

Effects of Nonreactive Resins on the Properties of a UV-Curable Methacrylated Urethane Resin

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Received 22 September 1997; accepted 22 January 1998

ABSTRACT: The effects of two nonreactive conventional-type resins, a bisphenol-A-based phenoxy resin PAPHEN-301 and aromatic-based PETROLEUM RESIN, on the mechanical, thermal, and physical properties of methacrylated urethane resin-based UV-curable formulations were studied. A methacrylated urethane prepolymer was synthesized from isocyanatoethyl methacrylate (IEM) and polytetrahydrofurandiol (PTHF) via a one-step reaction. An increase in PAPHEN-301 content caused an increase both in tensile strength and elongation values of UV-cured polymeric films. On the other hand, an increase in PETROLEUM RESIN content caused a decrease both in tensile strength and elongation values of the polymeric films. However, thermooxidative properties were not affected by the introduction of either resin. It was also found that the water-absorption capacities of the UV-cured methacrylated urethane films depended on the type and amount of the nonreactive resins. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1837–1845, 1998

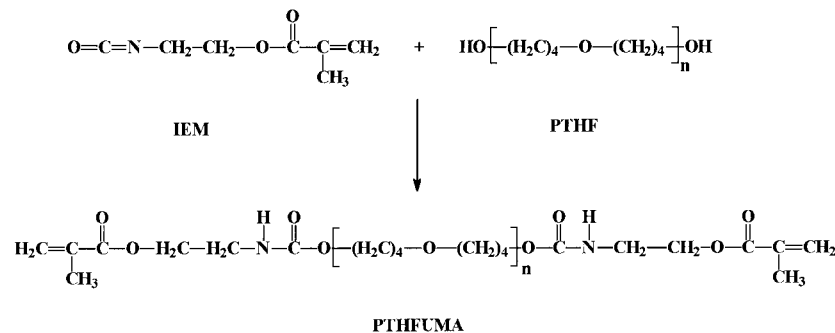
Key words: UV-curable resins; methacrylated urethanes

INTRODUCTION

Radiation-curable coating applications have been continuously increasing because of the many advantages of this technology including lower energy consumption, less environmental pollution, and very rapid curing even at ambient temperatures.^{1–3} In general, UV-curable coating formulations consist primarily of three major components: a reactive oligomer end-capped with an acrylic functional group, a mono- or polyfunctional reactive diluent, and a photoinitiator. Additionally, nonreactive additives such as pigments, adhesion

promoters, and surface active agents are also introduced into formulations depending on the specific application. Reactive oligomers are the major ingredients in these formulations which govern the mechanical properties of a UV-curable system.^{1–5} Acrylated urethane oligomers, as a class, have the potential to combine the high abrasion resistance, toughness, tear strength, and good low-temperature properties of polyurethanes with the superior optical properties and weatherability of polyacrylates.^{1–5} In general, commercial acrylated urethane oligomers are synthesized by a two-step reaction procedure. In these systems, polyols are first reacted with diisocyanates, such as toluene diisocyanate (TDI), slightly below twice the equivalent amount. In the second stage, the remaining isocyanate groups are capped with

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Scheme 1

hydroxyl groups containing methacrylates, such as hydroxyethyl methacrylate.

Nitrocellulose is one of the oldest and widely used gloss-providing decorative resins for printing and coating applications. In our previous work,⁶ it was demonstrated that nitrocellulose could be successfully introduced into the UV-curable formulations as a nonreactive component.

In this work, a methacrylated urethane prepolymer was synthesized from isocyanatoethyl methacrylate (IEM) and polytetrahydrofurane-diol (PTHF) which constituted the soft-segment component (Scheme 1). To make use of their inherent properties in a UV-curing system, two other nonreactive resins, one aromatic hydrocarbon and one phenoxy-based, respectively, PETROLEUM RESIN and PAPHEN-301, were introduced into the UV-curable resin formulations at varying amounts between 5 to 20 wt %. PETROLEUM RESIN is an aromatic hydrocarbon resin which is widely used in the printing ink industry. It is compatible with different types of resins and is soluble in a large variety of common solvent systems. It has a low viscosity and is used to obtain the required rheological properties⁷ in ink formulations.

