

Techniques to monitor the UV curing of potential solvent-free film-coating polymers

Jean Z.Y. Wang, Robin H. Bogner *

University of Connecticut, School of Pharmacy, U-92, Storrs, CT 06269, USA

Received 25 March 1994; modified version revised 15 June 1994; accepted 24 June 1994

Abstract

A methodology has been established for systematically evaluating polymer films produced by UV curing. Cast films of 1,3-bis[(*p*-acryloxymethyl)phenethyl] tetramethyldisiloxane (I) and norborenylpolydimethylsiloxane (II) were cured by UV irradiation. The films were evaluated from real-time FTIR studies, a non-rheologically destructive method for determining microviscosity, dynamic mechanical thermal analysis (DMTA) and leaching and swelling studies. Real-time FTIR indicated that while conversion from prepolymer to network was complete for II, conversion was only 80% for I with 0.05% benzoin methyl ether (BME), an initiator, and only 60% with 0.5% BME. Results of DMTA show the glass transition temperatures (T_g values) of the films to have an inverse rank order correlation with conversion. Along with microviscosity results, this is indicative of a diffusion rate-limited curing reaction. Results of leaching and swelling studies demonstrated greater rates and extents of leaching and swelling from films prepared with a lower concentration of initiator (0.05% BME). These observations were in good agreement with the results from the microviscosity and DMTA studies which showed larger free volumes and lower T_g values as well as slightly lower crosslinking densities in films prepared with less initiator. The methods presented in this paper have been shown to be useful in quantifying the reaction of this new class of film formers and in identifying the mechanisms of film formation.

Keywords: UV curing; Film coating; Polymer film

1. Introduction

Coating techniques have long been used in the pharmaceutical industry to achieve elegant and functional dosage forms. With advances in materials science, the pharmaceutical industry has seen the introduction of organic based polymer film

coatings and aqueous based emulsion coatings. The latter were introduced to circumvent the use of organic solvents to comply with requirements of the Environmental Protection Agency and the Occupational Safety and Health Administration (Kislalioglu and Banker, 1984).

Further advances in the materials science field now make it possible to apply a solvent-free coating in which the transition from liquid to solid film is mediated by a chemical reaction of the liquid coating material. One technique which can

* Corresponding author. Tel. 203-486-2136; Fax 203-486-4998; email/internet BOGNER@uconnvm.uconn.edu.

achieve such a conversion is photocuring of suitably functionalized prepolymers. This technique has been successfully used in the paint and adhesives industries for decades (Roffey, 1982). Photocuring is also used in a variety of medical and dental applications (American Dental Association, 1985; Dempsey and Thirucote, 1990; Bachmann and Alvarez, 1992). UV-curable coating materials generally consist of low viscosity prepolymers with functional groups which react to form a network upon UV irradiation in the presence of initiators, sensitizers and/or catalysts. Crosslinking sets the coating on the substrate surface to form a solid film. Thus, it is possible to eliminate organic and aqueous solvents, as well as heat, from the film-coating process.

It has been reported that oxygen has the ability to slow down and/or reduce the extent of curing in some acrylate-functionalized silicone systems by quenching excited states and scavenging free radicals from the initiator and the growing polymer network (Decker et al., 1980). To reduce this complication, UV-curable systems are usually purged with nitrogen. Studies have shown that UV curing processes use only 5–50% as much energy as conventional curing methods (Shahidi and Powanda, 1975). The advantages of photocuring over other conventional curing methods include a potentially shorter application time, elimination of solvents, a savings of raw materials and energy, and a reduction in thermal stress on substrate materials (Yang, 1993). As with any new technology, photocuring has potential disadvantages as well. For example, it may not be useful for coating light-sensitive drugs.

UV curing is similar to polymerization reactions which involve free radical, cationic or anionic mechanisms depending on the functional groups of the prepolymer and initiators or catalyst used (Phillips, 1983; Kutal et al., 1991). Among UV-curable materials which have been studied, acrylate-functional prepolymers are the most widely used. These have been extensively investigated in terms of reaction mechanisms, kinetics and mechanical properties (Otsubo et al., 1984; Thanawalla and Victor, 1985; Kloosterboer, 1988). In the present study, two siloxane containing prepolymers were chosen since the siloxane

backbone would be expected to provide flexibility to the film in the absence of plasticizers. The reaction mechanism in our UV-curing system is free radical polymerization. In addition, polydimethylsiloxane (PDMS) has been recently investigated for its use in film-coating tablets (Dahl and Tan et al., 1988; Sue, 1990; Li and Peck, 1991, 1992). The long-term goal of this research is to develop novel film-coating systems by applying UV-curing technology. This paper will present methods for quantitatively evaluating the UV curing process and resulting films.

