

Ultraviolet-Curing Behavior and Mechanical Properties of a Polyester Acrylate Resin

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Received 12 August 2003; accepted 4 November 2003

ABSTRACT: Ultraviolet (UV) curing technology has been widely used in many applications because it has several distinct advantages compared to solvent-based processes or thermal-curing technology. The effects of photoinitiator types and their contents as well as reactive diluent types and their contents on the UV-curing behavior and mechanical properties of a UV-curable polyester acrylate resin were investigated in this study. Three photoinitiators, Irgacure 184, Darocur 1173, and benzophenone, were used in this study. Hexanediol diacrylate, tripropylene glycol diacrylate,

and trimethylol propane triacrylate were used as reactive diluents to modify the properties of the acrylate resin. The change of chemical structure during UV curing was monitored by FTIR. A universal testing machine was used to measure the tensile properties of various UV-cured acrylate films of different compositions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3921–3928, 2004

Key words: UV curing; polyester acrylate; films; mechanical properties; initiators

INTRODUCTION

Ultraviolet (UV) radiation technology is widely used in many industrial applications including electronics, chemicals, water and food treatment, as well as medical treatment. UV radiation technology includes curing of monomeric or oligomeric materials with the aid of UV light. UV light initiates free-radical polymerization with very low activation energy. This allows high polymerization rates at room temperature because the rates are not temperature dependent in the early stages.¹ The principal uses of photopolymers are coatings, specialty films, paints, varnishes, inks, and adhesives, and the most common chemicals used for such applications are acrylates.

UV light-initiated polymerizations are precise reactions that require a match between the wavelength of the light source and the light-absorbing and reacting molecules. A direct relationship exists between the chemical structure of a particular molecule and the UV light energy that it is capable of absorbing.² UV sources can be capable of producing high power radiation from the near UV ($\lambda = 354$ nm) to the vacuum UV ($\lambda = 108$ nm).^{3–7} Suitable light sources for photopolymerization and photocuring are light sources with emission in the range of wavelengths from 254 to 450 nm.⁸

The UV-curing process is a very attractive alternative to conventional curing processes because it offers

several distinct advantages over solvent-based processes or thermal-curing processes^{9–12}: high-speed, operation at room temperature, lower energy consumption, and environmental compatibility. The liquid resin is transformed in a very short time into a solid polymer that is absolutely insoluble in organic solvents and has a high level of thermal and mechanical properties.¹³ Monomers determine the properties of reacting systems and final cured products by their chemical structures.¹⁴ Apart from the monomers there are other factors that influence the photopolymerizations, such as photoinitiator type and its concentration, reactive diluent type and its concentration, presence of oxygen, temperature, spectral distribution, and intensity of UV light source.^{15–17}

Photocuring processes usually occur in two stages.¹⁸ The primary reaction is that which is directly ascribed to the absorbed photons or quanta involving electronically excited states. This process has been found to be independent of temperature. The secondary reaction is the reaction of radicals, radical ions, ions, and electrons that are produced by the primary reaction. Thus, even after the UV light source is turned off, nonterminated radicals survive and can continue to propagate polymerization. The result of these secondary reactions can affect the physical properties of the finally cured polymer.

In this study the UV-curing behavior and mechanical properties of a UV-curable polyester acrylate resin system were investigated. The effects of photoinitiator types and their contents as well as reactive diluent types and their contents on the UV curing and mechanical properties of the polyester acrylate resin sys-

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tem were investigated. UV-curing behavior was analyzed using FTIR spectroscopy data and mechanical test data. Mechanical properties of UV-cured films made of the resin system were measured using a universal testing machine.

