

Reactive Diluent Effect on Properties of UV-Cured Films

K. M. IDRIS ALI,^{1,*} MUBARAK A. KHAN,¹ M. M. ZAMAN,² and M. A. HOSSAIN²

¹Radiation Chemistry Division, Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission, P.O. Box 3787, Dhaka, Bangladesh; ²Department of Applied Chemistry and Chemical Technology, University of Dhaka, Dhaka-1000, Bangladesh

SYNOPSIS

Polymer films were prepared with UV radiation from urethane acrylate oligomer (LR 8739) mixed with a photoinitiator (Irgacur 184) and a number of reactive diluents chosen from monofunctional monomers (such as *N*-vinyl pyrrolidone, ethylhexyl acrylate, methoxyethyl acrylate, and hydroxyethyl methacrylate), difunctional monomers (hexane dioldiacrylate, butanediol diacrylate, and tripropylene diacrylate), and a trifunctional monomer (trimethylol propane triacrylate). The optimum concentrations of the photoinitiator, oligomer, and diluents were determined. Various properties of the cured films such as pendulum hardness, gel content, swelling ability, tensile strength, and elongation at break were also determined. The glass transition temperatures (T_g) of the diluents were correlated with tensile properties and those of the film. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymer is a versatile material that has diversified applications from space material to kitchen spoons. These applications are dependent on the various properties of the polymer prepared out of a formulated solution composed of different ingredients required to modify the polymer properties according to the need of its utility. Reactive diluents are some of these ingredients. These diluents have twofold functionalities: One is to dilute the oligomer to reduce its viscosity in order to conveniently coat on a suitable substrate prior to making the polymer film, and the second function is the participation of the diluent in the reactive process of the oligomer with a view of making a polymer with a desired property for some specific purpose. The 2-ethylhexyl acrylate monomer used as the diluent makes the film softer with reduced mechanical strength, whereas *N*-vinyl pyrrolidone and multifunctional monomers induce higher mechanical strength to the film with relatively hard character. Polymer is generally prepared by curing the formulated solution coated on a sub-

strate. The curing can be done by using thermal or radiation energy. The present work was the preparation of polymers from formulated solutions composed of urethane oligomer mixed with reactive diluent monomers of different functionalities and the curing was done with ultraviolet radiation. The influence of these diluents on the properties of the polymers, so formed, is also studied.

EXPERIMENTAL

Urethane acrylate oligomer (LR 8739) supplied by IAEA was used. Irgacur 184 was used as the photoinitiator. Four monofunctional monomers such as *N*-vinyl pyrrolidone (NVP), methoxyethyl acrylate (MEA), 2-ethylhexyl acrylate (EHA), and hydroxyethyl methacrylate (HEMA); three difunctional monomers like hexanedioldiacrylate (HDDA), butanedioldiacrylate (BDDA), and tripropylene glycol diacrylate (TPGDA); and one trifunctional monomer, trimethylol propane triacrylate (TMPTA), were used as reactive diluents and were procured from E. Merck.

Solutions were prepared with variable concentrations of oligomer (55–75%), monomers (20–40%), and photoinitiator (1–10%) in order to optimize

* To whom correspondence should be addressed.

their concentrations so that the subsequent experiments could be carried out at those concentrations. The solutions, so formulated, were coated on glass plate (6×10 cm) with the help of a bar coater no. 0.28 in of Abbey Chemicals Co. (Australia). The coating was cured under ultraviolet (UV) radiation using UV-minicure (1ST-Technik, Germany): The intensity of the lamp was 2 kW at 9.5 amps current and the wavelength was 254–313 nm. The cured film was then subjected to various characterization tests. The pendulum hardness of the films was determined using a digital Pendulum Hardness Tester (Model 5854, Byk Labotron). The gel content was measured by extracting the cured film for 20 h with hot acetone in a Soxhlet. The difference in weight of the film after and before the extraction determines the gel content. The ability of the cured film to swell by absorbing acetone yields the swelling ratio. A known weight of the gel was soaked in acetone at normal conditions for 24 h. The difference in weight of the film gel before and after the soaking determines the swelling ratio. The tensile properties of the cured film were determined directly from the Instron (Model 1011).

