

# Photopolymerization of Dendritic Methacrylated Polyesters. III. FRP Composites

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## SYNOPSIS

In two previous articles, the preparation, modification with epoxy methacrylate and methacrylic anhydride, and properties of dendritic aromatic polyesters with structural symmetry, a high degree of branching, and a high density of terminal functionality were described. The resulting polyester resins were cured by addition of benzildimethylketal (Irgacure 651) as the photoinitiator and trimethylolpropane triacrylate (TMPTA) as the comonomer and irradiated with UV light as laminates with 35 wt % glass fiber mats. After short irradiation times (0.02–0.10 s) at room temperature, the laminates with excellent mechanical properties which are comparable with the thermally cured linear unsaturated polyester in styrene and UV-cured linear epoxy acrylate-modified unsaturated polyester composites were obtained. The addition of 10–40 wt % TMPTA had only small effects on the mechanical properties, except on tensile strength, which decreased about 15%. The dendritic polyesters have low viscosity and a much higher curing rate than those of corresponding linear unsaturated polyesters and are, therefore, of great interest for industrial applications. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Composite materials based on glass fiber-reinforced polyester resins have replaced metals for many applications, such as in vehicle, furniture, and construction industries, due to their mechanical strength, low weight, high corrosion resistance, and low fabrication cost.<sup>1</sup> In traditional maleate-based unsaturated polyester resins for thermally curable or radiation-curable systems, styrene is preferred as a reactive diluent because of the lower cost. The advantages of photochemical crosslinking, mainly short curing time, energy saving, complete automation, and strong reduction of pollution, compared with thermal processes are presently studied for the manufacture of glass fiber-reinforced polyester composites. Some photopolymerizable unsaturated polyester resin systems with styrene or acrylates as

reactive diluents have been described.<sup>2,3</sup> However, there is growing concern about the health risks of the volatile compounds used in the maleate or maleate-acrylate-based photopolymer systems, especially for the large amount of styrene or multifunctional acrylate monomers added for the primary function of viscosity control. Allylic or vinyl ether monomers are preferred to replace or reduce the amount of styrene or acrylate monomers. However, a slow polymerization rate or high price can be obtained with the former's systems. Therefore, development of a thermosetting oligomer which would both decrease the viscosity of the resin formulation and increase the cure speed, while also improving the physicochemical properties of radiation cured materials, has thus become a real challenge.

The viscosity of an oligomer is related to the dynamic extension of the molecules and the segment density within the volume of a molecule. Therefore, oligomers with a dendritic structure and a high number of functional groups are expected to give low viscosity and a high curing speed.<sup>4</sup> However, in highly branched substituted aromatic maleate-based unsaturated polyesters, there are steric effects around the vinylene double bonds located at the

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middle of the chains. This may reduce their ability to crosslink with the added comonomers. A new kind of oligomer with a star-shaped molecular structure has recently been developed for many applications, including coating and adhesive systems. In two previous articles,<sup>5,6</sup> we synthesized dendritic methacrylated polyesters and investigated the structure and properties of these dendritic polyesters including the photopolymerization characteristics in the UV-curing process. These modified dendritic polyesters containing about 8, 12, and 16 double bonds per oligomer molecule, designated as D-1, D-2, and D-3, respectively, have low viscosity, a high curing rate, and a high degree of curing and the final product has excellent mechanical properties.

We now report the use of the methacrylated dendritic polyesters as reactive oligomers in glass fiber-reinforced composites instead of the traditional maleate-based unsaturated polyester compositions. The effects of radiation time and comonomer content, as well as the functionality of the dendritic polyester on the tensile and flexural properties, and the impact strength of the UV-crosslinked composites were investigated. This work also describes the differences in tensile and impact behavior between the linear and dendritic polyesters with various amounts of comonomer added and compares the mechanical properties of thermally cured styrene-containing and UV-cured epoxy acrylate-modified unsaturated polyester composites.

## EXPERIMENTAL

### Materials

The composites in this investigation are made of modified dendritic polyesters and unsaturated polyesters (MUP) with multifunctional comonomer added and cured with a mat of chopped E-glass fibers. The dendritic polyester was prepared from pentaerythritol and 1,2,4-benzenetricarboxylic anhydride, end-capped by glycidyl methacrylate and methacrylic anhydride in a stepwise divergent preparation.<sup>5</sup> Three dendritic methacrylated oligomers with about 8, 12, and 16 terminal methacrylic double bonds were numbered D-1, D-2, and D-3, respectively. The idealized formula scheme of the dendritic methacrylated polyester with 16 double bonds at the ends of the molecular chains is given in Figure 1.

