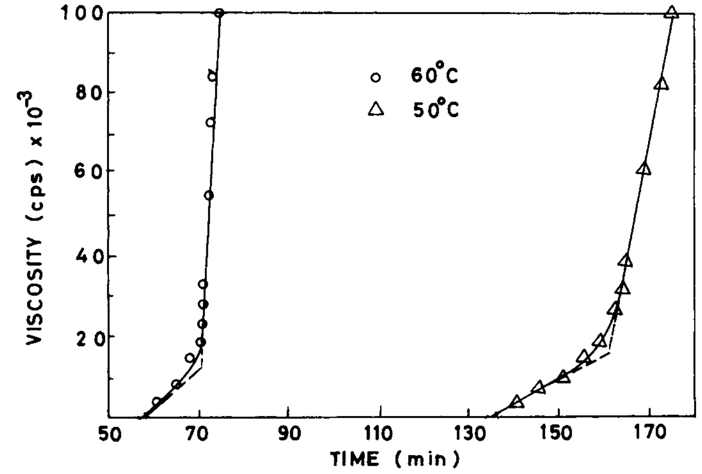

Figure 2 Plots of viscosity vs. time for the polymerization of MMA containing 1% AIBN (w/w) at 50 and 60°C.

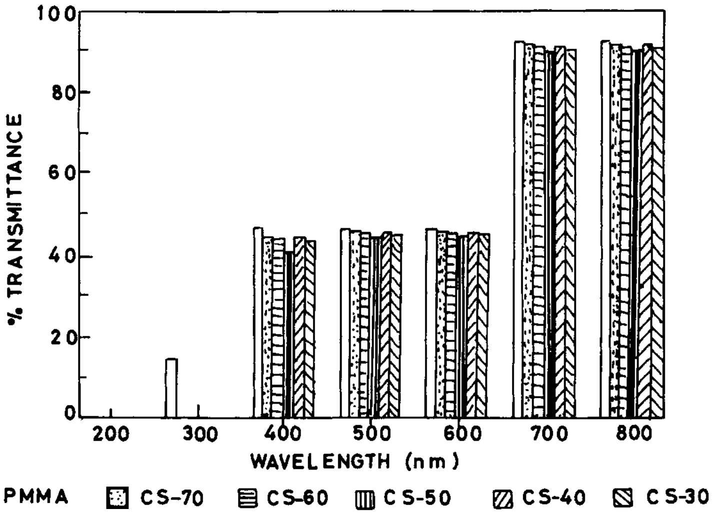

Figure 3 Plot of percent transmittance at various wavelengths for different copolymer samples.

A gage length of 56 mm, a full scale load of 500 kg, a chart speed of 200 mm/min, and a crosshead speed of 10 mm/min was used. A minimum of five samples were tested for each composition and the average was taken.

Dynamic Mechanical Properties

Dynamic mechanical measurements of various polymer samples were carried out in the temperature range of −50 to +70°C, using a Polymer Laboratory Dynamic Mechanical Thermal Analyzer (model MK II) in a bending mode. A heating rate of 5°C/min, a frequency of 1 and 10 Hz, and a sample size of 12 × 5 × 2 mm^3 were used in each experiment. The equipment has built-in computerization facilities, and dynamic moduli (both storage and loss moduli) and damping (loss factor) were calculated by the built-in software and were plotted by the plotter.

Thermal Behavior

Powdered samples of various copolymer samples were prepared by sizing the copolymer sheets. Thermal stability was evaluated using a DuPont 1090 thermal analyzer, having a 951 TG module. A heating rate of 10°C/min and sample size of 10 ± 1 mg were used.