2. Experimental

2.1. Materials

Prepolymer I, 1,3-bis[*p*-acryloxymethyl]phenethyl] tetramethylsiloxane (Huls America, Piscataway, NJ) and the initiator, benzoin methyl ether (BME, 96% with benzoin as the major impurity, Aldrich, St. Louis, MO) were stored in a desiccator and used without further purification. BME was dissolved directly in prepolymer I at concentrations of 0.05% and 0.5% (w/w) and stored in a desiccator in the dark. Prepolymer II, norborenylpolydimethylsiloxane, was kindly provided by Loctite Corp. (Newington, CT). It was preformulated with 1% crosslinking agent, thiol, and 2% initiator, 2-hydroxy-2-methyl-1-phenylpropan-1-one. This preparation was stored in the refrigerator until use. The structures of these chemicals are shown in Fig. 1.

2.2. Bulk viscosity measurement

A cone/plate viscometer (Brookfield Engineering, Stoughton, MA) was used to measure viscosities of UV-curable prepolymer preparations. A volume of 0.5 ml was placed into the thermostatted sample cup and measured at 25°C.

2.3. Real-time FTIR

UV-curable prepolymer preparations were spread to a uniform thickness of 30–50 μm on aluminum-coated glass plates and placed on the

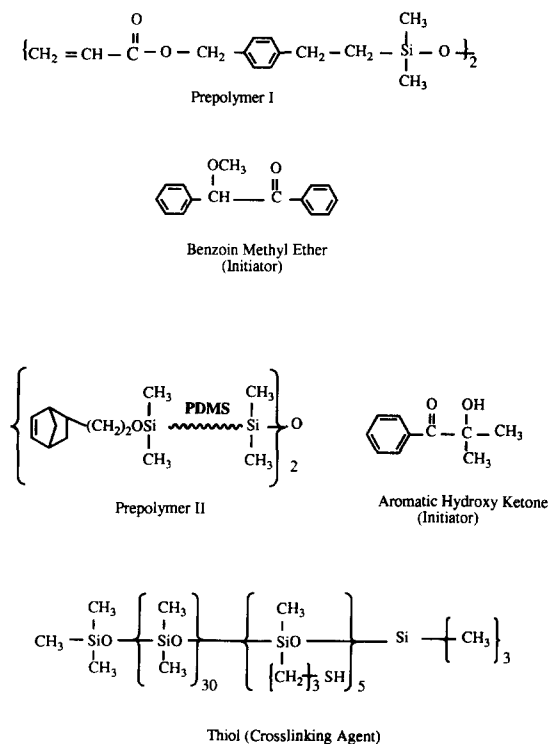


Fig. 1. Structures of the prepolymer I and its initiator, benzoin methyl ether, and prepolymer II, its crosslinking agent and initiator.

horizontal sample holder of a Fourier Transform Infrared Spectrometer (Model 1600, Perkin Elmer, Norwalk, CT) with nitrogen streaming over the surface of the sample. A mercury vapor UV lamp (PortaCure 1000, UV Process Supply, Chicago, IL) set at 125 W/inch^2 was positioned 16 inches above the sample. Using a four mirror glancing angle accessory, the curing process was monitored. The angle of the accessory was adjusted to allow the incident beam to penetrate the entire thickness of the film in order to monitor bulk curing (Yang, 1993). After 10 min of curing, samples were shielded from UV irradiation and continuously monitored for post-irradiation curing. Measurements were made at room temperature.

2.4. Real-time microviscosity

A viscosity-sensitive fluorescent probe, 9-dicyanovinyljulolidine, DCVJ (Molecular Probes,

Eugene, OR), was homogeneously mixed into the UV-curable prepolymer I preparations (0.5 and 0.05% (w/w) BME) from a 10^{-4} M ethanol stock solution. Prepolymer solutions containing DCVJ ($4 \times 10^{-5} \text{ M}$) were placed in UV-transparent cuvettes under nitrogen streaming and irradiated vertically while a horizontal monochromatic laser beam (514.5 nm, 30 mV) simultaneously excited the DCVJ. Fluorescence emission from the DCVJ was collected at 90° from the laser incident beam. The integrated fluorescent peaks reflected relative quantum yields which increased as local viscosity increased.

