UV Curing of Composites Based on Modified Unsaturated Polyester

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SYNOPSIS

Synthesis and photocrosslinking of glass fiber-reinforced composites, based on epoxy acrylate-modified unsaturated polyester, have been investigated. The efficiency of the photocrosslinking process for glass fiber laminates of the polyesters that contain different comonomers has been evaluated by measuring mechanical properties. The data show (i) that 2 mm thick laminates, containing 30-40% glass fiber mats, are cured with UV irradiation for 15 sec at room temperature in air; (ii) that multifunctional acrylate or acrylether monomers added to the polyester resin improve the tensile and flexural properties of the photocured product to a greater extent than do added allylic monomers, due to the different photocrosslinking mechanisms; (iii) that the physical properties of the photocrosslinked laminates are well correlated with the molecular weight of the polyester, the amount of multifunctional monomer added, and the glass fiber content. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The advantageous commercial potential in the aerospace, construction, furniture, and transportation industries, for inexpensive composite materials based on glass fiber-reinforced unsaturated polyester resin, has been apparent for many years, due to its light weight, dimensional stability, electrical insulation, and excellent mechanical properties.¹ Markets for unsaturated polyesters are continually increasing and the polyesters have become the most widely used, fiber-reinforced thermosetting material composites for sheet molding, injection molding, resin transfer molding, and pultrusion applications. Most of these composites are thermally cured at elevated temperature (above 100°C), using initiators, such as t-butyl perbenzoate or methyl ethyl peroxide and 30 to 50% styrene monomer added to the polyester.^{2,3} A few photopolymerizable unsaturated polyester resins, with a styrene monomer, have been developed.^{4,5} They show high efficiency and savings

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of investment and energy. Styrene reduces the viscosity of the polyester and reacts by crosslinking the unsaturated polyester chains to a thermoset product. Styrene has been used widely in the composite materials industry because it is miscible with the polyester, shows a low degree of homopolymerization, and is inexpensive.⁶ However, the volatility may cause explosion, and the persistent odor and the skin penetration is a potential health hazard during the curing process in the plant and in the end use of the laminates. Thermally cured or photocured products often contain substantial amounts of residual styrene trapped in the network structure. The conversion to polystyrene in the thermal copolymerization process does not exceed 80% at 60°C for a resin system with a styrene/polyester molar ratio range of 2:1. It has been reported^{2,7} that postcuring at 210°C for 2 h increases the conversion of styrene to 95% and of the fumarate double bonds in the polyester to 85%. At an elevated temperature, residual styrene monomer may cause blisters and voids on the surface of molded products. The purpose of this study is to develop new unsaturated polyester resin systems, without styrene, which can be crosslinked to a higher conversion of polyester and monomer at room temperature within shorter reaction times than the polyester/styrene systems.

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We have studied the optimum conditions of oligomer-monomer systems and the use of nonvolatile monomers for photoinitiated curing of unsaturated polyester at a low temperature. Such systems are described in this article, which involve the use of modified unsaturated polyesters with reactive end groups, the addition of a polyfunctional acrylate or allyl monomer, a photofragmenting initiator, and the photoinitiation of the crosslinking reaction using UV irradiation.

EXPERIMENTAL

Materials

Fumaric acid, phthalic anhydride, propylene glycol, and neopentyl glycol, from the KEBO Lab, Sweden, are used for synthesis of the unsaturated polyesters. Benzyldimethylamine as a catalyst and glycidyl acrylate as a reagent from Fluka AG, Switzerland, are employed for modifying the unsaturated polyester by endcapping the chains with acrylate groups. The different multifunctional monomers, added to the polyester resin, are presented in Table I. Benzoyldimethylketol (BDK) and benzoyl-1-hydroxyl-1-cyclohexanol (Irgacure 184) from Ciba Geigy, Switzerland, are used as photofragmenting initiators. Mats of chopped E-glass fiber mats, weighing 450 g/m^2 , from Scandinavian Glass Fiber AB, are used as reinforcement. These mats yield composites that are sufficiently transparent to ultraviolet radiation. All the materials in this study are used as received without further purification.