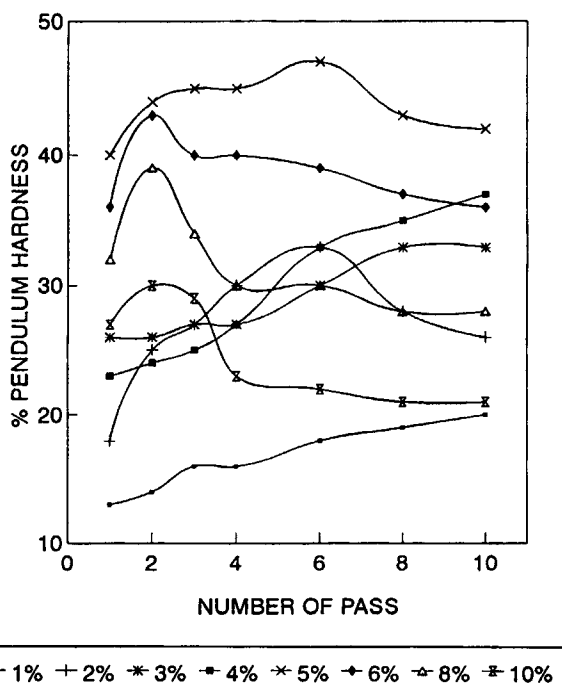


Figure 1 Pendulum hardness of UV-cured films of urethane acrylate and NVP is shown against the number of passes under the UV lamp as a function of concentration of the photoinitiator.

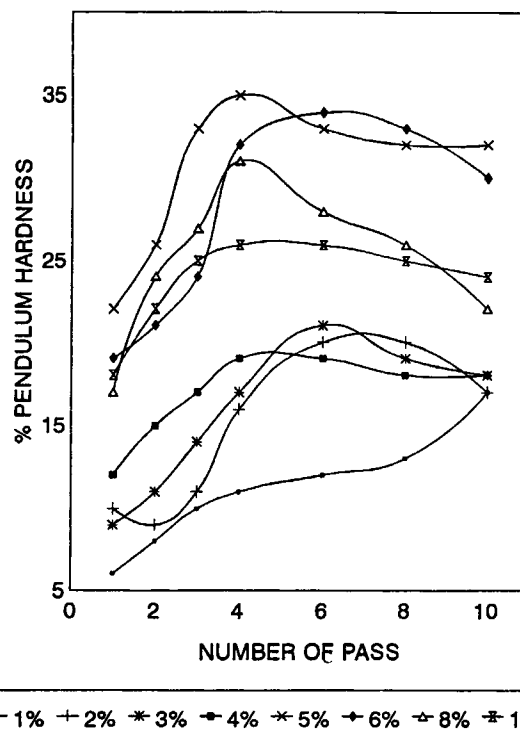


Figure 2 Pendulum hardness of UV-cured films of urethane acrylate and TPGDA is shown against the number of passes under the UV lamp as a function of concentration of the photoinitiator.

RESULTS AND DISCUSSION

Pendulum hardness of the films, prepared with the solutions containing oligomer (60% fixed), Irgacur 184 (1–10%), and NVP (39–30%) is given in Figure 1; the film was cured under UV radiation at different intensities represented by the number of passes. The hardness is related to the cross-linking density on the surface of the film. The highest pendulum hardness is obtained with 5% photoinitiator at the sixth pass, after which the hardness slightly reduces, indicating that higher radiation may have caused some degradation of the polymer. Concentration of photoinitiator higher than 5% induced the maximum hardness at the second pass, after which it reduces quite substantially. This reduction may have occurred by the effect of recombination of free radicals whose concentration becomes higher as the radiation intensity increases with a relatively high photoinitiator.