2.5. Curing free films

The UV-curable preparations were spread as homogeneous liquid films onto glass cover slips (18 mm diameter) or aluminum foil and placed in a nitrogen-purged quartz chamber for curing. The quartz chamber was fabricated from GE 124 quartz glass exhibiting 90% UV transmission above 290 nm. The liquid films in the chamber were irradiated for various periods using a medium pressure mercury vapor lamp (PortaCure 1000, UV Process Supply, Chicago, IL). Lamp power was set at 125 W/inch^2 and the distance between the lamp and samples was fixed at 16 inches. The actual radiation intensity at the sample surface was 1.5 mW/inch^2 . The mercury lamp's spectral distribution ranges from 200 to 440 nm with major energy peaks at 250, 310, 360 and 400 nm.

2.6. Dynamic mechanical thermal analysis (DMTA)

UV-cured films (0.8 mm thick) from prepolymer I and II preparations were cut into $4 \times 1 \text{ cm}$ strips and clamped rigidly at both ends in a dynamic mechanical thermal analyzer (MK II, Polymer Laboratories, Salop, U.K.). One end of the sample underwent torsional strain at a sinusoidal frequency of 1 Hz. Polymer chains which are perturbed in this way store a portion of the imparted energy elastically and dissipate some portion as heat. The resulting storage modulus from the deformation, a measure of the energy stored elastically, was monitored as a function of temperature.

2.7. Water vapor transmission

UV-cured films approx. 300 μm thick were prepared from prepolymer I (0.05 and 0.5% BME) and II preparations in a nitrogen-purged, quartz chamber. Exact film thickness was measured with a micrometer. Similar to the methods reported by other investigators (Woodruff et al., 1972; Joshi et al., 1989; Sprockel et al., 1990), an 18 mm diameter film was cut and fitted onto an open top phenolic screw cap and secured in place with a rubber gasket. The unit was then screwed onto a sample vial containing distilled water. The vial was placed into a desiccator containing CaSO_4 and was maintained at $30 \pm 1^\circ\text{C}$ for 24–28 h. The area for water vapor transmission was 68 mm^2 . At each sampling time, the vial was removed from the desiccator and weighed to record the loss of water vapor. The studies were performed in triplicate.

2.8. Leaching and swelling

Aliquots of prepolymer I containing 0.05 and 0.5% (w/w) BME or the prepolymer II formulation were spread to an average thickness of 300 μm on glass cover slips and cured as described above. The irradiation time for prepolymer I preparations was 10 min and that for prepolymer II preparations was 3 min. The films on their substrates were immediately weighed and placed in sealed vials containing 10 ml of acetone at 25°C . Acetone was used to achieve measurable swelling while minimizing the cracking of relatively brittle prepolymer I films. At each sampling time over a 48 h period, the swollen films were quickly weighed and re-immersed in fresh acetone. The data were analyzed as previously described (Bogner et al., 1988). In addition, the leachates were dried, weighed and reconstituted in tetrahydrofuran for analysis by gel permeation chromatography (Model 840, Waters, Milford, MA) at a flow rate of 1.0 ml/min through five polystyrene/divinylbenzene columns (10^2 , 10^3 , 10^3 , 10^5 and 10^5 Å) using UV and refractive index detectors.

3. Results

The viscosities of prepolymer I and II preparations were 34 and 645 cps, respectively, at 25°C with the coexistence of initiator and crosslinking agents. The UV-cured films were solid and transparent. Prepolymer I films prepared with both levels of initiator showed good resistance to bending and scratching, while prepolymer II films were very flexible. Cross-sections of the films appeared homogeneous in texture on visual inspection. The remainder of this section presents quantitative techniques to evaluate film formation. The first two methods – real-time FTIR and real-time microviscosity – are used to follow the reaction as it proceeds. The final four methods – DMTA, water vapor transmission, leaching and swelling – are used to evaluate characteristics of the formed film.

3.1. Real-time FTIR

Fig. 2 illustrates typical IR spectra of prepolymer I with 0.05% BME during UV curing. The absorption peak for C = C of the acrylate (peak I) occurs near 1630 cm^{-1} and that for C = O of the acrylate (peak II) at 1730 cm^{-1} . As the curing reaction proceeds, the concentration of C = C groups is depleted while that of the C = O groups

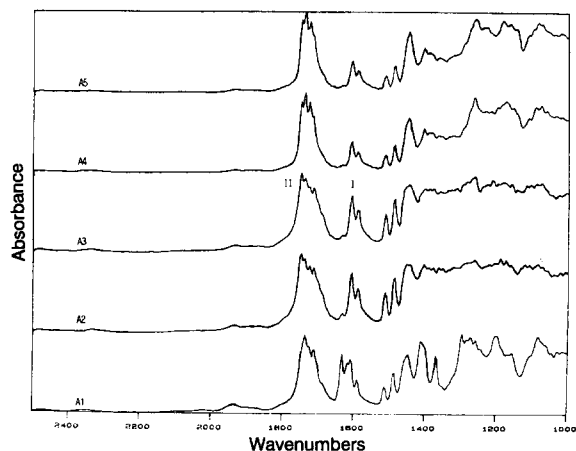


Fig. 2. IR spectra of prepolymer I using glancing angle accessory. A1, no UV irradiation; A2, 5.2 min UV irradiation; A3, 10.2 min UV irradiation; A4, 14.3 min irradiation; A5, 16.3 min irradiation.