EXPERIMENTAL

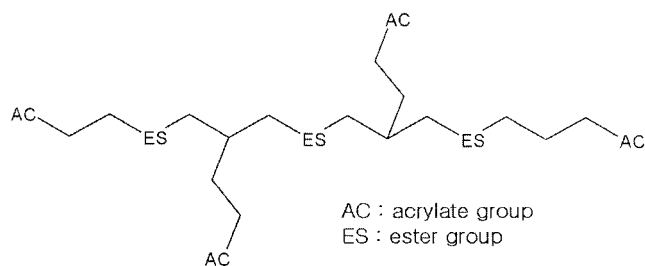
Materials

The UV-curable polyester acrylate resin (EB 80), having four acrylate functional groups per molecule, was supplied by SK-UCB Co. (Ulsan, Korea). The molecular weight of the resin was about 1000 and viscosity was 3000 cP at room temperature. Reactive diluents, having two functional groups, HDDA (hexanediol diacrylate) and TPGDA (tripropylene glycol diacrylate), and having three functional groups, TMPTA (trimethylol propane triacrylate), were supplied by SK-UCB Co. The reactive diluents were introduced to conveniently coat the resin on a suitable substrate by reducing the viscosity of the resin system before UV curing in the film-making process, and to modify the properties of UV-cured polymer films. The content of each reactive diluent was changed up to 40 phr (parts per hundred of the polyester acrylate resin). The chemical structures of the polyester acrylate resin and the reactive diluents are shown in Figure 1.

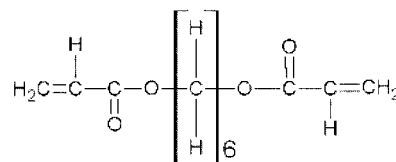
Photoinitiators used were Irgacure 184 (1-hydroxycyclohexyl acetophenone), Darocur 1173 (2-hydroxy-2-methyl-1-phenylpropan-1-one), and benzophenone, all supplied by SK-UCB Co. One of the photoinitiators was mixed with the acrylate resin system containing a reactive diluent in a mixer at room temperature. The content of each photoinitiator was changed up to 5 phr. The mixer was covered with aluminum foil to prevent premature polymerization that might occur by light exposure. The chemical structures of the photoinitiators are shown in Figure 2.

UV-curing instruments

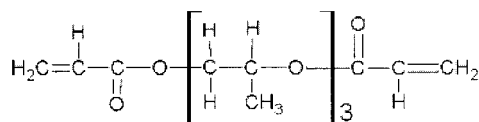
Two UV cabinets, one (UVItec CL-508G Cabinet, UVItec Ltd., Cambridge, UK), having five 8-W UV lamps, and the other (UVC-925 UV Multi-Purpose Cabinet, Myungsung Science Co., Busan, Korea), having five 25-W UV lamps, respectively, were used to cure the acrylate resin systems. Each lamp in the cabinets radiates UV light having a wavelength of 254 nm. The UV intensity at the position where UV curing proceeds was 1.24 mW/cm² for the cabinet having 8-W lamps and 5.45 mW/cm² for the cabinet having 25-W lamps. The acrylate resin system containing one of the photoinitiators was coated on a glass plate, using a bar applicator, to obtain a film about 80 μm thick, and cured immediately in one of the UV cabinets.



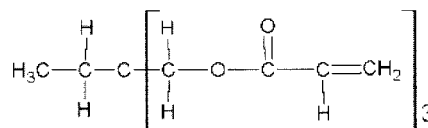
Polyester acrylate resin (EB80)



Hexanediol diacrylate (HDDA)



Tripropylene glycol diacrylate (TPGDA)

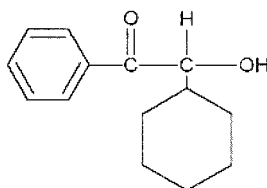


Trimethylol propane triacrylate (TMPTA)

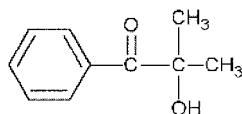
Figure 1 Chemical structures of the polyester acrylate resin and the reactive diluents.