When the monofunctional monomer NVP is replaced with TPGDA, a difunctional monomer in the

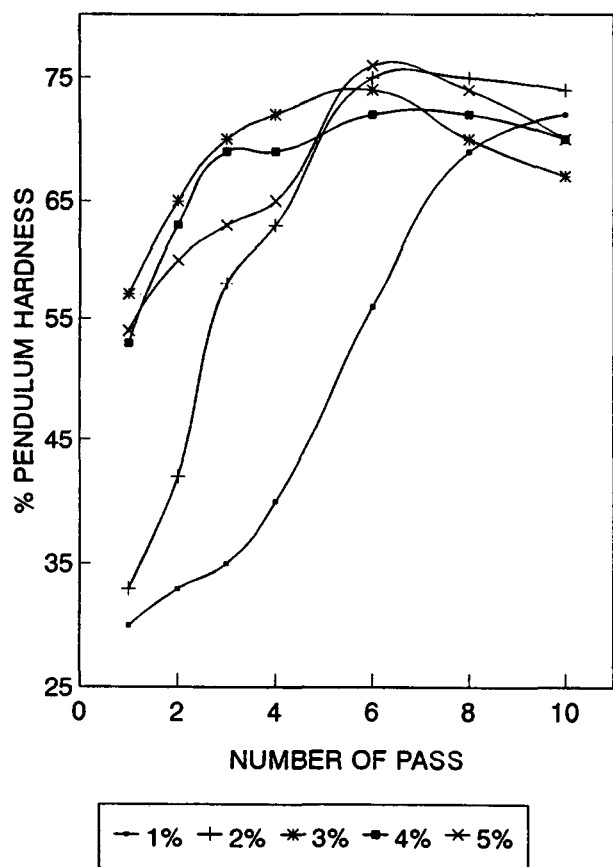


Figure 3 Pendulum hardness of UV-cured films of urethane acrylate and TMPTA is shown against the number of passes under the UV lamp as a function of concentration of the photoinitiator.

above solutions, the highest hardness is observed with the film produced in the presence of 5% photoinitiator at the fourth pass as well as of 6% Irgacur at the sixth pass (Fig. 2). After attaining the highest hardness either at the fourth or at the sixth pass, almost all the films (Fig. 2) show a decline in the hardness as the radiation intensity increases except with the film produced by the presence of 1% photoinitiator. In this case, hardness increases with UV intensities.

Figure 3 shows the pendulum hardness of the films containing variable proportions of TMPTA, a trifunctional monomer, in place of NVP or TPGDA against the number of passes. The highest hardness is again exhibited in the presence of photoinitiator at 5% with the sixth pass. However, the profile of the 1% photoinitiator is different from the rest of the profile curves. After the sixth pass, most of the films showed reduced hardness as with other cases of NVP and TPGDA.

TMPTA induced the highest pendulum hardness (Fig. 4) compared to those of NVP and TPGDA. This is because TMPTA has trifunctional acrylated groups that have a branching effect^{1,2} and can yield more cross-linking in the cured film. NVP, being a monofunctional monomer, exhibited more reduced hardness than that of TMPTA, but higher hardness than that of TPGDA. NVP is a unique monomer containing a carbamide functional group attached to the vinyl double bond, which causes significant enhancement in rheological properties of the film³ and the composite,⁴ a cellulose reinforced polymer. All these results (Fig. 4) were obtained at the sixth pass under UV radiation and the concentration of oligomer was 60% with variable concentrations of monomers (NVP, TPGDA, and TMPTA) and photoinitiator. It is clearly observed in Figures 1–3 that 5% photoinitiator induces the highest hardness irrespective of the functionality of the reactive diluents.