remains unchanged. As a result, the area under peak I can be used to quantitate the change in the concentration of C = C using the C = O peak as a reference or internal standard. Similar peaks are used for the quantitation of the conversion of prepolymer II where the C = C is contained in the norbornenyl endgroup, while the C = O is contained in the initiator. The physical properties and microenvironment around the C = C groups change during curing due to the transition from liquid to solid film. The IR spectra are seen to be somewhat affected by this transition, particularly in the shapes of the peaks being quantified. Therefore, areas of the peaks rather than peak heights were used to quantify curing from FTIR spectra. The ratio of the area under peak I to that under peak II was used to measure the % conversion of the prepolymer to network at room temperature (Eq 1):

$$X(t) = (1 - R_t/R_0) \times 100 \quad (1)$$

where $X(t)$ represents % conversion of prepolymer to polymer at time t , R_t is the ratio of peak I area to peak II area at time t and R_0 denotes the ratio of peak I area to peak II area at time 0.

The spectra were quantified using this method to calculate the percentage of prepolymer conversion. Prepolymer I does not achieve complete conversion at room temperature regardless of the apparent formation of the solid film. Relative to

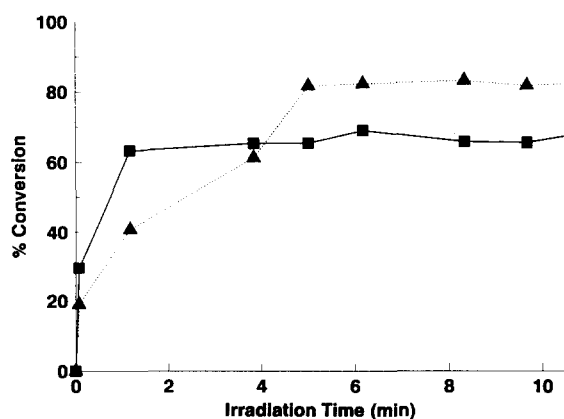


Fig. 3. Representative profiles of percentage conversion of the prepolymer II preparations at room temperature as a function of UV irradiation time calculated from the real-time FTIR spectra. (▲) 0.05% BME; (■) 0.5% BME.

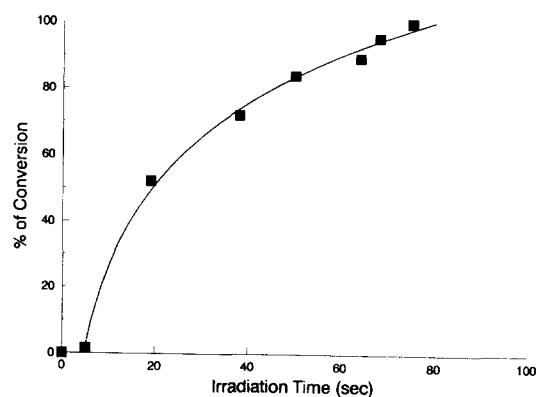


Fig. 4. Representative profile of percentage conversion of the prepolymer I to film network at room temperature as a function of irradiation time calculated from FTIR spectral analysis.

the higher initiator concentration, 0.05% BME appears to cause a slightly slower initial curing rate, yet yields a higher percentage conversion of 82% compared to 63% conversion for the 0.50% BME-containing film (Fig. 3). In contrast, prepolymer II achieved 100% conversion in under 80 s of UV irradiation as shown in Fig. 4.

3.2. Real-time microviscosity

A viscosity-sensitive fluorescent probe (DCVJ) was used to monitor changes in viscosity during the curing of prepolymer I with the two levels of initiator. The molecular internal rotation of the malonitrile group within DCVJ depends on local viscosity of the medium or free volume of the network. This rotation is the major route of nonradiative decay of the excited state of DCVJ. Thus, the fluorescence quantum yield increases with increasing local resistance which provides a barrier to the rotation of the malonitrile group (Loutfy, 1981, 1982). As seen in Fig. 5, the fluorescence of the probe in prepolymer I films increases as the curing proceeds due to the increase in viscosity. After a lag time, there is a sudden increase in fluorescence of the probe, particularly at the higher initiator concentration. A similar sharp increase has been reported to occur at gel formation (Loutfy, 1981). The higher fluorescent intensity of the probe in the 0.50%

BME system indicates that this network has less free volume and is stiffer, while the lower initiator level allows the formation of a more flexible network with greater free volume.