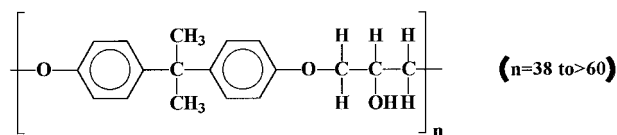
PAPHEN-301 is a tough, ductile thermoplastic resin with good cohesive strength and good impact resistance. Its ether linkage and pendant hydroxyl groups promote wetting and bonding to polar substrates and fillers. It is compatible with many polymers and is an efficient flexibilizer for crosslinked formulations. It improves the performance of metal primers and coatings for metal, wood, and flexible substrates. It imparts outstanding properties in magnetic tape, adhesive, and molding and extrusion applications. It is useful as a plastic additive to enhance the structural integrity of plastic systems and contributes to polymer alloy properties⁸ (Scheme 2).

Due to its powerful solvating effect, *N*-vinyl-2-pyrrolidone (NVP) was used as the reactive diluent. Diethylene glycol dimethacrylate (DEGDA) was used as the crosslinking agent. Isobutyl benzoin ether (IBuBE) and dibutyltin dilaurate (DBTDL) were used as the photoinitiator and catalyst, respectively.

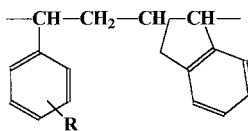
EXPERIMENTAL

Materials

Isocyanatoethyl methacrylate (IEM, Dow Chemical Co., Midland, MI) was used without further purification. Purity was determined analytically to be 99.3%.⁹ Polytetrahydrofuranediol (PTHF, BASF Inc., Ludwigshafen, Germany) was dried under a vacuum before use. Its hydroxyl number was determined to be 104 mg KOH/g.¹⁰ *N*-Vinyl-2-pyrrolidone (NVP, GAF Corp., Surrey, England) was dried over a 4 Å molecular sieve before use.



PAPHEN-301



PETROLEUM RESIN

Scheme 2

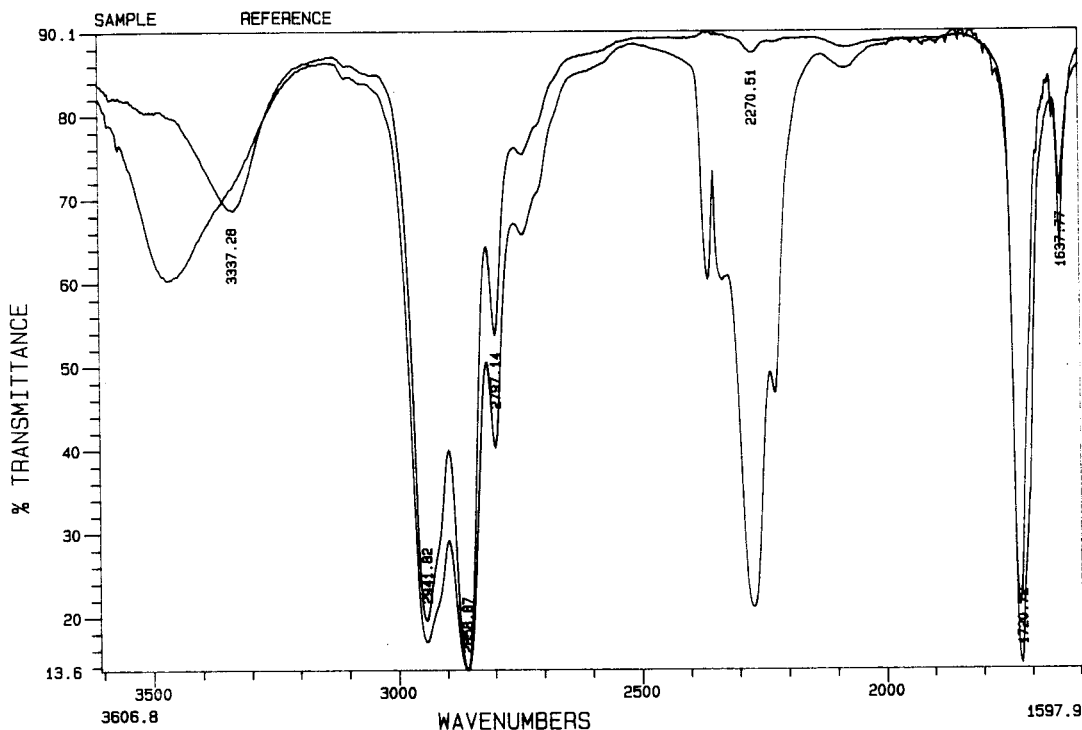


Figure 1 Disappearance of the characteristic —NCO peak at 2275 cm^{-1} in the FTIR spectrum.