FTIR spectroscopy

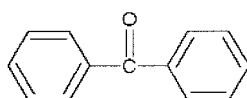
One of the most commonly used techniques to analyze UV-curing processes is FTIR spectroscopy, which gives information on the chemical structure change of a UV-curing system by monitoring the IR absorption spectra. Infrared spectra of the acrylate resin systems containing one of the photoinitiators were measured during UV curing with an FTIR spectrophotometer (Bomem MB100, Bomem Inc., Quebec, Canada) in the wavenumber range of 4000–400 cm⁻¹. An acrylate resin sample, coated on a KBr plate and cured in the UV cabinet having 8-W lamps, was removed from the cabinet sequentially with a proper time interval, and analyzed immediately by FTIR. During the UV-curing process, the chemical structure of the acrylate resin changes and so do the IR spectra. By monitoring the disappearance of the specific IR absorption for a functional group, the chemical conversion of the acrylate resin can be determined.¹⁹



1-Hydroxycyclohexyl acetophenone (Irgacure 184)



2-Hydroxy-2-methyl-1-phenylpropan-1-one (Darocur 1173)



Benzophenone

Figure 2 Chemical structures of the photoinitiators.

Universal testing machine (UTM)

Thin films were prepared by coating the acrylate resin systems on each glass plate followed by UV curing in

the UV cabinet having five 25-W UV lamps. Tensile tests of the acrylate films were performed according to ASTM D-882 using a UTM (LR-30K, JJ Lloyd Instruments, Hampshire, UK) at a crosshead speed of 10 mm/min. An average of at least five measurements was taken to report the tensile properties of the acrylate films. Dimensions of film specimens for tensile tests were $15 \times 5 \times 0.08$ mm.

RESULTS AND DISCUSSION

FTIR spectroscopy was used to observe the change of chemical structure during a UV-curing process of the acrylate resin system containing 1 phr of Irgacure 184. At first the content of the photoinitiators was fixed to 1 phr by referring to the recommendations reported in the literature.^{18,19} The UV-curing process of the resin system was carried out in the UV cabinet having five 8-W UV lamps. The IR spectra of the resin system obtained during curing at various curing times are shown in Figure 3. The absorption peak at 810 cm^{-1} , attributed to the alkene CH stretching in the acrylate resin, became almost negligible after UV curing for 180 min. The other absorption peaks at 984 cm^{-1} (vinyl group, $\text{CH}_2=\text{CH}-$), 1408 cm^{-1} ($\text{CH}_2=\text{CH}$), and 1635 cm^{-1} (acrylic group, $\text{C}=\text{C}$) also gradually disappeared with UV-curing time. It took a relatively long time to cure the resin system using the cabinet because the UV radiation power of the cabinet was low. However, the slow UV-curing process was reasonable in monitoring UV-curing behavior of the resin system.