3.3. Dynamic mechanical thermal analysis (DMTA)

DMTA provides a reliable determination of the glass transition temperature of the film network, because it gives a measure of the segmental motions of polymer chains in the films. In DMTA measurements, the glass transition temperature (T_g) is defined as the temperature corresponding to the maximum rate of decline of the storage modulus in the glass to rubbery transition region (Sperling, 1992). Films prepared from prepolymer I containing 0.50% BME were characterized by a T_g of 45°C while films prepared with 0.05% BME had a T_g of 33°C as shown in Fig. 6. Thus, films prepared with a lower level of initiator are more flexible as compared to those with higher initiator concentration. Films from the prepolymer II preparation had a T_g of -120°C.

The plateau value in the rubbery state after the glass transition zone allows estimation of the crosslinking density of the film. Fig. 6 shows the plateau for the film prepared with a higher initiator level to have a higher value for the storage modulus in the plateau region, indicating that the higher level of initiator yields a more densely crosslinked film.

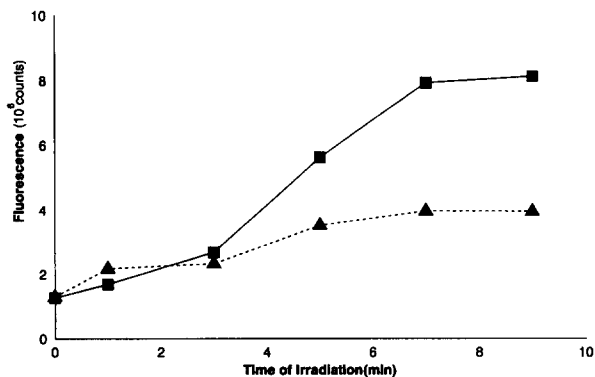


Fig. 5. Representative plots of the fluorescence intensity of the viscosity-sensitive probe, DCVJ (4.0×10^{-5} M) in prepolymer I as a function of irradiation time. (▲) 0.05% BME; (■) 0.50% BME.

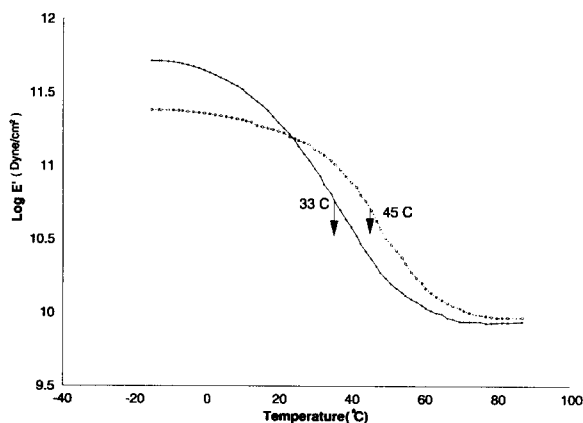


Fig. 6. Representative plots of the log storage modulus, log E' , of UV-cured films as a function of temperature monitored using DMTA. (*) film with 0.05% BME; (○) film with 0.5% BME.

3.4. Water vapor transmission studies

Water vapor transmission rates give evidence for film integrity as well as a measure of the ability of water vapor to permeate the films. Water vapor transmission constants for the cured films are 1.13×10^{-6} , 1.11×10^{-7} and 1.12×10^{-7} $\text{g h}^{-1} \text{cm}^{-1} \text{mmHg}^{-1}$ for prepolymer II and prepolymer I containing 0.05 and 0.5% BME, respectively. Coefficients of variation for these data are less than 7%. The results show that prepolymer I films were poorly permeable to water vapor as compared to other commercially available celluloses (Woodruff et al., 1972; Joshi et al., 1989; Sprockel et al., 1990). In contrast to prepolymer I, prepolymer II films were 10 times more permeable to water vapor and closer to the values of commercially available coatings.

3.5. Leaching and swelling

Leaching and swelling are traditional techniques used to evaluate the structure of the film network. Since the prepolymer I films were somewhat less flexible, a poorer solvent was used to reduce film cracking during the swelling studies. However, there was some cracking of the films even under these mild conditions which caused relatively large standard deviations in the results.

Prepolymer II films were not damaged under the experimental conditions.