Keeping the photoinitiator concentration at 5%

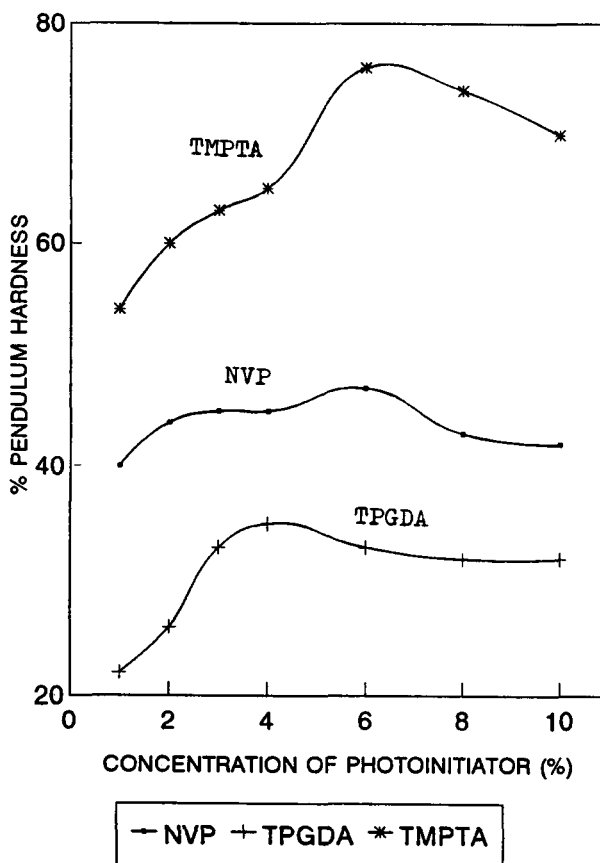


Figure 4 Pendulum hardness is shown as a function of concentration of the photoinitiator for the film of oligomer/(monomer + photoinitiator) = 60/40, w/w, and cured with six passes under the UV lamp.

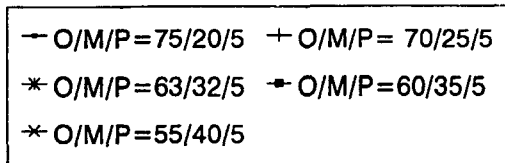
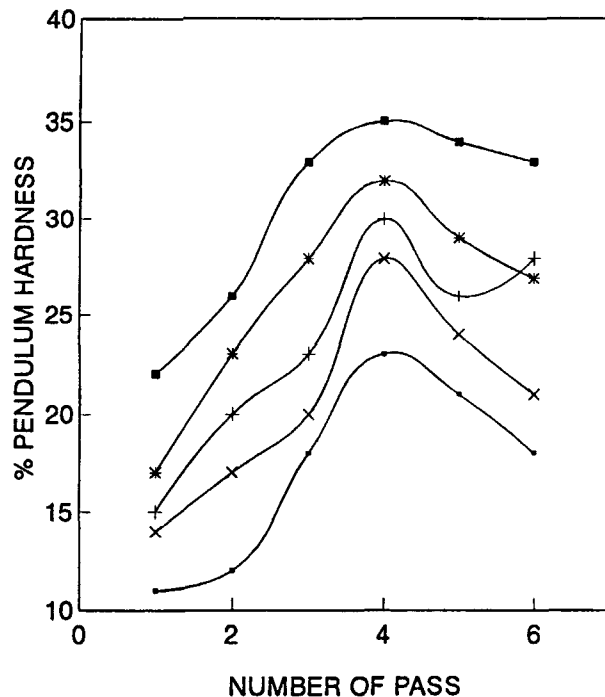


Figure 5 Pendulum hardness is plotted against the number of passes under the UV lamp for the films prepared with variable concentrations of oligomer (O) and monomer TPGDA (M) at a fixed concentration (5%) of the photoinitiator (P).

fixed, the proportions of oligomer and monomer (TPGDA) were varied. The pendulum hardness of the cured films are plotted (Fig. 5) against the number of passes under UV radiation. It is observed that 60% oligomer or 35% monomer produces the maximum hardness compared to other concentrations of oligomer (55–75%). On having optimized the concentrations of photoinitiator (5%), monomer (35%), and oligomer (60%) and the UV radiation intensity (up to six passes), eight different solutions were prepared with eight different monomers, using the same oligomer LR 8739 and photoinitiator Ir-gacur 184. The pendulum hardness of these films cured under the UV lamp at different passes is plotted against the number of passes (Fig. 6). TMPTA exhibited the highest pendulum hardness followed by other reactive diluents; the order is TMPTA

> BDDA > NVP > HDDA > TPGDA > HEMA > MEA/EHA. Because of the branching effect associated with the trifunctionality of TMPTA, it is likely to have more cross-linking density, creating hardness to the cured film.