The MUP was synthesized from fumaric acid, phthalic anhydride, propylene glycol, and neopentyl glycol and modified by glycidyl methacrylate, with the formula as follows<sup>7</sup>:

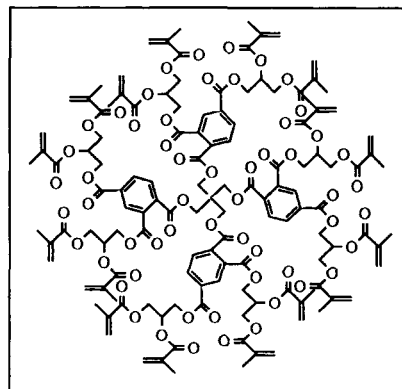


The comonomer used in all formulations was trimethylolpropane triacrylate (TMPTA) (supplied by Aldrich, Germany). The glass fiber mats were of randomly oriented chopped fibers bonded in mat form (450 g/m<sup>2</sup>) with an organosilane coupling agent (supplied by Scandinavian Glass Fiber AB). The photoinitiator was benzildimethylketal (BDK or Irgacure 651, supplied by Ciba Geigy), which produces two radical species upon UV irradiation. The polyester resins with 3% BDK and 15% TMPTA by weight were prepared as composites with 35 wt % glass fiber mats.

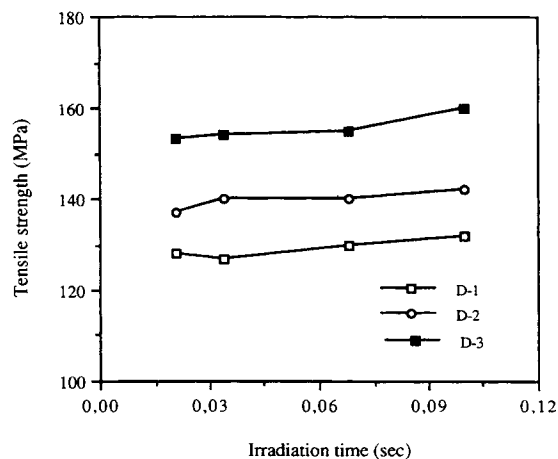
### Preparation of Cured Composite Samples

Given amounts of the multifunctional acrylate monomer TMPTA and photoinitiator BDK were added to the methacrylate-modified dendritic polyester using a glass rod for stirring. For fabrication of the polyester laminates, a mold made of stainless steel with a thin Mylar polyester film at the bottom was used. To obtain a 2 mm-thick sheet, four or five layers of the E-glass fiber mats were placed one by one, pouring a preweighed amount of resin on top of each layer and allowing it to penetrate thoroughly. Finally, another Mylar film was applied as a cover for the smooth surface of the laminates, preventing the diffusion of oxygen from the air. A roller was employed to remove air bubbles and enhance the impregnation of the fiber mats with the resin.

Both sides of the laminate were UV-irradiated separately in air on a conveyor belt with a variable speed and passed under a 300 W/in. (120 W/cm) Model F300 D bulb in the exposure chamber (Fusion



**Figure 1** Idealized formula of the dendritic polyester with 16 double bonds.



**Figure 2** Tensile strength of the composites vs. irradiation time.

UV Curing Systems). After curing, the Mylar films were stripped off and laminate sheets with smooth surfaces were obtained.

The cured laminates were shaped into test samples of 88 mm length and 12 mm width using a diamond-tooled circular cutting saw blade. For the tensile testing, aluminum end tabs were attached to the laminate samples before cutting.

### Measurements

For tensile testing, the specimen was clamped into a 100 KN Instron universal tester with a jaw separation of 50 mm. The specimen was extended at a rate of 0.5 mm/min to failure. For bending testing, the specimen was loaded in a three-point holder with a 50 mm span and strained at a rate of crosshead motion of 0.2 mm/min. The Charpy impact strength was measured with a 1.67 kg pendulum of 100 kg/cm capacity to break unnotched specimens.