Diethyleneglycol dimethacrylate (DEGDA, Poly-science, Inc. Warrington, PA), PAPHEN-301 (Phenoxy Associates, Rock Hills, SC), and PETROLEUM RESIN (Gibaka Trading & Industrial Co., Zoetermeer, Holland) were used as received. Isobutyl benzoin ether (IBuBE, Stauffer Chemicals, Westport, CT) and dibutyltin dilaurate (DBTDL, Merck, München, Germany) were used without further purification.

Preparation of IEM/PTHF Prepolymer

PTHF (20.00 g, 0.0396 mol) was charged into a flame-dried three-necked 250-mL round-bottom flask equipped with a nitrogen inlet and a dropping funnel. DBTDL (0.08% by weight) was added into the reaction flask as a catalyst and the contents of the flask were stirred by a mechanical stirrer. The reaction temperature was kept between 15 and 20°C with a temperature-controlled water bath. IEM (6.76 g, 0.0396 mol) was added dropwise to the reaction mixture over a period of 1 h. The reaction was completed after 8 h. Completion of the reaction was confirmed by the disappearance of the characteristic —NCO peak at 2275 cm^{-1} in the FTIR spectrum (Fig. 1). The reaction scheme of the IEM/PTHF oligomer polytetrahydrofuran ura-

thane methacrylate (PTHFUMA) is shown in Scheme 1.

Sample Preparation for Characterization

The formulations of UV-curable methacrylated urethane systems were prepared by mixing the PTHFUMA oligomer with NVP and IBuBE homogeneously. The amounts of commercial resins added were varied from 5 to 20 wt % and the IBuBE concentration was kept constant at 2 wt %, all on the basis of the final formulation. Air bubbles formed during mixing were removed under a moderately reduced pressure at room temperature.

Polymeric films approximately $200\ \mu$ thick were prepared by pouring the viscous liquid formulations into a Teflon-coated mold. To decrease the viscosity and thus obtain a reasonable flow of the formulation, the experiment was conducted at 35°C . Moreover, to prevent the inhibition effect of oxygen, liquid formulations were covered with a $25\text{-}\mu$ -thick transparent Teflon film. Before irradiation, a quartz glass plate was placed over the Teflon film to obtain a smooth surface with the desired thickness. Finally, the formulation was irradiated for 210 s under a high-pressure UV