Among the difunctional diluents (BDDA, HDDA, and TPGDA), BDDA showed the highest pendulum hardness, indicating maximum cross-linking density. These three difunctional molecules have different molecular volumes associated with different molecular shapes and geometries. Diffusion of these molecules into the oligomer chain at the time of the equilibrium conditions needed for the cross-linking reactivity is different. BDDA has the smallest molecular volume among the difunctional diluents and can be easily diffused into the system compared to those of HDDA and TPGDA. The later (TPGDA) has the bulkiest molecule and is, thus, the slowest in reactivity compared to other difunctional monomers. Among the four monoacrylated monomers, NVP exhibited the highest hardness. This value is

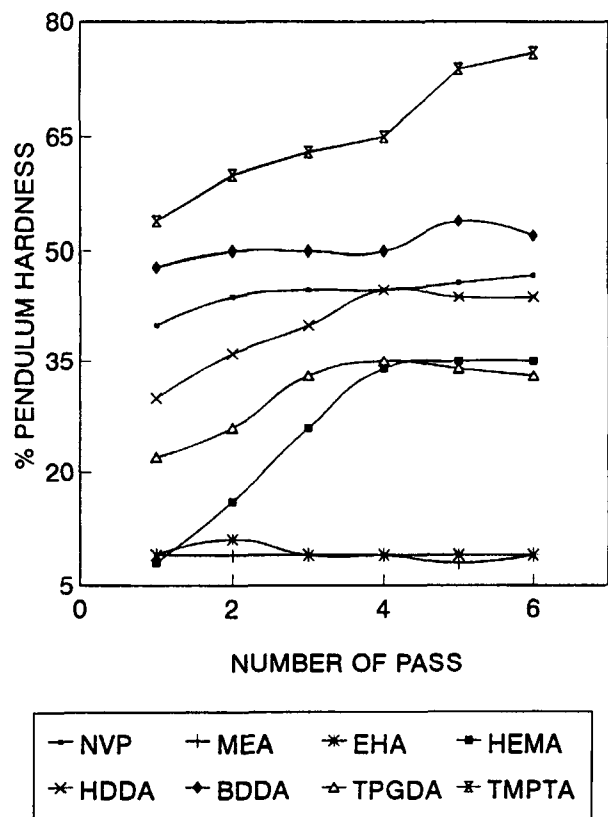


Figure 6 Pendulum hardness is shown against the number of passes under the UV lamp for the films of oligomer : monomer : photoinitiator = 60 : 35 : 5, w/w.

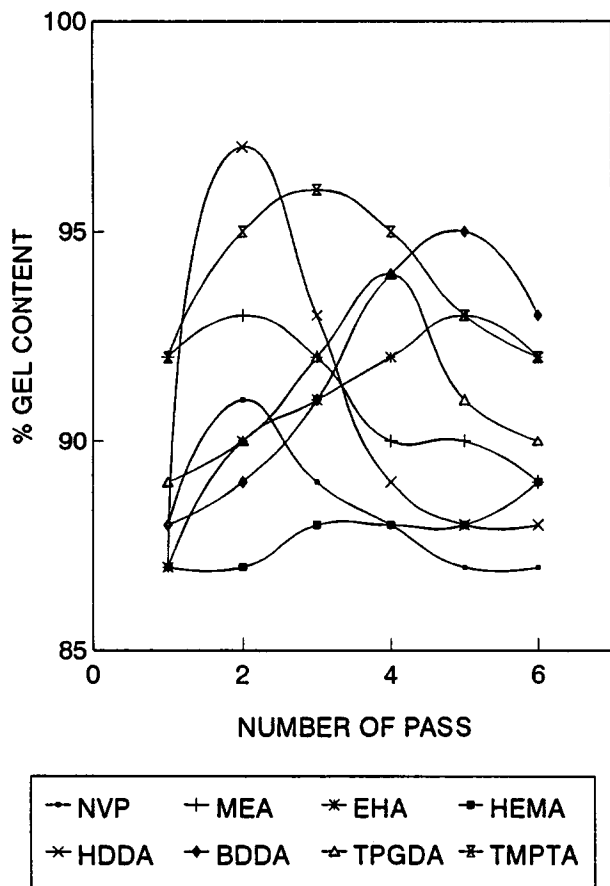


Figure 7 Gel content is plotted against the number of passes under the UV lamp for the films of oligomer : monomer : photoinitiator = 60 : 35 : 5, w/w.

even more than that of the diacrylated monomers (HDDA and TPGDA). This unique character of NVP has already been explained and it is due to the carbamide group present in the NVP molecule.