Polyester Preparation

The unsaturated polyesters in this study are prepared by a two-step condensation polymerization. In the first step, an excess of glycol components are esterified with phthalic anhydride in toluene as solvent, which, towards the end of the reaction, removes the water by azeotropic distillation. With stannous chloride as a catalyst at 190–220°C under nitrogen atmosphere, the reaction is continued until an acid number of less than 5 mg KOH/g polyester has been reached. In the second step, fumaric acid is added to the prepolymer at 110°C, and the reaction is continued at 140–170°C in the presence of hydroquinone until a still lower hydroxyl number is obtained. The excess of acid monomer determines the molecular weight of the carboxyl group terminated polyester. The number-average molecular weight (M_n) is calculated from the sum of acid and hydroxyl numbers, determined by end-group titration.

The carboxyl end groups of the polyester are modified by a reaction with glycidyl acrylate (a 2% excess is added) at about 70°C in the presence of benzyldimethylamine as catalyst until no carboxyl groups can be detected. Finally residual toluene is removed by evacuation below 30 mm Hg at 40°C. No IR band for carboxyl at 3224 cm⁻¹, and anhydride at 1776 and 1850 cm⁻¹, are observed for the final product, as shown in Figure 1. The acrylate end-capped unsaturated polyester that is obtained is a slightly yellow and translucent viscous liquid, which is stored under refrigeration until used.

Preparation of Cured Composites

Amounts of multifunctional acrylate ester and photoinitiator are added to the molten acrylate-modified unsaturated polyester, using a glass rod for stirring. For preparation of the laminate, a mold made of stainless steel is used, with a thin, smooth, transparent Mylar polyester film at the bottom. To obtain a 2 mm-thick sheet, four or five layers of the E-glass fiber mats are placed, one by one, pouring a preweighed amount of resin on top of each layer, and allowing the resin to penetrate thoroughly. Another Mylar film is then applied as a cover. A roller is employed to squeeze out air bubbles and to enhance the impregnation of the glass fiber mats with resin.

Table I Multifunctional Monomers Used in This Work

Name	Abbreviation	Supplier
Trimethylolpropane tri(meth)acrylate	TMPT(M)A	UCB, Belgium
Hexanediol diacrylate	HDDA	UCB, Belgium
Trimethylolpropane triallylether	TMPTAE	Perstorp AB, Sweden
Pentaerythritol tri-/tetra-allylether	PETAE	Perstorp AB, Sweden
Triallylcyanurate	TAC	Aldrich, Germany
Trimethylolpropane triacrylether	TP30	Perstorp AB, Sweden
Pentaerythritol tetraacrylether	XP5105	Perstorp AB, Sweden

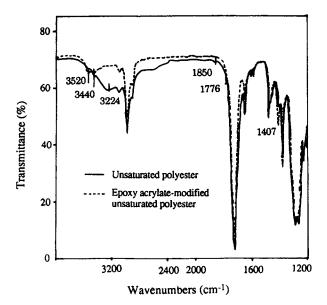


Figure 1 FTIR spectra for modified unsaturated polyester.

Both sides of the laminate are UV-irradiated separately with a high-pressure mercury lamp (2 KW, HPM-15 from Philips, Holland) built into a UV-CURE device, constructed in our laboratory, as shown in Figure 2, at a distance of 10 cm from lamp to specimen at room temperature. After curing and through-hardening, the Mylar films are stripped off and a laminate plate with smooth surfaces is obtained.

The cured laminates, with aluminium end tabs attached, are shaped into test specimens that are 88 mm in length and 12 mm in width for tensile measurement using a diamond-tooled circular cutting saw blade.

Measurements

IR and UV Spectra

Infrared spectra of the uncured polyester resins are recorded on a Perkin-Elmer Model 1710 Fourier Transform Spectrometer by smearing an acetone solution of the resin on a NaCl prism to form a thin film. UV absorption spectrum measurements of the photoinitiators and the mylar film (used as a cover) are carried out with a Hewlett Packard 8451A Diode Array spectrophotometer.

Mechanical Properties

For tensile testing, the specimen is clamped into a 100 KN Instron universal tester, with a jaw separation of 50 mm. The specimen is extended at a rate

of 0.5 mm/min to failure. For bending testing, the specimen is loaded in a three-point holder of an Instron 1122 instrument with a 50 mm span and is strained at a rate of crosshead motion of 0.2 mm/ min. The Charpy impact strength is measured with a 1.67 Kg pendulum of 100 Kgcm capacity to break unnotched specimens.