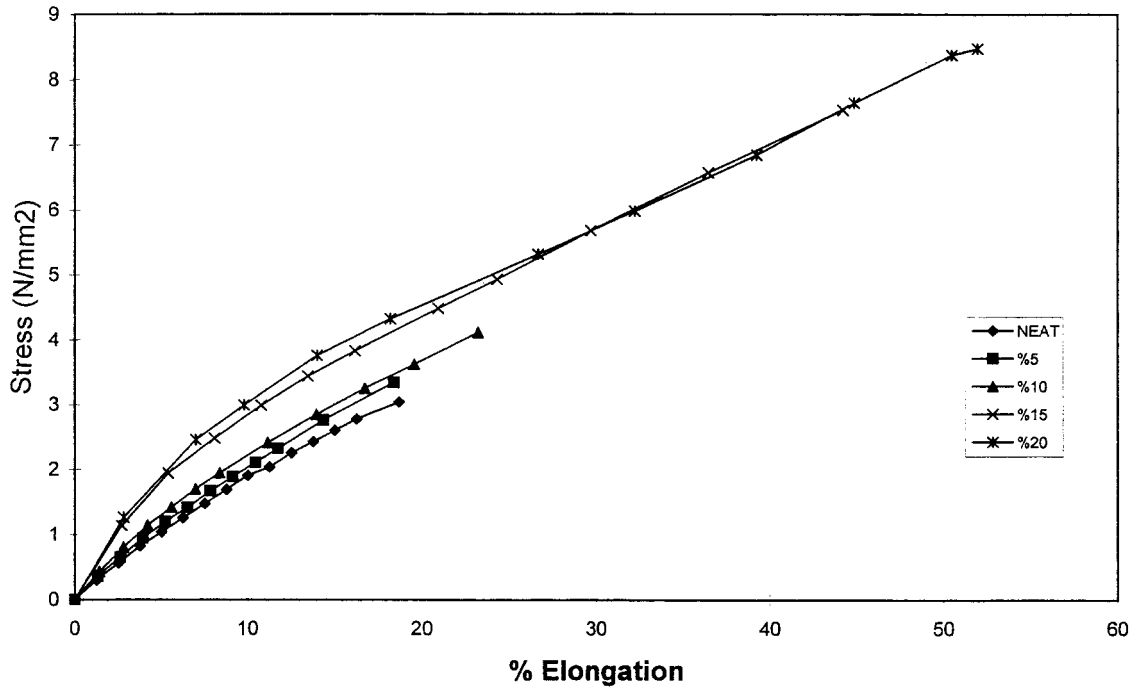


Figure 2 Effects of PAPHEN-301 content on tensile properties of PTHFUMA-based polymeric films (wt %).

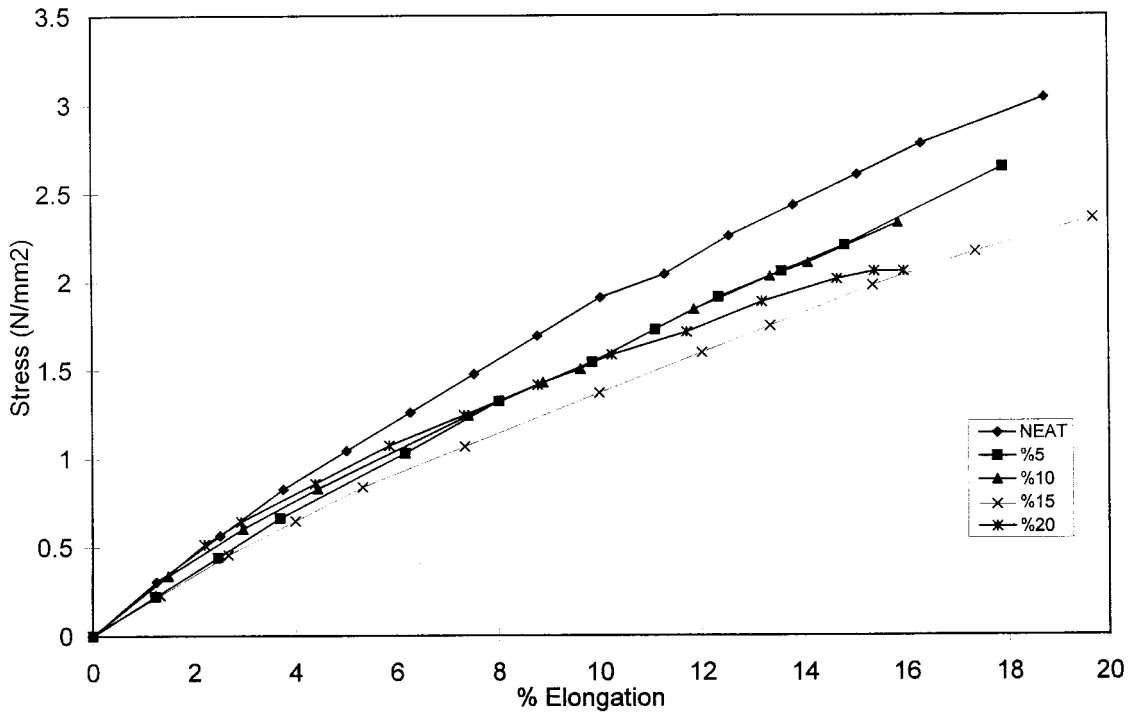


Figure 3 Effects of PETROLEUM RESIN content on tensile properties of PTHFUMA-based polymeric films (wt %).

Table I Effects of PAPHEN-301 Content on Tensile Properties of IEM/PTHF-Based Polymeric Films

Sample	Ultimate Tensile Strength (N/mm ²)	Elongation at Break (%)
68PTHFUMA/10DEGDA/ 20NVP/2IBuBE/0PAPHEN	3.04	18.73
63PTHFUMA/10DEGDA/ 20NVP/2IBuBE/5PAPHEN	3.34	18.43
58PTHFUMA/10DEGDA/ 20NVP/2IBuBE/10PAPHEN	4.12	23.20
53PTHFUMA/10DEGDA/ 20NVP/2IBuBE/15PAPHEN	7.54	44.23
48PTHFUMA/10DEGDA/ 20NVP/2IBuBE/20PAPHEN	8.48	51.96

lamp (OSRAM-300W). The exposure time of 210 s was initially determined in a separate experiment for the disappearance of unsaturated methacrylates. For quantification, a 763 cm⁻¹ band which was raised by aromatic rings within IBuBE was used as an internal standard against the 810 cm⁻¹ band of the unsaturated methacrylate.