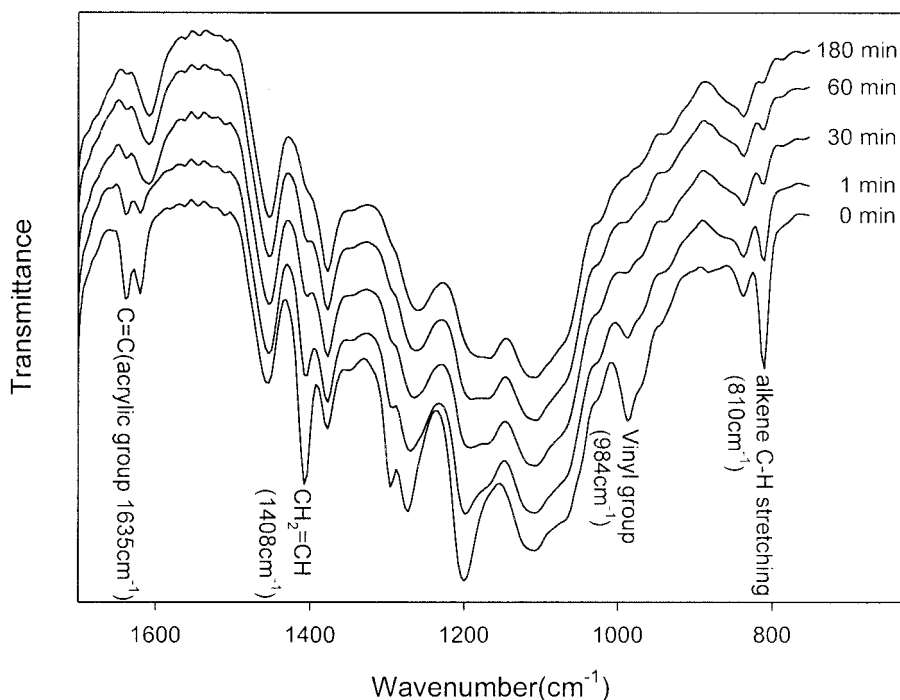


Figure 3 FTIR spectra of the acrylate resin system at different UV curing times. The cabinet having five 8-W UV lamps was used to cure the resin system.

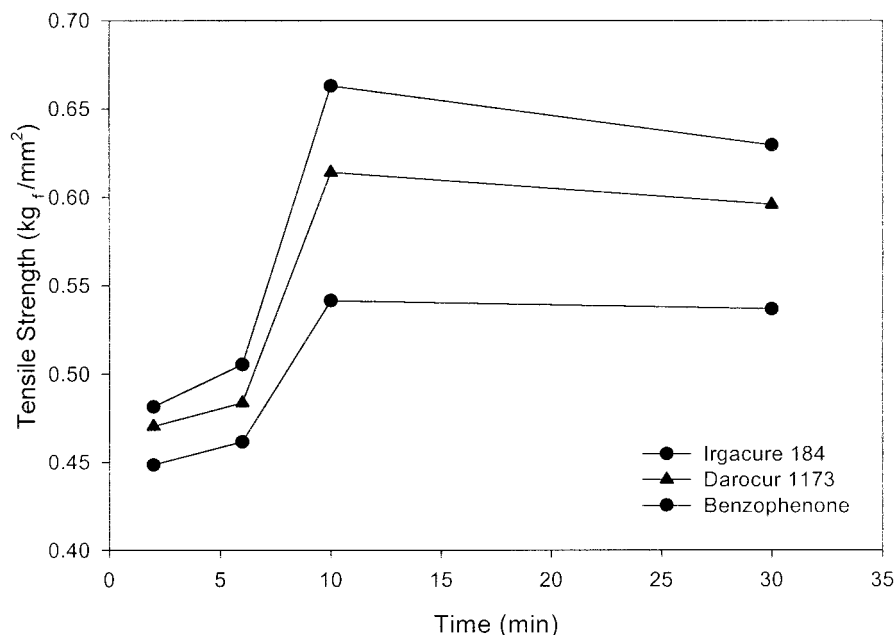


Figure 4 Tensile strength versus UV curing time for the acrylate films containing different photoinitiators. The films were cured for 10 min using the cabinet having five 25-W UV lamps.

From the FTIR spectra, it was confirmed that the photopolymerization of the acrylate resin could be finished in about 180 min when the UV cabinet of lower UV power was used.

Figure 4 shows the tensile strength of the acrylate films cured using the cabinet having five 25-W UV lamps as a function of UV-curing time. Various types of photoinitiators were added to the acrylate resin, in a sequence of experiments, to investigate the effect of photoinitiator type on the mechanical properties of the acrylate films. As shown in Figure 4, the tensile strength of the acrylate films, cured by the photoinitiation of Irgacure 184, Darocur 1173, and benzophenone, respectively, increased with UV-curing time until about 10 min, and after 10 min the tensile strength of the acrylate films did not increase with UV-curing time. FTIR analysis provided evidence that the UV-curing reaction under this condition was finished within 10 min. From this result, it was considered that a curing time of about 10 min is adequate for attaining good mechanical properties of acrylate resin systems when the UV cabinet of higher UV power was used. To obtain high chemical conversion is very important for good physical properties of polymers produced by step polymerization because the physical properties of polymers increase drastically at high conversion range. Therefore, attaining high conversion is also important for the acrylate resin system used in this study because the resin system also polymerizes by step polymerization to produce network polymers.