Other Measurements

The water absorption is measured by weighing the samples after immersion in distilled water at room temperature for 24 h. The glass fiber/resin ratio is analyzed by ashing the laminate samples in a muffle furnace at a final temperature of about 700°C for half an hour.

RESULTS AND DISCUSSION

Photoinitiation and Photocrosslinking of Unsaturated Polyester

The effect of various photoinitiators in the photocuring polyester systems was studied. Curing of unsaturated polyesters using photo-fragmenting initiators, such as benzoin ethers, which produce free radicals on UV irradiation, has been applied on a large industrial scale for printing ink and surface

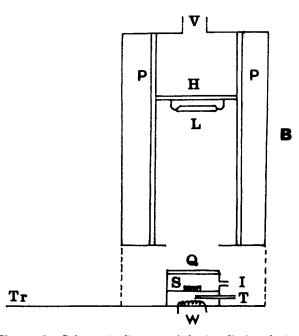


Figure 2 Schematic diagram of the irradiation device UV CURE: (V) ventilation, (P) stands, (H) holder, (L) lamp, (Q) quartz plate, (S) sample, (I) N² entrance, and (Tr) track.

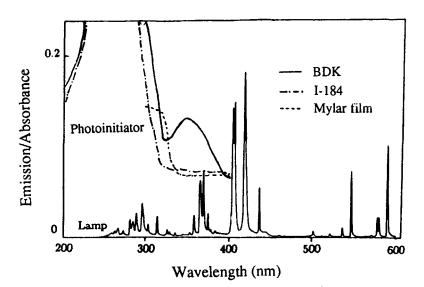


Figure 3 UV spectra of the photoinitiators in chloroform (10^{-3} M) and mylar film and emission spectrum from Philips HPM-15 lamp.

coating.⁸ However, we have found that BDK is a more efficient initiator in our polyester/glass fiber system than Irgacure 184 because both the benzoyl (I) and the methyl (II) radicals from the BDK photocleavage are reactive enough to initiate polymerization of vinyl groups, while the Irgacure 184 only forms one initiating radical (benzoyl), since the other radical (III) only acts as a chain terminator at relatively high radical concentrations and does not initiate polymerization, as shown in the following equations,

Irgacure 651 (BDK)

Irgacure 184

$$PhCOC_{6}H_{10}OH \rightarrow Ph^{\circ}CO + C_{6}H_{10}OH \quad (3)$$
(III)

Moreover, BDK has a broad absorption peak at 315 to 390 nm, which is in the same range as the UV spectrum of the HPM-15 lamp, as shown in Figure 3. BDK is a photoinitiator, which undergoes a Norrish Type I photocleavage. The radicals produced from BDK can initiate the photopolymerization reaction rapidly. The Mylar film, which has practically no absorption in the range of the UV spectrum, has low permeability for oxygen. Therefore, the mylar film protects the laminate from atmospheric oxygen and does not interfere with the UV light during photocuring.

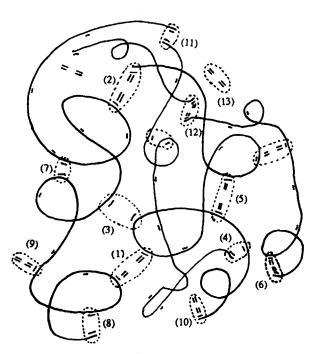


Figure 4 Schematic diagram, showing some possible ways of bonding in the unsaturated polyester-multifunctional monomer copolymerization. I. Intermolecular crosslinking: $E' - (M)_n - E''(1)$ and (2), and E' - E''(3) and (4); II. Intramolecular cyclization: $E - (M)_n - E$ (5) and (6), and E - E(7) and (8); III. Branching growth and chain extension: $E - (M)_n$ (9) and (10), E' - E''(11), and $E' - (M)_n - E''(12)$; IV. Multimolecular monomer homopolymerization: M - M (13).