Both MEA and HEA behave virtually in the similar manner irrespective of the dose intensity. Both these compounds have their glass transition temperature (T_g) lower than 0°C (T_g of MEA = -110°C and EHA = -50°C).⁵ It is universally known that monomers of low T_g values produce soft polymer. HEMA is a methacrylated monomer. The presence of the $-\text{CH}_3$ group at the acrylated moiety always requires more energy to activate the molecule for interaction. Once it is activated, the methacrylated monomer produces a stronger film. Thus, HEMA produced a cross-linking density that is almost the same as that created by TPGDA, a difunctional monomer, at the fifth pass under the UV lamp. The gel content with HEMA similarly increases with UV

intensity (Fig. 7). The pendulum hardness represents the hardness obtained on the surface of the cured film and, thus, corresponds to the cross-linking density on the surface area, whereas the gel represents the entire cross-linking density of the film. The phenomena of pendulum hardness obtained with all the cases after the fourth pass (Fig. 6) are different. The hardness either reduces or remains almost steady up to the sixth pass. The gel determination of all these films (Fig. 7) shows that the gel content reduces after the fourth pass in most of the cases except with HEMA, MEA, and EHA. This means that degradation of the polymer has occurred during the UV radiation after the fourth pass and this is true when the photoinitiator used is 5%. The phenomena might be different if the concentration was changed, as observed in Figures 1–3. The overall gel content varies between 82 and 97% depending on the reactive diluents used. As the gel content

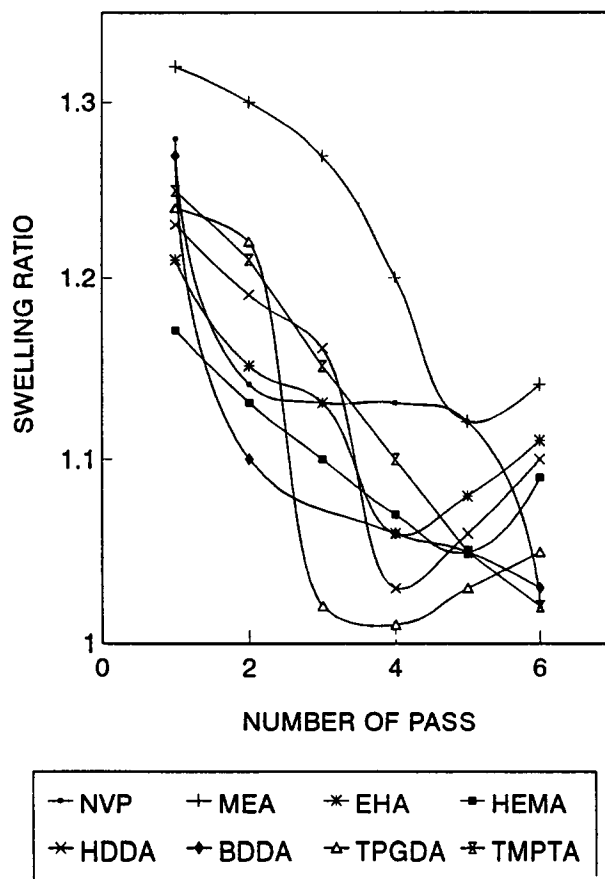


Figure 8 Swelling ratio is plotted against the number of passes under the UV lamp for the films of oligomer : monomer : photoinitiator = 60 : 35 : 5, w/w.