The effect of photoinitiator type on the tensile strength of the acrylate films is also shown in Figure 4.

By comparing the three sets of tensile strength data for the acrylate films cured for at least 10 min, using the cabinet having five 25-W UV lamps, the acrylate resin system containing Irgacure 184 showed the best tensile properties among the acrylate systems containing three different photoinitiators, respectively. Irgacure 184 was the best among the photoinitiators tested in this work in producing UV-cured acrylate films of high tensile properties. Therefore, Irgacure 184 was chosen as a photoinitiator for the acrylate resin in this study.

The content of Irgacure 184 included in the acrylate resin system was varied from 0.5 to 5 phr to determine the most adequate composition of the photoinitiator. Figure 5 shows the tensile strength of the acrylate films cured using the cabinet having five 25-W UV lamps for various contents of Irgacure 184. The acrylate resin system containing 1 phr of Irgacure 184 showed the best tensile properties among the acrylate resin systems containing various amounts of the photoinitiator. A relatively large amount of a photoinitiator must be included within a resin system for fast and efficient UV curing, but too high levels of the photoinitiator can cause problems of insufficient dissolving or mixing within the resin system. Even in the system wherein a large amount of a photoinitiator is compatible, most of the photoinitiator will remain chemically unbounded in the final cured product, causing deteriorative effects on the properties of the cured materials. To overcome these disadvantages oligomers and monomers having built-in photoinitiators, which are autopolymerizable through UV radiation, might be

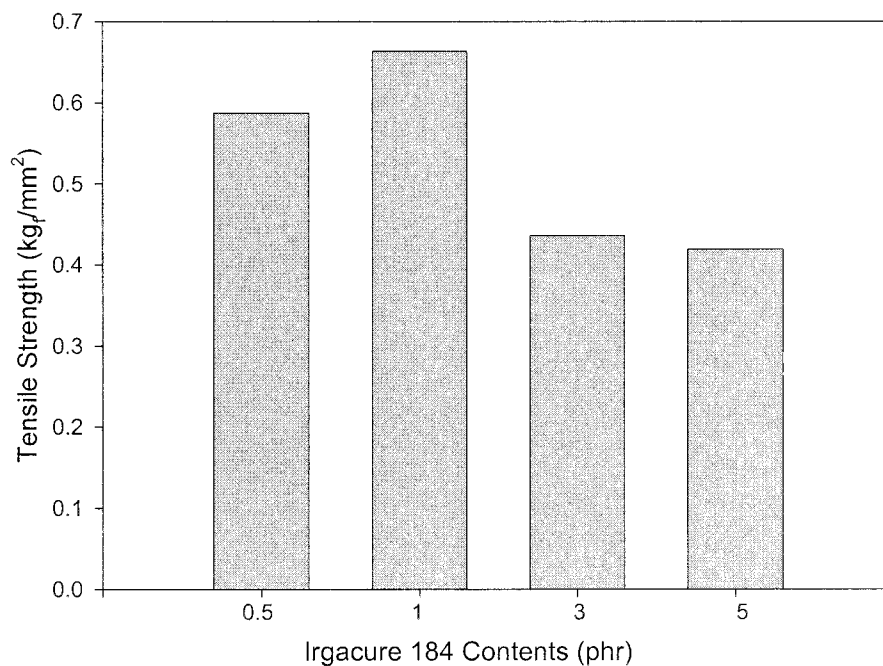


Figure 5 Tensile strength of the acrylate films containing various contents of Irgacure 184. The films were cured for 10 min using the cabinet having five 25-W UV lamps.

used. The synthesis of UV-autocurable polyester multiacrylate oligomers and the effects of chemical structure, molecular weight, and acrylic functionality on their properties were reported.²⁰ An optimum content of a photoinitiator depends on various factors such as wavelengths of UV light, absorption spectrum of the photoinitiator, and reflection characteristics of the materials. According to the tensile strength data shown in

Figure 5, the content of the photoinitiator was fixed to 1 phr in this study.