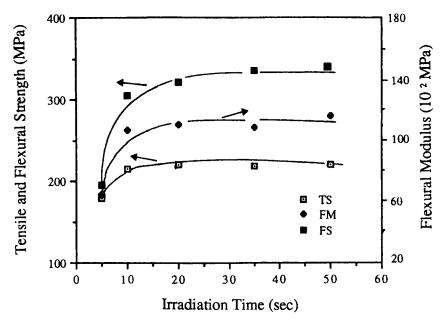


Figure 5 Change of mechanical properties of the laminate with irradiation time.

The epoxy acrylate-modified unsaturated polyester is rapidly crosslinked by UV irradiation in the presence of an effective photoinitiator and a multifunctional monomer. The photocrosslinking process includes three major reactions: monomermonomer, monomer-polyester, and polyester-polyester, and it includes intermolecular crosslinking, intramolecular cyclization, branching growth, polyester chain extension, and multifunctional monomer homopolymerization. Figure 4 shows a schematic diagram for some possible ways of bonding in the polyester-monomer reactions. It exhibits a more complicated behavior than thermally a crosslinking styrene-polyester system, due to the introduction of acrylate double bonds at the unsaturated polyester chain ends.⁹ The reaction of the end-double bonds of the polyester with vinylene fumarate, on the same or another polymer chain, can also form crosslinks with a polymerized TMPTA chain, in addition to the coupling between fumarate groups in the polymer chain.

The properties of the laminate are strongly dependent on the degree of crosslinking. The effect of irradiation time on the mechanical properties and water absorption is shown in Figures 5 and 6, respectively, for 2 mm thick laminate, containing 55% glass fiber, 42.5% polyester with MW 1440, and 7.5% HDDA, to which 1 wt % BDK, based on the resin, is added. It can be seen that "level off" properties have been reached after 10 sec irradiation time on each side. This means that the crosslinking reaction is almost complete at that curing time, and that a relatively high degree of crosslinking has been reached. The rapid increases of mechanical strength and water resistance, in the beginning of the irradiation, are due to high reaction rates when the concentration of the multifunctional monomer is high.

Effect of Molecular Weight of Unsaturated Polyester and Glass Fiber Content

Table II lists the composition and molecular weight (M_n) of three samples of unsaturated polyester, UP-1, UP-2, and UP-3, and it presents the molar ratio

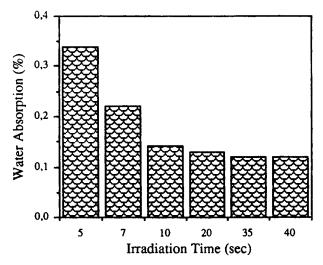


Figure 6 Change of water absorption of the laminate with irradiation time.

Unsaturated Polyester Resin Compositions (Molar Ratio)	UP-1	UP-2	UP-3
Fumaric acid	1.4	1.2	1.13
Phthalic anhydride	1.4	1.2	1.13
Propylene glycol	1.0	1.0	1.0
Neopentyl glycol	1.0	1.0	1.0
Glycidyl acrylate	0.8	0.4	0.25
M_n of modified polyester	1440	2400	3660
MW/mole fumarate $C = C$	337	358	378
Avg. no. of fumarate C==C per polyester	3.5	6.0	9.0
C = C ratio of acrylate to fumarate/polyester resin	0.57	0.33	0.22
Ingredients			
Unsaturated polyester:			
UP-1	37.5		
UP-2	_	37.5	_
UP-3			37.5
TMPTMA (%)	20	20	20
BDK (%)	1	1	1
Glass fiber (%)	42.5	42.5	42.5
Tensile properties			
TS ^a (MPa)	162	153	143
TM^{b} (10 ² MPa)	93	88	71

Table II Compositions of the Unsaturated Polyester and the Tensile Properties of Their Laminates

* (TS) tensile strength.