The prepolymer I films prepared using the lower level of initiator (0.05% BME) swelled to a greater extent than films with the higher level of initiator, as shown in Fig. 7. The large deviations in these data rendered the results inconclusive; however, they are suggestive of a slightly looser network or lower crosslinking density at the lower level of BME. The swelling results of prepolymer II films are also shown in Fig. 7. However, no comparisons can be drawn between prepolymer I and II films due to the difference in solvent polymer interactions in these films of different chemical composition.

Prepolymer I films prepared with 0.05% BME also showed a higher rate and extent of leaching in acetone than those prepared with 0.50% (Fig. 8). These films reached their maximum leaching within the first 24 h, while films prepared with 0.50% BME did not reach equilibrium within the 48 h test period. Gel permeation chromatography (GPC) showed that the leachate consisted of traces of initiator as well as low molecular weight material similar in size to the starting prepolymer I; no polymer molecules were detected in the leachate. The increased leaching from films prepared with the lower level of initiator was probably the result of forming a more flexible or loosely

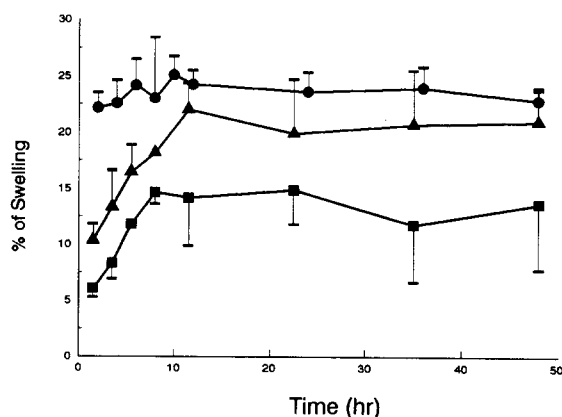


Fig. 7. Percentage swelling of the cured prepolymer I and II films in acetone at 25°C as a function of swelling time. (●) Prepolymer II; (▲) prepolymer I with 0.05% BME; (■) prepolymer I with 0.5% BME ($n = 3$).

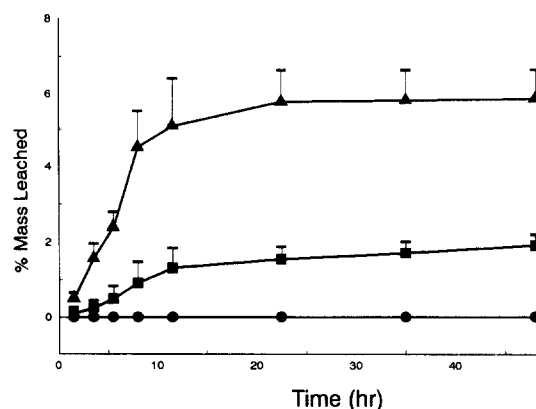


Fig. 8. Percentage leaching of the cured prepolymer I and II films in acetone at 25°C as a function of swelling time. (●) Prepolymer II; (▲) prepolymer I with 0.05% BME; (■) prepolymer I with 0.5% BME ($n = 3$).

packed network which allowed more solvent to penetrate forming larger pores for the components to leach out.

4. Discussion

Table 1 summarizes the data on conversion of prepolymer to polymer using FTIR and T_g using DMTA. The results show a rank order inverse correlation of % conversion with T_g . This is strong evidence that UV curing in the prepolymer I systems is a diffusion rate-limited reaction. Completely formed networks of prepolymer II with T_g values of -120°C are in the rubbery state at the reaction temperature 25°C and are therefore flexible. The reactants (prepolymer molecules and initiator as well as crosslinker) have greater diffusivities in the flexible network to reach reaction sites resulting in complete conversion. For prepolymer I, the T_g values for the 0.05 and 0.50% BME systems are 33 and 45°C, respectively, which

Table 1
Comparison of % conversion and T_g

Prepolymer	% conversion	T_g (°C)
I 0.5% BME	62	45
I 0.05% BME	82	37
II	100	-120

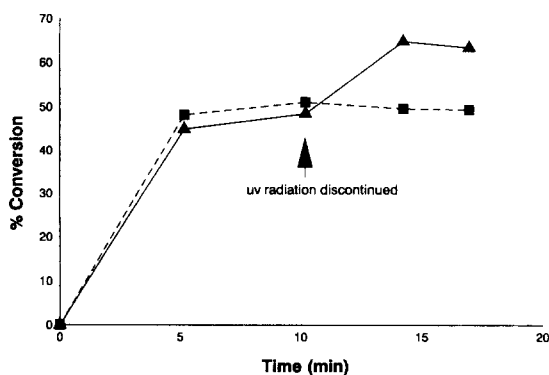


Fig. 9. Representative profile of post curing effects of prepolymer prepolymer I at room temperature shown by % conversion calculated from FTIR spectral analysis versus irradiation time. (▲) Prepolymer I with 0.05% BME; (■) prepolymer I with 0.5% BME.