Characterization

The gel content¹¹ of the UV-cured samples were determined by Soxhlet extraction for 12 h using an acetone–toluene solution (1/1, v/v). The insoluble gel fraction was dried under a vacuum for 24

Table II Effects of PETROLEUM RESIN Content on Tensile Properties of the IEM/PTHF-Based Polymeric Films

Sample	Ultimate Tensile Strength (N/mm ²)	Elongation at Break (%)
68PTHFUMA/10DEGDA/ 20NVP/2IBuBE/0PET.RES	3.04	18.73
63PTHFUMA/10DEGDA/ 20NVP/2IBuBE/5PET.RES	2.65	17.89
58PTHFUMA/10DEGDA/ 20NVP/2IBuBE/10PET.RES	2.33	15.86
53PTHFUMA/10DEGDA/ 20NVP/2IBuBE/15PET.RES	2.36	19.69
48PTHFUMA/10DEGDA/ 20NVP/2IBuBE/20PET.RES	2.06	15.97

h at 60°C and was weighed to calculate the gel content.

Stress–strain measurements¹² were performed on UV-cured free films using an Instron tensile testing machine according to ASTM D 882-91. All stress–strain measurements were carried out uniaxially at ambient conditions.

The UV-cured samples were dried for 24 h at 50°C before immersing them into deionized water at 25 ± 0.5°C for 24 h. The water-absorption capacities¹³ of the cured samples were calculated from the weight differences between the water-swollen and dry films.

Thermal characterization of the UV-cured polymeric films with and without the nonreactive resins were determined by a DuPont 990 modular thermal analyzer system. Thermogravimetric analysis (TGA) was performed using a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min in air. Glass transition temperatures were determined by a DuPont 910 differential scanning calorimeter (DSC). Scans were run at a heating rate of 10°C/min under a nitrogen purge at a rate of 30 cm³/min. The reported values were obtained from a second heating after quenching with liquid nitrogen.

Table III Effect of Nonreactive Resin Content on Water Absorption of Polymeric Films

Sample	Water Absorption (wt %)
68PTHFUMA/10DEGDA/ 20NVP/2IBuBE/0PAPHEN	8.8
63PTHFUMA/10DEGDA/ 20NVP/2IBuBE/5PAPHEN	9.2
58PTHFUMA/10DEGDA/ 20NVP/2IBuBE/10PAPHEN	14.1
53PTHFUMA/10DEGDA/ 20NVP/2IBuBE/15PAPHEN	17.2
48PTHFUMA/10DEGDA/ 20NVP/2IBuBE/20PAPHEN	18.8
68PTHFUMA/10DEGDA/ 20NVP/2IBuBE/0PET.RES	8.8
63PTHFUMA/10DEGDA/ 20NVP/2IBuBE/5PET.RES	8.6
58PTHFUMA/10DEGDA/ 20NVP/2IBuBE/10PET.RES	8.6
53PTHFUMA/10DEGDA/ 20NVP/2IBuBE/15PET.RES	8.6
48PTHFUMA/10DEGDA/ 20NVP/2IBuBE/20PET.RES	8.6