^b (TM) tensile modulus.

of acrylate groups to fumarate vinylene groups, along the polyester chains. The contents of photoinitiator BDK, monomer TMPTMA, unsaturated polyester, and glass fiber were 1%, 20%, 37.5%, and 42.5% by weight, respectively, for the three samples. Due to its molecular weight, the UP-1 resin has a higher molar ratio of acrylate to polyester vinylene double bonds and lower average number of fumarate groups in the polyester molecule than the UP-2 and UP-3 resins. The average number of fumarate groups in the polyester molecule increases with increasing molecular weight of the polyester. On the contrary, the molar ratio of acrylate to fumarate decreases with increasing molecular weight. The acrylate double bonds on the ends of polyester chains are more responsive to UV irradiation than the maleic/fumaric double bonds along the polyester chains, which leads to higher polymerization rate, higher crosslinking density, and better mechanical properties of the photocured sample from the UP-1 resin. Another reason for the better performance is that the acrylate monomer is more compatible with the UP-1, due to the low molecular weight of the polyester (two OH groups per chain). It is not surprising that both the tensile strength and tensile modulus decrease with increasing molecular weight, as shown

Table III	Effect of Glass Fiber	on Mechanical	Properties of th	e Photocured Laminate
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Glass Fiber (wt %)	24.2	31.2	42.0	47.7	54.9	65.4
TS ^a (MPa)	75	120	152	173	232	182
TM^{b} (10 ² MPa)	42	53	77	77	98	74
FS ^c (MPa)	155	210	272	298	386	149
FM^{d} (10 ² MPa)	85	90	107	130	172	38

^a (TS) tensile strength.

^b (TM) tensile modulus.

^c (FS) flexural strength.

^d (FM) flexural modulus.

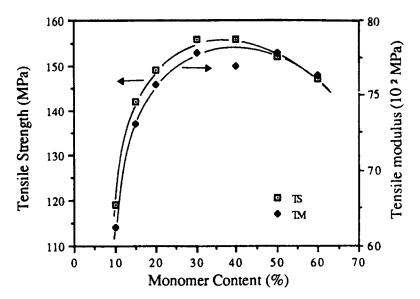


Figure 7 Effect of TMPTA concentration on tensile properties of the photocured laminate.

in Table II. However, a higher molecular weight of the polyester requires larger amounts of the reactive monomer in order to reach a useful casting viscosity. In the continued studies, we have, therefore, used polyesters in the lower molecular weight range.

The effect of increasing glass fiber content from 24.2 to 65.4% on the mechanical properties of photocured laminate is shown in Table III. In this case, the resin compound contains 70% polyester with MW 1440 and 30% HDDA, to which 1% BDK is added as photoinitiator. Both tensile and flexural strength properties increase with increasing glass fiber content to a maximum at about 54.9%, and then decrease at 65.4%. This can be interpreted as being due to increasing strength, provided by the glass fibers initially, and lack of resin for bonding of the glass fibers at the higher fiber content, which results in voids in the photocured product.

Effect of Reactive Comonomer

To obtain a low viscosity of the polyester resin system for casting or molding, a certain amount of multifunctional monomer is added. The monomer is converted to an integral part of the laminate by polymerization or copolymerization during the photocuring process. The rate of photocrosslinking can also be enhanced by the addition of a reactive diluent monomer. It is well known that acrylic groups, at unsaturated polyester chain ends and in TMPTA molecules, are highly active groups, which are rapidly homopolymerized or copolymerized on UV irradiation in the presence of a photofragmenting initiator. Figure 7 and Figure 8 show the effect on the mechanical properties of the laminates of TMPTA concentration from 10 to 60% in the MW 2400 polyester in the presence of 38% glass fiber. Tensile strength and tensile modulus reach a high level at 20 to 30% TMPTA, while impact strength increases more gradually. At more than 40% TMPTA, the tensile properties of the cured laminates decrease.

The effect of the different monomers on the tensile and flexural properties of the photocured laminates is shown in Figures 9 through 12. The laminates contain 55% glass fiber, 36% polyester MW

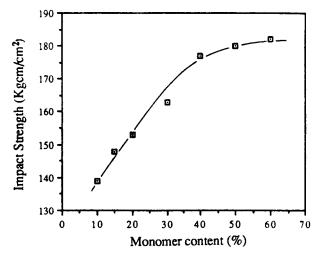


Figure 8 Effect of TMPTA concentration on impact strength of the photocured laminate.

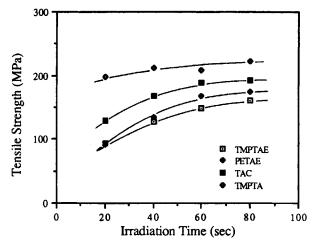


Figure 9 Effect of multifunctional monomers on the tensile strength of the photocured laminate.