Reactive diluents are usually added to modify the properties and/or to reduce the viscosity of the oligomeric resins. Three types of reactive diluents, HDDA, TPGDA, and TMPTA, were used in this study to improve the tensile properties of the acrylate films. Each acrylate film was cured using the cabinet having five

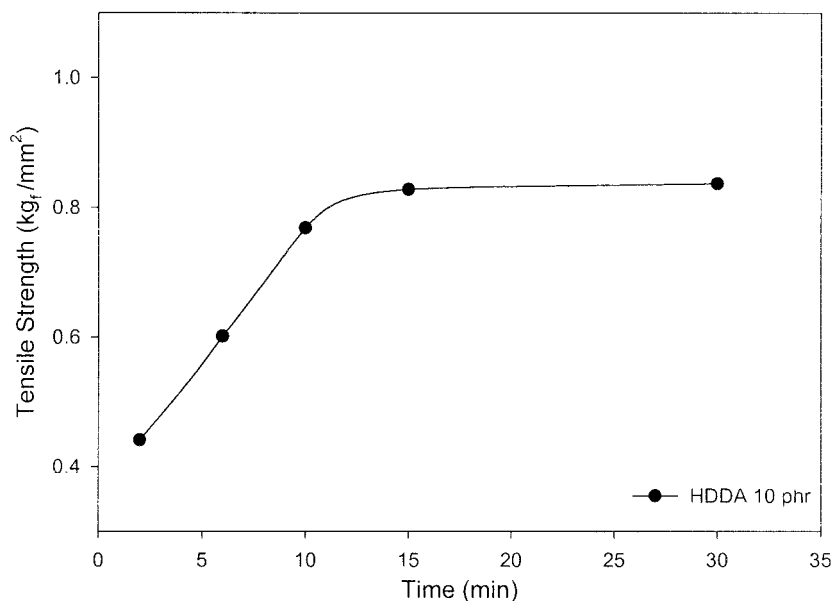


Figure 6 Tensile strength versus UV curing time for the acrylate films containing 10 phr of HDDA.

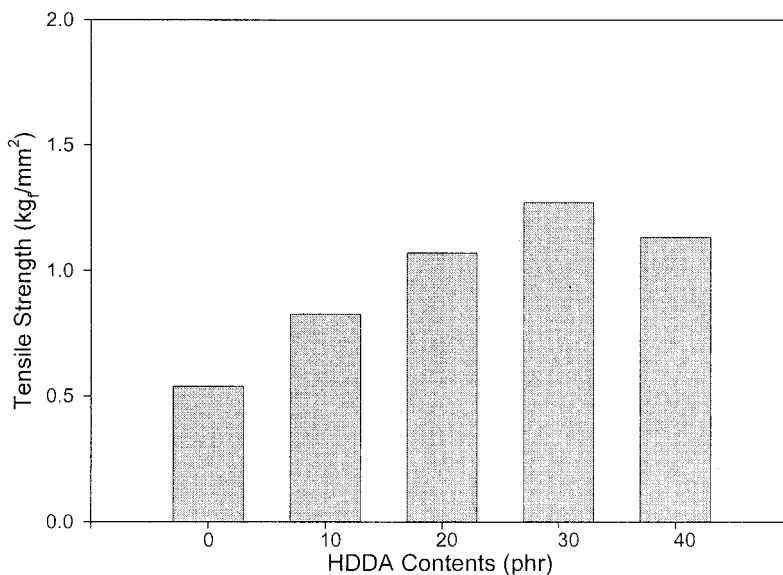


Figure 7 Tensile strength of the acrylate films containing various contents of HDDA.

25-W UV lamps for over 10 min. For example, it took about 15 min to fully cure the modified acrylate resin system containing 10 phr of HDDA, as shown in Figure 6. The UV-curing speed decreased slightly as the low molecular weight reactive diluents were introduced. This result is considered to be attributed to reduced photoinitiator concentration by introducing a reactive diluent because photoinitiator content was fixed to 1 part per hundred of the acrylate resin. The modified acrylate resin systems containing other reactive diluents also showed almost similar UV-curing behavior compared with the resin system containing HDDA, even though the resin system containing

TMPTA showed relatively slower curing speed. The modified acrylate resin systems, containing various amounts of the reactive diluents, were cured for 15 min using the cabinet having five 25-W UV lamps. FTIR spectroscopy provided evidence that the UV-curing reaction under this condition was finished within 15 min.