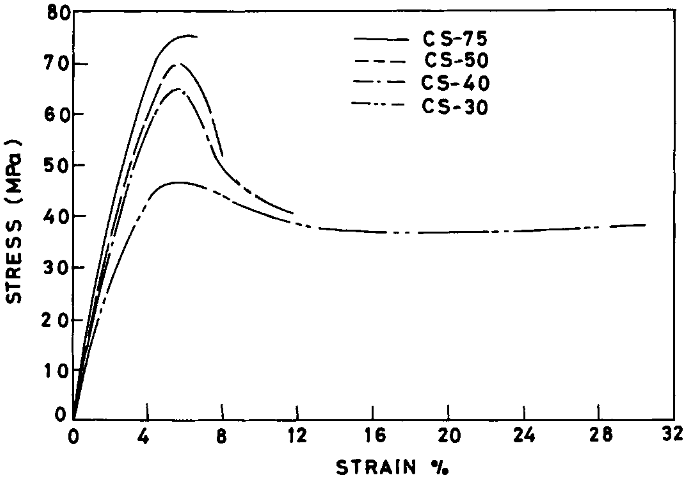

Figure 4 Stress–strain curves of copolymer samples.

Table I Effect of MMA on Mechanical Properties of Urethane-Methacrylates

Sample Designation	Tensile Modulus (MPa)	Percent Elongation at Break	Tensile Strength (MPa)	Work-of-Rupture (MPa)
CS-30	1029	30.8	46.9	11.46
CS-40	1407	11.8	65.1	5.37
CS-50	1425	8.3	69.8	4.07
CS-75	1567	6.7	75.7	3.45

RESULTS AND DISCUSSION

Due to polymerization, the viscosity of the medium was expected to increase. However, since the polymerization reaction was highly exothermic, an increase in temperature also took place, thereby reducing the viscosity. Thus, the isolation of these two opposing effects on viscosity had to be carefully understood. A knowledge of chemical kinetics is helpful in such studies.

Figures 1 and 2 show the viscosity vs. time plots for polymerization of CS-70, CS-80, CS-90, and MMA systems at 60°C. The temperature during this measurement was maintained constant by proper thermostatting. At an early stage of the reaction, the viscosity increased slowly, but later, it increased