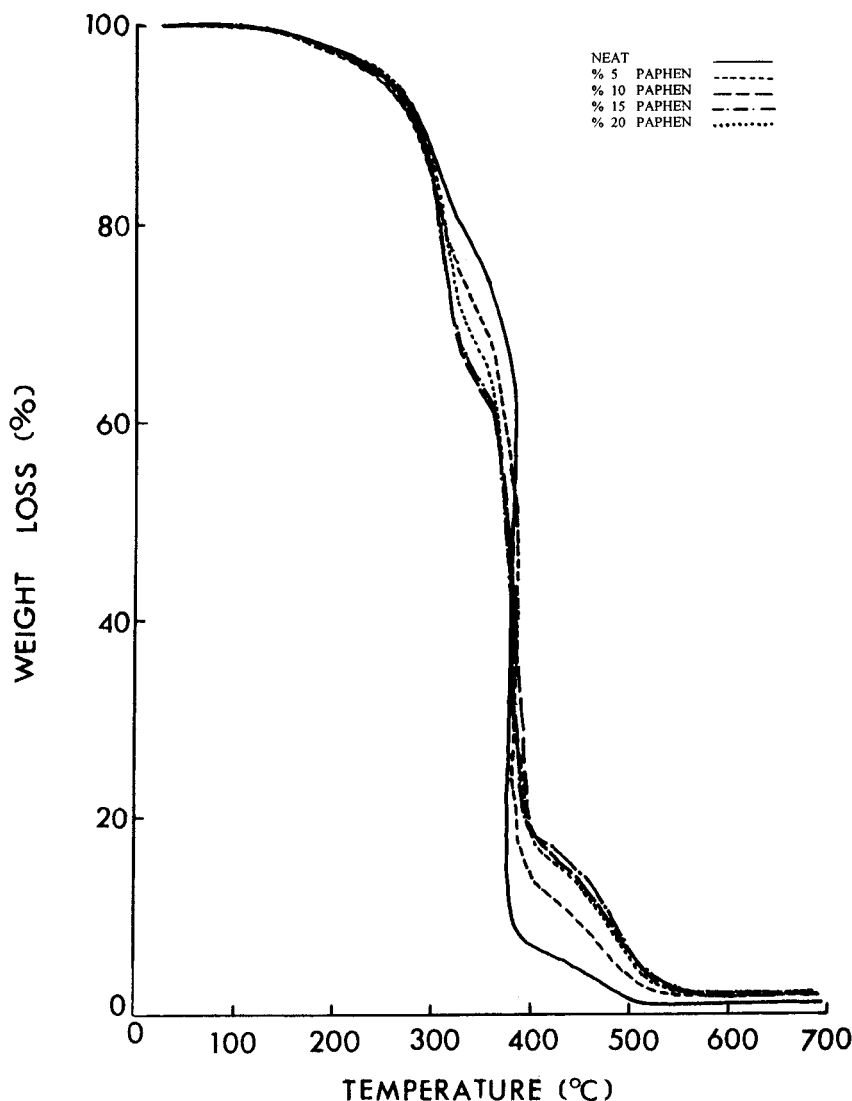


Figure 4 TGA thermograms of PAPHEN-301-based polymeric films.

RESULTS AND DISCUSSION

The compositions of the UV-curable methacrylated urethane formulations were changed by varying the content of two different nonreactive resins and PTHFUMA while keeping other ingredients (NVP, IBuBE, DEGDA) constant. The numbers in front of the designation codes used in the tables represent the weight percent content of each component of the final formulation.

The amount of the nonreactive resins were found to have a considerable effect on the mechanical properties of the UV-cured polymeric films. Stress-strain curves for two different nonreactive resins are shown in Figures 2 and 3 and the corresponding values are given in Tables I and II.

After 210 s of irradiation, the gel contents of all UV-cured urethane methacrylate films, except for the 20% PETROLEUM RESIN-containing film, were found to be 96%.

The addition of the nonreactive resins, namely, PAPHEN-301 and PETROLEUM RESIN, up to 20 wt % into the formulations showed different trends. Increase in the PAPHEN-301 concentration caused an increase in both the tensile strength and elongation while an increase in the PETROLEUM RESIN content caused a decrease both in the tensile strength and elongation of the UV-cured films. However, the elongation value (19.69) for the 15% PETROLEUM RESIN-containing film is an exception which cannot be explained.