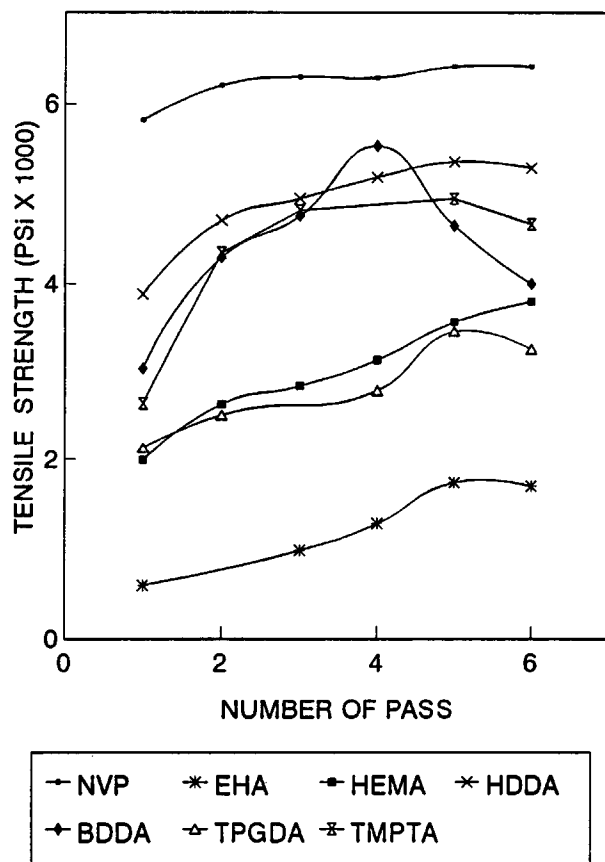


Figure 9 Tensile strength is plotted against the number of passes under the UV lamp for the films of oligomer : monomer : photoinitiator = 60 : 35 : 5, w/w.

increases, the swelling ability decreases. This is shown in Figure 8, where swelling ratio is plotted against the number of pass.

The tensile property is an important characteristic of a polymer. The application of a polymer is made in consideration of this property. A polymer may be made harder in the presence of a polyfunctional monomer like TMPTA, but its tensile strength may not necessarily be higher. On the other hand, incorporation of a reactive monomer diluent in the formulation may cause the film to be less hard with enhanced tensile property. Comparing pendulum hardness (Fig. 6) and tensile strength (TS) (Fig. 9), it is observed that TMPTA has the highest pendulum hardness, whereas NVP has the highest tensile strength. The TMPTA film is brittle and cracks easily, rendering less tensile strength, whereas NVP or HDDA film is elastic and has higher tensile strength. The EHA film has the lowest tensile strength because of its low T_g character. HEMA, being a monofunctional monomer, has exhibited

more tensile strength than that of TPGDA, a di-functional diluent; it is due to the presence of a $-\text{CH}_3$ group attached to an acrylated moiety. This group most probably forms a sort of hydrogen bonding in the cross-linking network. The higher tensile strength of NVP (Fig. 9) can be again explained in that the molecule contains a $-\text{N}-$ attached to a $=\text{C}=\text{O}$ group, which helps better augmentation of the reactive moiety for the overall texture of the polymer film. MEA film could not be peeled off the plate and, thus, no tensile property could be determined.

The elongation property at the break (E_b) is related to the elastic or brittle character of the film. TMPTA film has the most brittle character among all the films studied and has, thus, exhibited the lowest E_b (Fig. 10). As a film becomes cured, its elongation tends to reduce. This is the case with HEMA, but EHA film has gained higher E_b with dose intensity. This is due to its inherent character for higher elastic property. Figure 11 shows how the