Figure 7 shows the tensile strength of the acrylate films containing various amounts of HDDA. The acrylate films containing HDDA showed the maximum tensile strength at 30 phr of HDDA content. Figure 8 shows the tensile strength of the acrylate films containing various amounts of TPGDA. The acrylate films

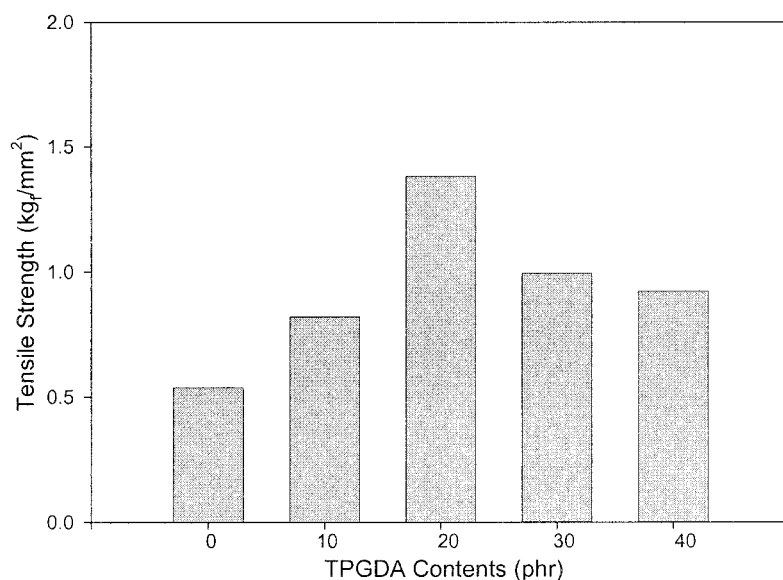


Figure 8 Tensile strength of the acrylate films containing various contents of TPGDA.

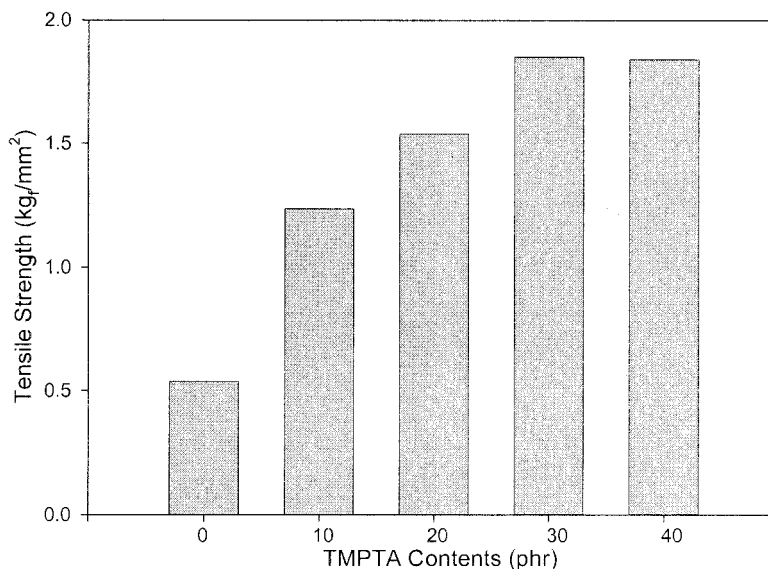


Figure 9 Tensile strength of the acrylate films containing various contents of TMPTA.

containing TPGDA showed the maximum tensile strength at 20 phr of TPGDA content. Figure 9 shows the tensile strength of the acrylate films containing various amounts of TMPTA. The acrylate films containing TMPTA showed the maximum tensile strength at 30 phr of TMPTA content.