Water-absorption values are given in Table

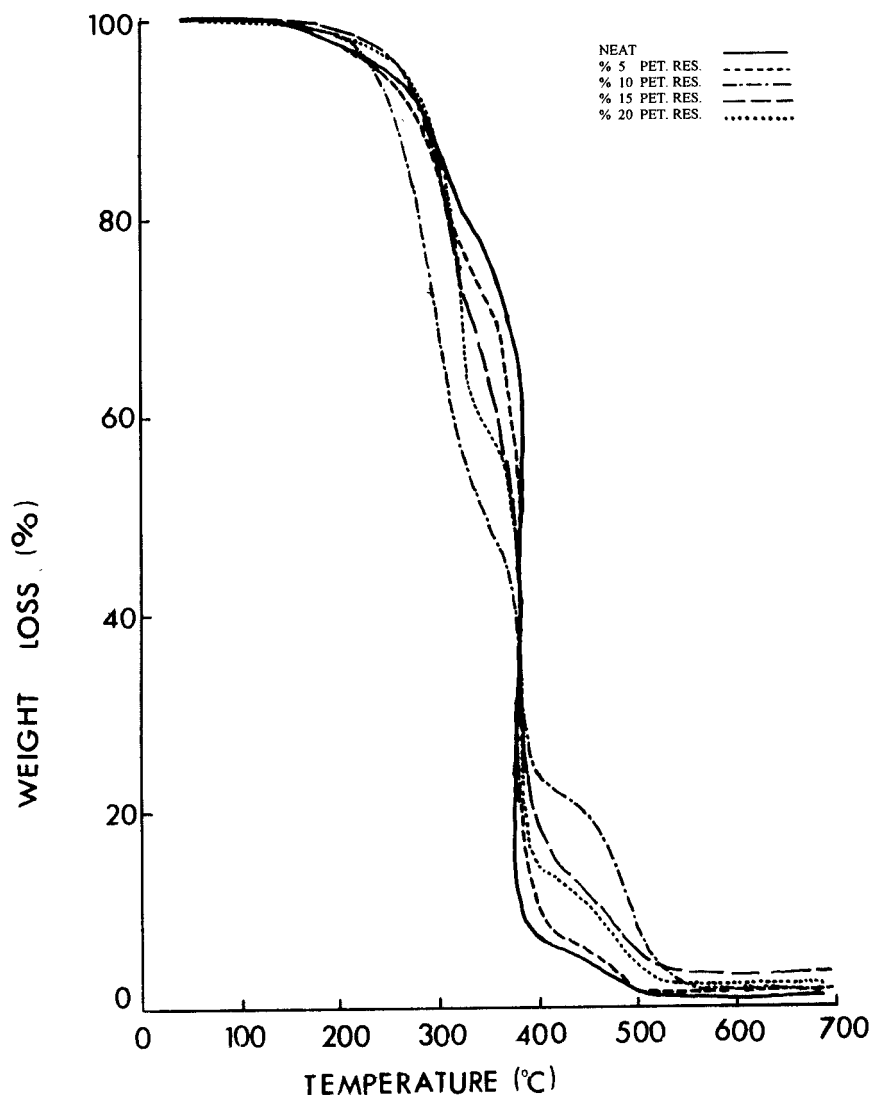


Figure 5 TGA thermograms of PETROLEUM RESIN-based polymeric films.

III. The water-absorption values for PAPHEN-301 were increased with the nonreactive resin content but there was no effect for PETROLEUM RESIN. These results can be explained by the chemical structures of the resins. The presence of hydroxyl groups and ether linkages in the structure of PAPHEN-301 increases the hydrophilicity, resulting in an increase in the absorption of water via strong hydrogen bonding. Since PETROLEUM RESIN does not contain any polar functional groups which can form hydrogen bonding with water, as expected, the water-absorption values of these formulations were relatively unaffected by an increasing PETROLEUM RESIN content.

TGA curves of the samples containing PAPHEN-301 and PETROLEUM RESIN are shown in Figures 4 and 5. As seen from these figures, the above-mentioned resins do not have any distinguishable effect on the thermooxidative stabilities of UV-cured neat films. All the films showed an approximately 5% weight loss at around 200°C and decomposed rapidly at around 300°C.

CONCLUSION

UV-curable ether-based, flexible methacrylated urethane resins were synthesized from PTHF and IEM in a one-step reaction. It was shown that two