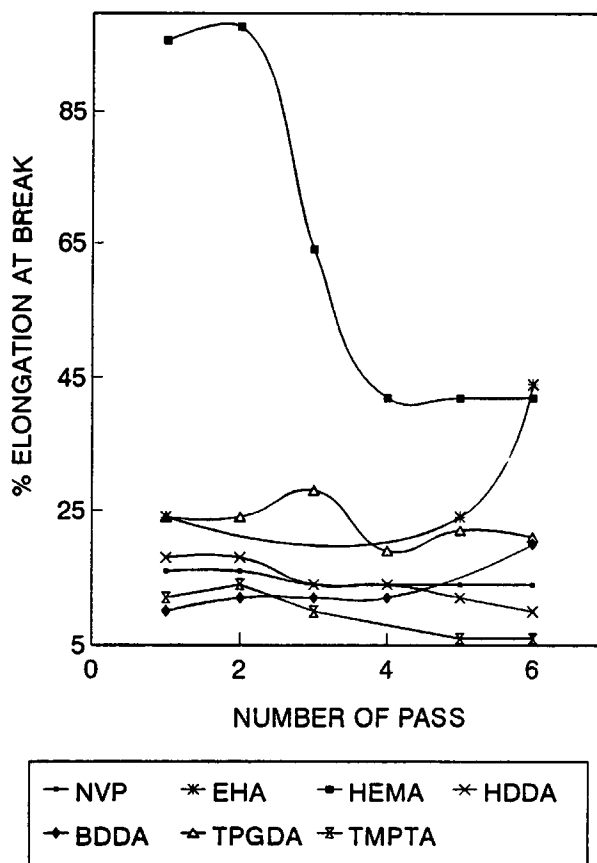


Figure 10 Elongation at break is plotted against the number of passes under the UV lamp for the films of oligomer : monomer : photoinitiator = 60 : 35 : 5, w/w.

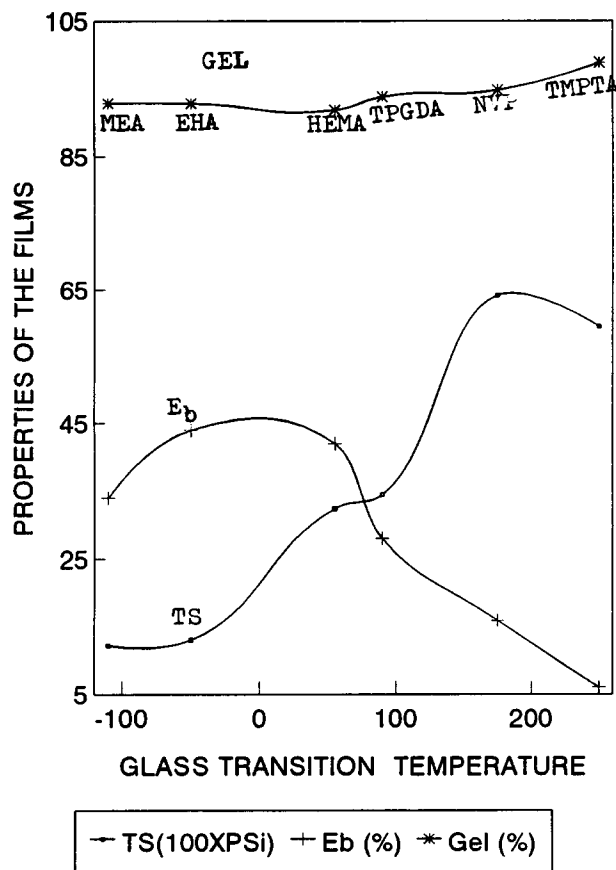


Figure 11 Relationship of glass transition temperature (T_g) of reactive diluent monomers with properties of the films prepared from oligomer:monomer:photoinitiator = 60 : 35 : 5, w/w, and cured with six passes under the UV lamp.

glass transition temperature (T_g) of the reactive diluents is related to the tensile properties (TS and E_b) and the gel content of the UV-cured films. The gel content slightly increases with increase of T_g values. The TS increases substantially with the T_g of the diluents and the E_b decreases quite significantly. The slight drop of the TS value at $T_g = 250^\circ\text{C}$ is due to the brittle character of the TMPTA film. The glass transition² temperature of the reactive diluents is an important factor in selecting the property of a film to be developed for some specific applications.

The authors are thankful to International Atomic Energy Agency (IAEA) for its partial financial support under Research Contract No. 5951/RB.

REFERENCES

1. M. A. Hossain, T. Hasan, M. A. Khan, and K. M. I. Ali, *Polym.-Plast. Technol. Eng.*, **33** (1), 1 (1993).
2. K. M. I. Ali, M. A. Ali, T. K. Saha, and M. A. Khan, *J. Appl. Polym. Sci.*, to appear.
3. K. Kawate and T. Sasaki, *Polym. Bull.*, **27**, 213 (1991).
4. M. A. Khan and K. M. I. Ali, *Radiat. Phys. Chem.*, **40** (6), 421 (1992).
5. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 3rd ed., Wiley, New York, 1974.

Received December 17, 1993

Accepted April 18, 1994