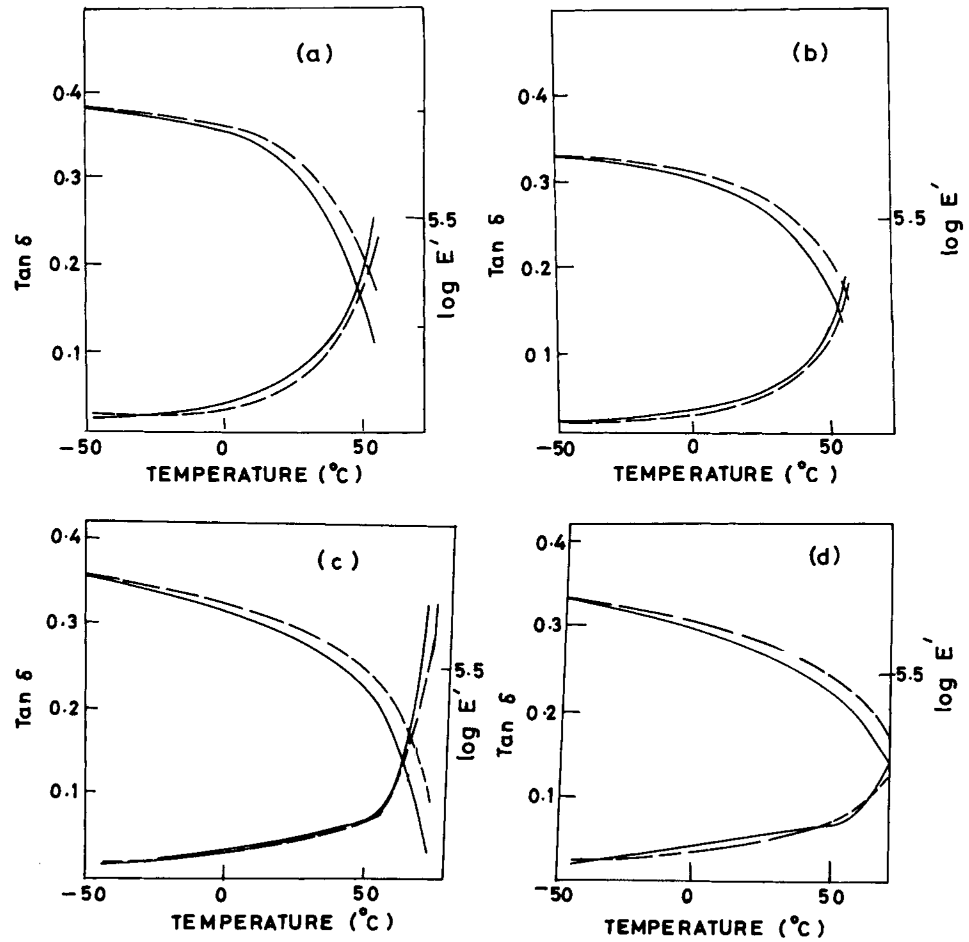

Figure 5 DMTA traces of various copolymers at frequencies 1 Hz and 10 Hz. (a) CS-30, (b) CS-40, (c) CS-50, and (d) CS-70.

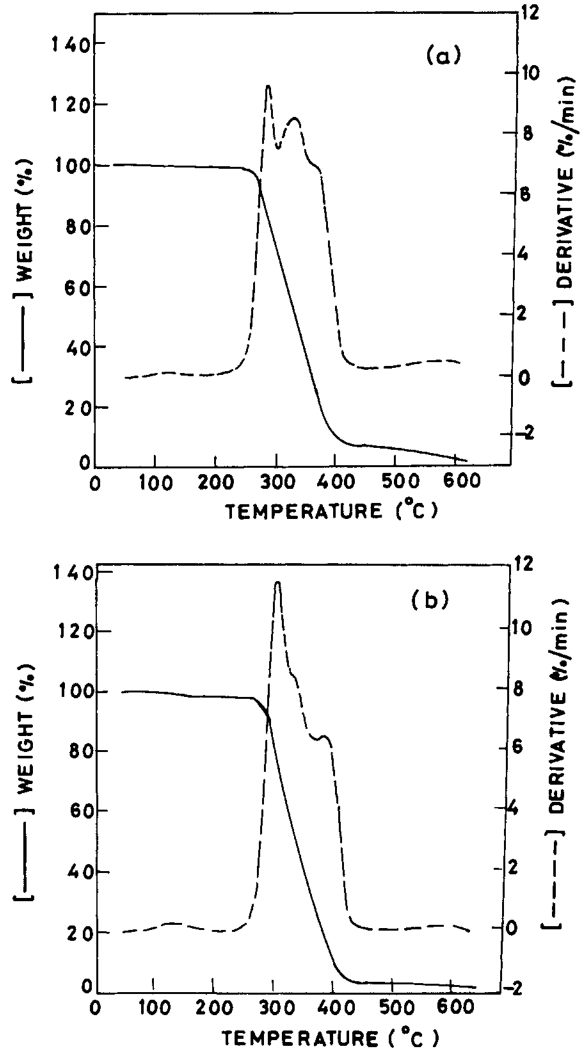

Figure 6 TG and DTG traces of (a) CS-40 and (b) CS-60 in nitrogen atmosphere at a heating rate of 10°C/min.

rapidly, tending to reach a high value as the reaction proceeded. The viscosity curve was characterized by a critical value of time and viscosity, corresponding to the upturn point, evaluated by extrapolation, of steep portion of viscosity vs. time plot. η_c (critical viscosity) characterized a given extent of growth of the polymer chains. At any temperature, after a period of time equal to critical time (t_c), the growth of the polymer chain was such that further polymerization would have caused a significant increase in the viscosity. Both η_c and t_c decreased with an increase in temperature. η_c of CS-70, CS-80, CS-90, and MMA at 60°C were found to be 155, 233, 266, and 133 poise, respectively, while the η_c for MMA at 50°C was found to be 167 poise. The t_c for CS-70, CS-80, CS-90, and MMA at 60°C were found to be 11.5, 11.8, 15.3, and 70 min, respectively, while for MMA at 50°C, the t_c was 161 min. The t_c values increased with an increase in MMA content in the monomer feed; this may be attributed to a reduction in average functionality of the system by incorporation of a bifunctional MMA in a tetrafunctional HEMA endcapped carbamate prepolymer.

The histograms of percent transmittance vs. wavelength for various copolymer sheets are given in Figure 3. All the copolymer sheets had a transmittance similar to the PMMA sheet in the wavelength range of 400–800 nm. However, a difference was observed at 300 nm. The reason for less transmittance in the wavelength at 300 nm for copolymer sheets may be attributed to the presence of aromatic rings in these carbamate polymers.