are above the reaction temperature 25°C. Upon reaching maximum conversion, 80% for 0.05 and 60% for 0.50% BME, prepolymer I networks became fairly stiff. Even though significant amounts of reactants still existed, diffusion to the reaction sites was limited in the vitrified samples such that the curing reaction was virtually terminated. This phenomenon is well-known in the photopolymerization field (Decker, 1987). Unreacted prepolymers and radicals become trapped inside the network. Atmospheric oxygen eventually diffuses into the network and scavenges the radicals.

Further evidence for the diffusion rate-limited conversion of prepolymer I was seen during post-illumination monitoring by FTIR. In this experiment the irradiation was attenuated at 10 min, while the FTIR spectra continued to be collected. Fig. 9 shows that conversion continued in the 0.05% BME system; however, conversion in the 0.50% BME system plateaued. Due to the formation of the more flexible network, reactants in the 0.05% BME system were still able to diffuse to reaction sites and propagate the reaction within the network after removal of UV irradiation. However, the reaction in the film prepared with the higher level of initiator was restricted by limited diffusion of reactants and achieved a lower % conversion. In fact, no post-curing was detected in the 0.50% BME system (Fig. 9). The

mechanism of diffusion rate-limited conversion is further supported by the real-time microviscosity data (Fig. 5) which show that as it cures the 0.50% BME system became more viscous or had less free volume, inhibiting the intramolecular rotation of DCVJ leading to greater fluorescence.

The DMTA measurement revealed that prepolymer I films with 0.05% BME have lower crosslinking density compared to those with 0.50% BME, as shown by the lower storage modulus in the rubbery states in Fig. 6. Due to the formation of a less dense network in the presence of lower initiator concentrations, these films have larger free volumes or flexibility and therefore reactants will have greater diffusivity to achieve higher conversion. This prediction is also consistent with the leaching and swelling studies. As shown in the real-time FTIR studies, approx. 35% unreacted prepolymer I remained in the system (0.50% BME), while the leachate only consisted of 2%. Due to the higher crosslinking density and lower flexibility of the prepolymer I films with higher BME concentrations, films prepared with 0.50% BME did not swell as much as the 0.05% BME films. The leaching process was kinetically limited by slow diffusion from the more tightly crosslinked network. The water vapor transmission studies could not distinguish the differences between the films prepared with different BME concentrations. However, there is rank order correlation between film flexibility and water vapor transmission.

5. Conclusions

Using the methodology described in this paper, polymers intended for solvent-free UV-curable coating can be evaluated. Real-time FTIR provides an effective tool to monitor the degree of prepolymer conversion during UV curing. DMTA and microviscosity measurements are very useful in providing information about the network structure and properties. Although more indirect, leaching and swelling measurements provide consistent results with the above three methods. In general, leaching and swelling results are dependent on a number of variables. This

makes these methods less reliable in evaluating networks; however, they can be used as secondary evidence in support of FTIR and DMTA results.

It is very desirable to achieve 100% conversion so as to reduce the amount of unreacted components and optimize the properties of the coatings. Based on our studies, two approaches can be applied to improve prepolymer to polymer conversion. One is to use a prepolymer that has a flexible backbone such as prepolymer II which can form a flexible network with a much lower T_g than the reaction temperature. In addition, a reduction in the crosslinking density of the formed networks results in a similar decrease in T_g . Using a reaction temperature above the T_g will assure that the film remains in its rubbery state throughout the course of the reaction thereby increasing diffusivity of reactive polymer chains and achieving higher conversion. Alternative approaches are to raise the reaction temperature far above the T_g of the network or add plasticizers to the system.

Acknowledgements

The authors wish to thank the University of Connecticut Research Foundation, American Cyanamid, and the American Association of Colleges of Pharmacy for funding this project and Loctite Corporation for their generous donation of the preformulated norbornenylpolydimethylsiloxane fluid. The technical support and helpful comments of Dr Michael S. Bradley are greatly appreciated. The authors would also like to thank Mr John Krech, Dr James Rusling, Dr Suga and Dr Montgomery Shaw for technical support and use of equipment.