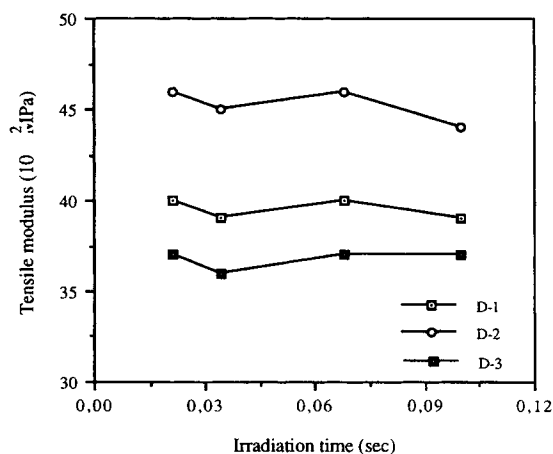
## RESULTS AND DISCUSSION

The physicochemical properties of fiber glass-reinforced polyester composites largely depend on characteristics of the resin matrix, the fiber, and the fiber/matrix interface. In engineering applications, the influence of the matrix on the mechanical behavior of the material has to be taken into account very carefully. The measurements of tensile and flexural properties are of particular importance for the monitoring of the cure process of the resin from a liquid of varying viscosity to a crosslinked solid.

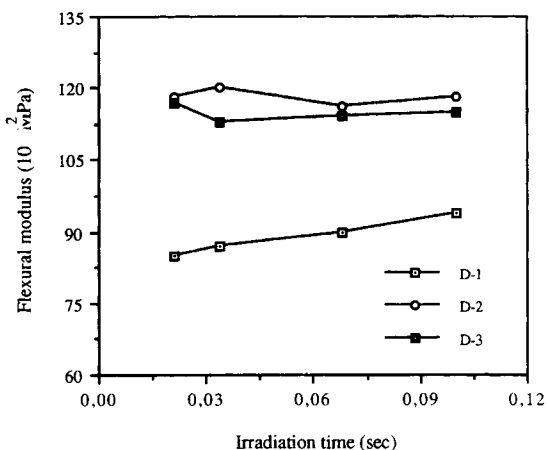
### Photocrosslinking Kinetics

The data in Figure 2 show the tensile strength of the UV-cured dendritic polyester composites with D-1, D-2, and D-3 polyesters. The cured composite with D-3 polyester has the lowest tensile modulus, as shown in Figure 3. After increasing the irradiation time, there are no big differences in tensile properties. This implies that the composites containing dendritic polyesters are UV-cured at a very high speed and reached optimal properties in a short irradiation time. Further irradiation has little influence on the tensile properties.

Acrylated epoxy resins prepared by reacting an ethylenically unsaturated monomer containing epoxy groups with a carboxylic acid have been reported to have a high cure rate due to the suppressing of the influence of oxygen in the resin on curing.<sup>8</sup> The cured epoxy acrylate resin films have excellent adhesion to a variety of substrates including glass, stainless steel, and aluminum, excellent mechanical properties, and high chemical and weathering resistance. The dendritic polyester composition in the resin matrix is a thermosetting methacrylated polyester which undergoes fast photopolymerization by a radical mechanism with a photofragmenting initiator. More than 95% of gel content for all three dendritic polyester systems in irradiation times longer than 0.03 s are obtained.<sup>6</sup> Therefore, the high tensile strength can be obtained in the early irradiation stage even if a large number of unsaturation groups are retained in the resin matrix. The tensile strength of the composite material increases with increasing functionality of the dendritic polyester, probably due to increased crosslink density.