The refractive indices for CS-30, CS-40, CS-50, CS-60, and CS-70 were found to be 1.5320, 1.5275, 1.5215, 1.5165, and 1.5115, respectively, while that of PMMA it was 1.4920. The refractive index decreased with increasing MMA content in the copolymers.

The stress–strain curves for various copolymers are shown in Figure 4. From the stress–strain curves, tensile strength (MPa), percent elongation at break, and modulus (MPa) were calculated and the results are summarized in Table I. Tensile strength and modulus decreased with decreasing MMA content, whereas percent elongation at break increased marginally in samples CS-40, CS-50, and CS-75. A significant increase in percent elongation was observed in the CS-30 sample. All the samples except CS-75 showed a ductile fracture. This shows a gradual change in the fracture mechanism from ductile to brittle upon increasing MMA content. The work-of-rupture was also calculated from the area under the stress strain curve (Table I). Work-of-rupture increased with increasing carbamate prepolymer. This is because of the increase in flexibility of the polymer chain introduced by PEG moeity of the carbamate prepolymer.

Table II Thermal Behaviour of Carbamate Copolymers in a Nitrogen Atmosphere

Sample Designation	IDT (°C)	T_{max} (°C)	T_f (°C)
CS-30	294	340, 380	385
CS-40	280	295, 340, 375	390
CS-50	285	315, 385	395
CS-60	281	305, 330, 390	400
CS-70	275	305, 340, 390	405

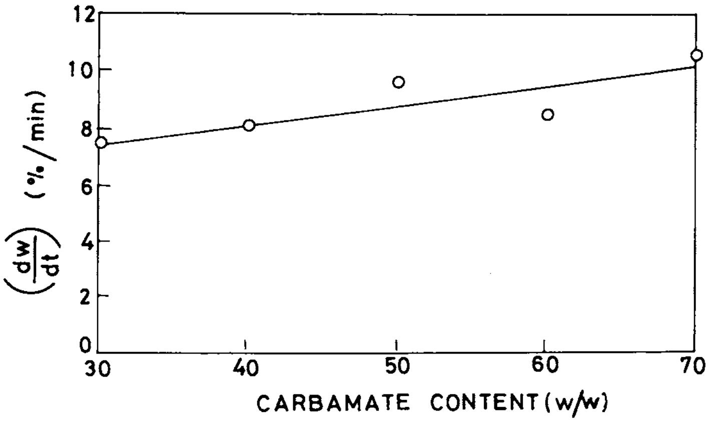

Figure 7 Effect of copolymer composition (carbamate content) on maximum rate of weight loss at 340°C.

DMTA curves are shown in Figure 5 for various copolymer sheets. In PMMA, β-relaxation has been reported around 20°C (1 Hz). This relaxation is due to the torsional liberation of the ester group. However, in carbamate copolymers, this transition was not observed.

Figure 6 shows the TG and DTG traces for various copolymer samples. The initial decomposition temperature (IDT), temperature of maximum rate of weight loss (T_{max}), and final decomposition temperature (T_f) are shown in Table II. IDT increased with increasing carbamate content. This could be due to the increase in the crosslinking density. Percent char yield was approximately 2 in all the copolymer samples.

DTG curves show 2–3 stages of degradation. T_{max} for each decomposition step was noted. Two steps of degradation were observed for CS-30 and CS-50, whereas all other samples showed three steps. The first step was observed at approximately 300°C, second at 340°C, and third at approximately 390°C. The rate of weight loss at 340°C (T_{max}) was noted. The results were plotted as a function of percent carbamate content in the copolymer (Fig. 7). A decrease in rate with increasing MMA content was observed. This could be due to the breakdown of urethane into isocyanate and alcohol.[5] The T_f increased with decreasing carbamate content.

CONCLUSION

It can be concluded from these studies, that the mechanical properties of urethane acrylate can be altered by varying the content of reactive diluent (MMA). An increase in MMA content resulted in a decrease in percentage elongation and increase in modulus and tensile strength. Optical properties are not markedly affected by decreasing MMA content in the urethane acrylate sheets.

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