1440, and 9% multifunctional monomer. The resin contains 1% BDK added. It can be seen that the best mechanical properties of the cured samples are obtained with the TMPTA systems at all irradiation times. In comparison, the addition of allylic multifunctional monomer into unsaturated polyester, such as pentaerythritol tri-/tetraallylether (PE-TAE) (45/55) or trimethylolpropane triallylether (TMPTAE) or triallylcyanurate (TAC), shows slower polymerization rates than TMPTA at the beginning of irradiation. Lower mechanical strengths are observed for the laminates with allylic monomer. In order to interpret these observations, we list the molecular structures of comonomers used in this work (Table IV).

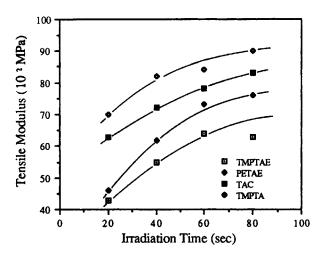


Figure 10 Effect of multifunctional monomers on the tensile modulus of the photocured laminate.

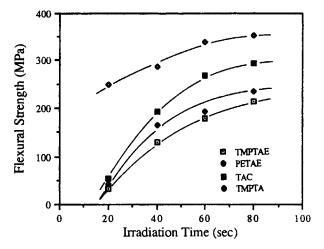


Figure 11 Effect of multifunctional monomers on the Flexural strength of the photocured laminate.

The benzoyl (Ph—'CO) and methyl ('CH₃) radicals, formed from the initiator BDK on cleaving by UV irradiation (Reactions 1 and 2), initiate polymerization reactions by the addition to the double bonds of both polyester and comonomer acrylate molecules. Acrylic monomers are the most reactive vinyl monomers in free radical polymerization. The double bonds in maleic and fumaric units in the polyester chains are much less reactive in free radical polymerization. The allylic comonomers (Table IV) react mainly by hydrogen abstraction with the initiator radicals (I') (Reaction 4) and to a minor extent by addition (Reaction 5). The allyl radicals formed yield crosslinks or terminate by combination to a dimer with another radical (R'') (Reaction 6).

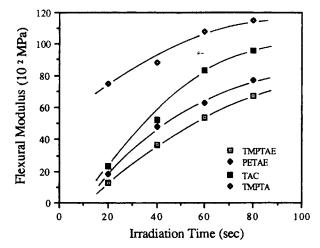


Figure 12 Effect of multifunctional monomers on the Flexural modulus of the photocured laminate.

Compounds	Molecular Structure			
TMPTA	$CH_3C(CH_2OCOCH = CH_2)_3$			
TMPTAE	$CH_3C(CH_2OCH_2CH=CH_2)_3$			
PETAE	$HOCH_2C(CH_2OCH_2CH=CH_2)_3/C(CH_2OCH_2CH=CH_2)_4$ (45/55)			
TAC	$C_3N_3(OCH_2CH=CH_2)_3$			
TP30	$CH_3C(CH_2OCH_2OCOCH = CH_2)_3$			
XP5105	$C(CH_2OCH_2OCOCH=CH_2)_4$			

Table IV Molecular Structures of Monomers Used in This Work

This explains the slow radical polymerization observed for allylic monomers.¹⁰⁻¹²