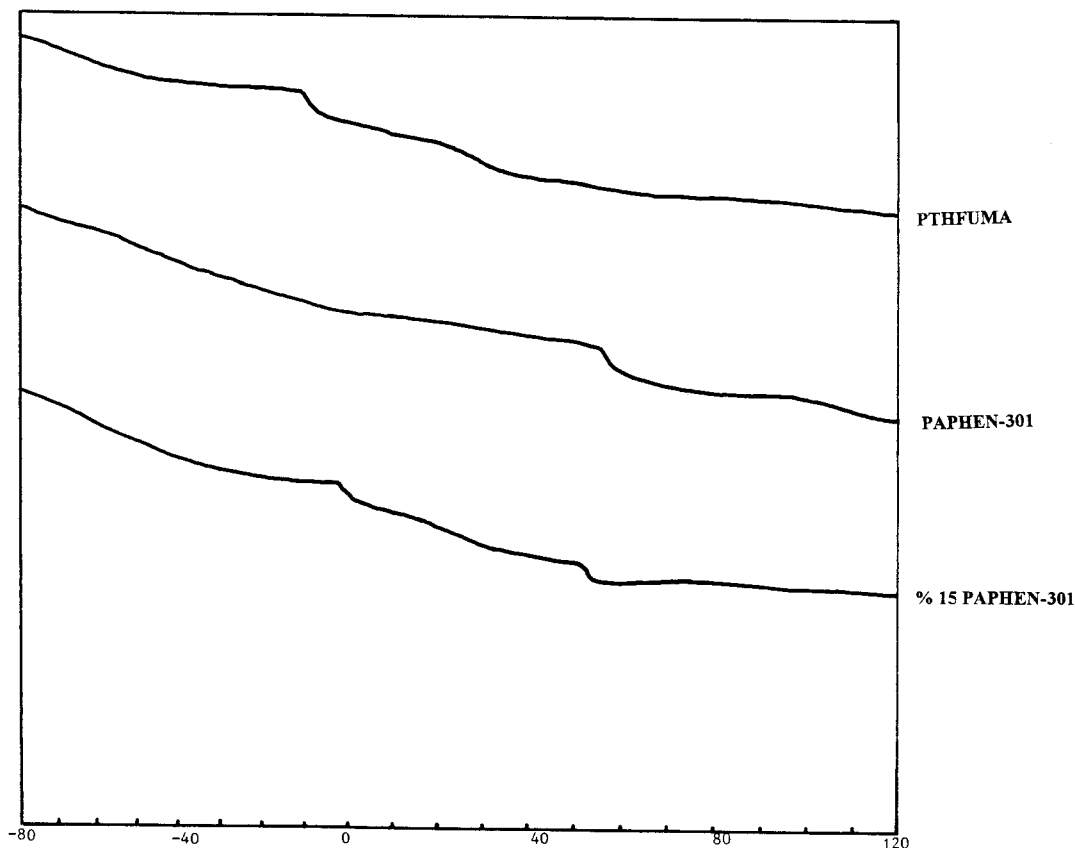


Figure 6 DSC thermograms of PTHFUMA, PAPHEN-301, and 15% PAPHEN-containing polymeric films.

nonreactive commercial resins with considerably different chemical structures can successfully be introduced into the above-mentioned UV-curable methacrylated urethane formulations via utilizing the powerful solvating effect of NVP.

All the films containing nonreactive resins showed good clarity and flexibility. The gel contents of the films prepared from neat resin and the 20% PAPHEN-containing formulation were both found to be 96%, while the gel content of the 20% PETROLEUM RESIN containing film was 80%. This can be attributed to the trapping of PAPHEN-301 in the network due to its higher polarity and much higher molecular weight compared to the PETROLEUM RESIN ($M_n = 10,000$ – $16,000$ g/mol for PAPHEN-301⁸ and $M_n = 1100$ g/mol for PET.RES⁷) and as well to the formation of intermolecular hydrogen bonding in the urethane matrix. This fact was supported by the DSC curves of the related resins, namely, the PTHFUMA, PAPHEN-301, and 15% PAPHEN-containing one. As can be seen from Figure 6, the

T_g of PTHFUMA at -11°C increased to 2°C for the 15% PAPHEN-containing formulation due to the intermolecular attractions, while there was no significant change for the T_g of PAPHEN.

While an increase in PAPHEN concentration caused an increase in both tensile strength and elongation, an increase in the PETROLEUM RESIN content caused a decrease both in the tensile strength and elongation of the UV-cured films. The introduction of PAPHEN-301 into the formulation, distinctly increased the water-absorption properties of the UV-cured films prepared from the neat resin. On the other hand, PETROLEUM RESIN showed almost no effect. The thermooxidative stabilities of the UV-cured films were relatively unaffected by the concentration of the nonreactive diluents.

The authors are pleased to acknowledge Phenoxy Associates (Rock Hill, SC) BASF, GAF Corp. (U.S.A.), Stauffer Chemicals Corp. (U.S.A.), and Gibaka Trading & Industrial Corp. (Zoetermeer, Holland) for their kind

support for the chemicals and Banu Yaşar, Mr. Zekayi Korlu, and Mr. Mustafa Candemir for their technical assistance.

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