A comparison between the tensile strength of the unmodified (pure) acrylate film and that of each modified acrylate film, containing one of the three reactive diluents, is shown in Figure 10. The tensile strength of each acrylate film, showing the best tensile strength by containing the optimum amount of its reactive di-

luent, 30 phr for HDDA, 20 phr for TPGDA, and 30 phr for TMPTA (as shown in Figs. 7–9), was compared. The acrylate film containing 30 phr of TMPTA showed the highest tensile strength among the films having three different reactive diluents, respectively. The tensile strength of the acrylate films containing 30 phr of TMPTA was about three times higher than that of the acrylate films containing no reactive diluents. The tensile strength of the acrylate films containing HDDA, or TPGDA, was about two times higher than that of the acrylate films containing no reactive diluents. This result seemed to be attributable to the fact

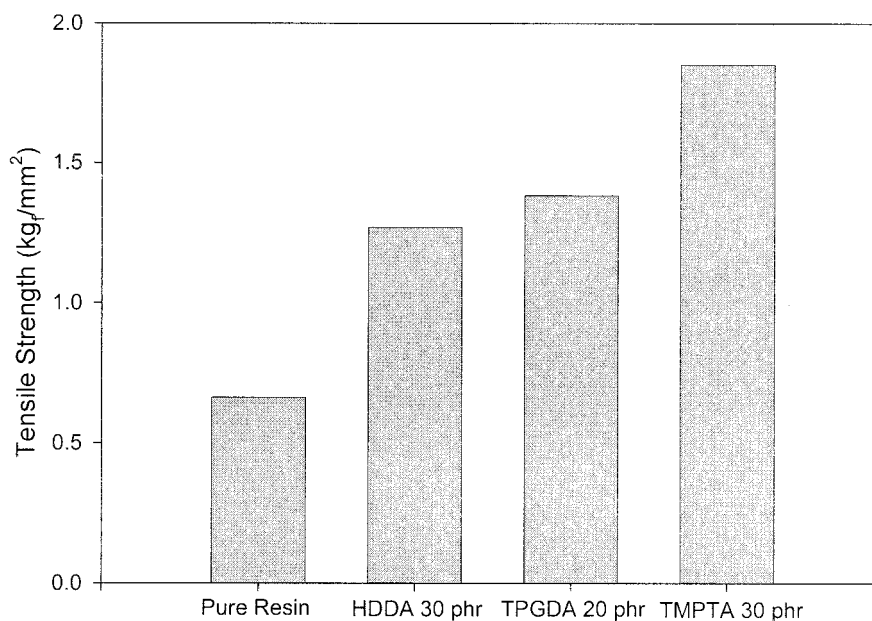


Figure 10 Comparison of the maximum tensile strengths of the acrylate films containing different reactive diluents.

that TMPTA has three acrylate functional groups and others have two acrylate functional groups. Compared to the difunctional acrylate diluents, the trifunctional acrylate diluent TMPTA would be cured together with the acrylate oligomers, resulting in a cured polymer network of higher crosslinking density.

CONCLUSIONS

UV curing behavior and tensile properties of a UV-curable polyester acrylate resin system, containing different photoinitiators and reactive diluents at various levels of contents, were investigated. FTIR spectra showed that the change of chemical structure of the acrylate resin system was almost finished within 180 min during UV curing using the cabinet having five 8-W UV lamps. Irgacure 184 showed the highest curing rate among the photoinitiators used in this study, and was the best for the good mechanical properties of cured acrylate films. The optimum content of Irgacure 184, determined from the results of tensile property measurements for the acrylate resin system, was 1 phr. UV curing speed decreased slightly when one of the reactive diluents was added to the acrylate resin system. TMPTA was the most effective among the reactive diluents used in this study in improving the tensile properties of the acrylate resin. The highest tensile strength of cured acrylate films was observed at the TMPTA content of 30 phr, and was about three times higher than the tensile strength of the cured acrylate films containing no reactive diluents.

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