$$I' + R - O - CH_2 - CH = CH_2 \rightarrow$$

$$R - O - CH - CH = CH_2 + IH \quad (4)$$

$$I' + R - O - CH_2 - CH = CH_2 \rightarrow$$

$$R = O = CH_2 = CH_2 = CH_1 = CH_2 \quad (5)$$

$$R - O - CH - CH = CH_2 + R' \rightarrow$$

$$R - O - CHR' - CH = CH_2 \quad (6)$$

On the other hand, the allyl radicals add oxygen molecules in the resin and form peroxy radicals, which may abstract hydrogen from other allyl groups (Figs. 13 and 14). In this way, allyl groups are scavengers for residual oxygen in a photocuring paint or lacquer.¹³ The different radical reactions of acrylic and allylic comonomers, with the initiating radicals, provide an interpretation of the results in Figures 9 through 12. The triacrylate ester TMPTA yields a higher initial rate of crosslinking and also higher resulting mechanical strength than all allyl ethers studied (TMPTAE, PETAE, and TAC) as comonomers in the unsaturated polyester. Moreover, the miscibility of reactive comonomer, added with unsaturated polyester, affects the crosslinking efficiency considerably. TMPTA is expected to be more soluble in the resin than the other monomers, which would promote copolymerization with the epoxy acrylate-modified unsaturated polyester. The resin systems, with the PETAE monomer, yield better mechanical properties than those with TMPTAE because of the hydroxyl group in pentaerythritol triallylether, which leads to better solubility in the modified polyester. The PETAE has one more allylic double bond than TMPTAE, which leads to higher crosslinking density. In the case of TAC, the photocrosslinking mechanism is essentially similar to that for PETAE and TMPTAE. However, the resin samples with TAC yield better physical properties

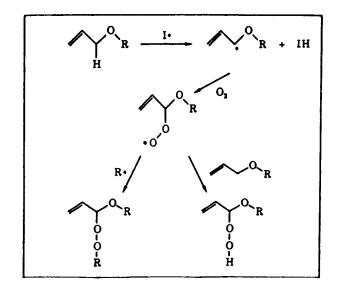


Figure 13 Oxidative crosslinking and hydrogen abstraction of allylether.

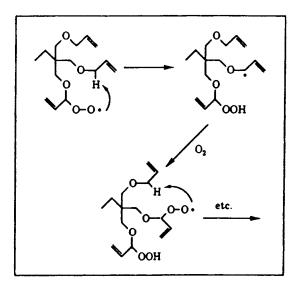


Figure 14 Intramolecular hydrogen abstraction of allylic peroxy radical.

Mechanical Strength	Monomer	Monomer Content (%)			
		10	20	30	40
TS (MPa)	TMPTA	183	188	187	184
	TP30	195	197	192	187
	XP5105	191	195	194	190
TM (10^2 MPa)	TMPTA	89	91	90	87
	TP 30	97	95	94	93
	XP5105	96	97	98	91

Table V Effect of Multifunctional Monomer on Mechanical Strength of the Photocured Laminate

than those with PETAE and TMPTAE, which may be due to high reactivity in hydrogen abstraction and steric hinders in peroxy radical reactions.

The multifunctional comonomers are highly reactive in radiation curing. A disadvantage is that they are a skin irritant and may cause allergy. For this reason, acrylether compounds have been prepared and found to be less toxic. The two acrylether comonomers we have studied, trimethylolpropane triacrylether (TP30) and pentaerythritol tetraacrylether (XP5150), are prepared by Perstorp AB, Sweden. As comonomers added to unsaturated polyester, they are as reactive as the conventional acrylic esters. In addition, the mechanical properties of the photocured laminates are improved by the acrylate ester monomers containing ether linkages. The tensile properties of photocured laminates of the MW 1440 polyester with 50% glass fibers are shown in Table V. The tensile properties of the photocured laminates are independent of the monomer content in the studied range of 10 to 40%. This is different from the data for acrylic monomers shown in Table III and Figure 7, which show strong the dependence of the monomer addition on the mechanical properties. Similar results have been reported for partial replacement of propylene glycol with diethylene glycol in the polyester chains, which vields increased tensile and flexural strength of the thermally cured unsaturated polyester with styrene as a comonomer.⁶ The main advantage of the ether linkage in the acrylether esters is the lower toxicity and lower skin irritation than the conventional acrylic esters.

CONCLUSION

1. Unsaturated polyesters, endcapped with acrylate groups and diluted with reactive multifunctional acrylic and allylic monomers in the presence of photoinitiator, can be photocrosslinked with UV irradiation as glass fiber-reinforced laminates in a rapid process.

- 2. The rate of crosslinking of acrylate-modified unsaturated polyester with UV irradiation increases with decreasing molecular weight of the unsaturated polyester. The photocrosslinking efficiency of the resin systems, with different comonomers, decreases in the order: acrylether monomer > acrylate monomer > allylic monomer.
- 3. Excellent mechanical properties and water resistance are obtained for laminates containing 20-50% multifunctional acrylate (especially acrylether) monomer, 40-55% glass fiber, and 1% photoinitiator.
- 4. The photocrosslinked product, obtained in this study, thereby can be applied for the end user with cleaner, healthier, and safer working atmosphere. These polyester compounds are promising for technical application and commercial use.

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