References

- American Dental Association, Council of dental materials, instruments and equipments, visible light-cured composites and activating agents. *J. Am. Dent. Assoc.*, 110 (1985), 100–103.
- Bachmann, A.G. and Alvarez, R.T., UV curing adhesives for medical device assembly. *Med Device. Technol.*, May (1992) 22–26, 28, 20, 32–35.
- Bogner, R.H., Lui, J.C. and Chien, Y.W., Kinetics of curing and physicochemical behavior of silicone membrane. *Int. J. Pharm.*, 42 (1988) 199–209.
- Dahl, T.C. and Sue, I.T., The effects of heat and desiccation treatment on the controlled release properties of aqueous silicone latex coated tablets. *Drug Dev. Ind. Pharm.*, 16 (1990) 2097–2107.
- Decker, C., UV curing chemistry: Past, present and future. *J. Coat. Technol.*, 59 (1987) 97–106.
- Decker, C., Fizet, M. and Faure, J., O₂ effects on UV curing and photodegradation of organic coatings. *Org. Coat. Plas. Chem.*, 42 (1980) 710–715.
- Dempsey, D., Thirucote, R., Sharge, L. and Dasse, K., Development of a novel UV curable polyurethane drug delivery matrix: Characterization of chlorhexidine gluconate wound dressings. *Proc. Int. Symp. Controlled Release Bioact. Mater.*, 17 (1990) 455–456.
- Joshi, H.N., Kral, M.A. and Topp, E.M., Microwave drying of aqueous tablet film coatings: A study on free films. *Int. J. Pharm.*, 51 (1989) 19–25.
- Kislalioglu, M.S. and Banker, G.S., Factors affecting diffusional controlled release from aqueous pseudolatex generated film coatings. *Proc. Int. Symp. Controlled Release Bioact. Mater.*, 11 (1984) 6–7.
- Kloosterboer, J.G., Network formation by chain crosslinking photopolymerization and its applications in electronics. *Adv. Polym. Sci.*, 84 (1988) 1–61.
- Kutal, C., Grutsch, P.A. and Yang, D.B., A novel strategy for photoinitiated anionic polymerization. *Macromolecules*, 24(1991) 6872–6873.
- Li, L.C. and Peck, G.E., Water based silicone elastomer controlled release tablet coating: V. A statistical approach. *Drug Dev. Ind. Pharm.*, 17 (1991) 27–37.
- Li, L.C. and Peck, G.E., Water based silicone elastomer controlled release tablet coating: IV. The effect of tablet shapes. *Drug Dev. Ind. Pharm.*, 18 (1992) 333–343.
- Loutfy, R.O., Fluorescence probes for polymerization reactions: Bulk polymerization of styrene, *n*-butyl methacrylate, ethyl methacrylate, and ethyl acrylate. *J. Polym. Sci. Polym. Phys. Ed.*, 20 (1982) 825–835.
- Loutfy, R.O., High-conversion polymerization fluorescence probes: 1. Polymerization of methyl methacrylate. *Macromolecules*, 14 (1981) 275–279.
- Otsubo, Y., Amari, T. and Watanabe, K., Rheological behavior of epoxy acrylate prepolymer during UV curing. *J. Appl. Polym. Sci.*, 29 (1984) 4071–4080.
- Phillips, R., *Sources and Applications of Ultraviolet Radiation*, Academic Press, London, 1983, p. 67.
- Roffey, C.G., *Photopolymerization of Coatings*, Wiley, New York, 1982, pp. 230–259.
- Shahidi, I.K. and Powanda, T.M., Ultraviolet curing: A review of the technology. *Am. Inkemaker*, 53 (1975) 20–21, 23–24, 26, 46.
- Sperling, L.H., *Introduction to Physical Polymer Science*, 2nd Edn, Wiley, New York, 1992, p. 311.
- Sprockel, O.L., Prapaitrakul, W. and Shivanand, P.J., Permeability of cellulose polymers: Water vapor transmission rates. *J. Pharm. Pharmacol.*, 42 (1990) 152–157.

- Tan, E.L., Liu, J.C. and Chien, Y.W., Controlled drug release from silicone coated tablets: Preliminary evaluation of coating techniques and characterization of membrane permeation kinetics. *Int. J. Pharm.*, 42 (1988) 161–169.
- Thanawalla, C.B. and Victor, J.G., Reactivity of some acrylates in UV formulations versus extent of their cure. *J. Rad. Curing*, October (1985) 2–8.
- Woodruff, C.W., Peck, G.E. and Banker, G.S., Effects of solids-loading on moisture permeability coefficients of free films. *J. Pharm. Sci.*, 61 (1972) 1956–1959.
- Yang, D.B., Kinetic studies of photopolymerization using real time FT-IR spectroscopy. *J. Polym. Sci., A: Polym. Chem.*, 31 (1993) 199–203.