**Figure 3** Tensile modulus of the composites vs. irradiation time.

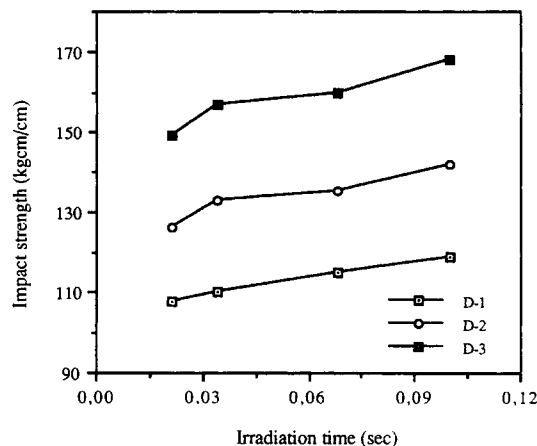


**Figure 4** Flexural modulus of the composites vs. irradiation time.

The flexural modulus of the composites increase slightly with prolonging irradiation time, as shown in Figure 4. There is not much difference between D-2 and D-3, but there is between D-1 and D-2/D-3. The impact strength of the composites with D-1, D-2, and D-3 polyesters increases gradually at increased irradiation time, apparently related to the functionality of the dendritic polyesters, as shown in Figure 5. In the previous article, we reported that at increasing functionality of the dendritic polyester the maximum degree of curing decreases.<sup>6</sup> In the resin with D-2 or D-3 polyester, there are about 40% methacrylic double bonds trapped in the crosslinking networks. In this case, it may be interpreted as due to the intramolecular plasticization from unreacted double bonds in the matrix with D-2 and D-3 polyesters; thus, the high impact strength of the composites with those polyesters is obtained.

#### Effect of Comonomer on Physical Properties

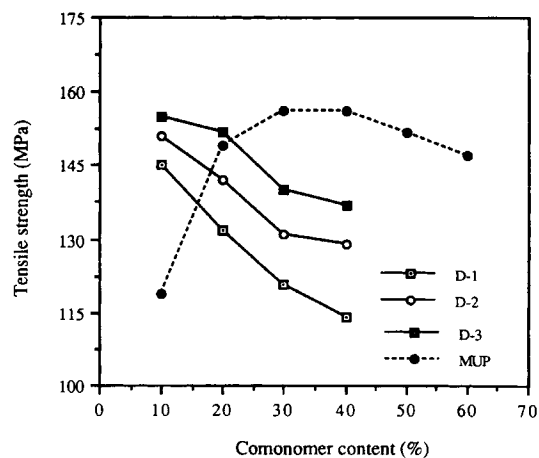
A well-known feature in the photopolymerization process of radiation-curable systems is that the chain propagation stops before the reaction is complete. This is due mainly to the gelation of the medium and the related restrictions in mobility of the reactive sites in the cured material. The viscosity of the formulation is a very important factor responsible for incomplete curing. Therefore, a comonomer of low viscosity is added to the viscous oligomer to improve the processibility of the material and increase the degree of polymerization of the oligomer. In the thermally cured composite systems, 30–40% styrene as a reactive diluent is added to the unsaturated polyester prepolymer.<sup>9,10</sup> About 30% multifunctional acrylate monomer is added to the epoxy



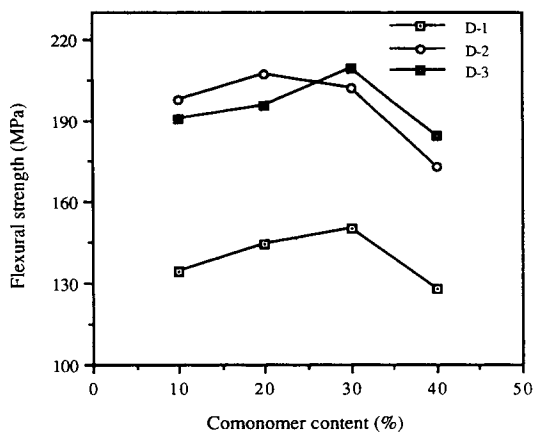
**Figure 5** Impact strength of the composite vs. irradiation time.

acrylate-encapped unsaturated polyester to improve processibility and obtain good mechanical properties of the UV-cured composites.<sup>7</sup>

It has been found that the pendulum hardness of the UV-cured dendritic polyester films is not largely affected by the addition of the comonomer TMPTA to the resins, even at 40 wt % for the resin with polyester D-3.<sup>6</sup> The tensile strength of the UV-cured dendritic polyester composites and the MUP composite (dotted line), as a function of the comonomer TMPTA added, shows different behavior (Fig. 6). The tensile strength of the composites with the three dendritic polyesters decreases rapidly with increased amounts of comonomer added, while the tensile strength of cured MUP composite increases to an optimum at about 30% TMPTA. The decrease of the tensile strength of the composite due to addition of the comonomer to the resin matrix implies that



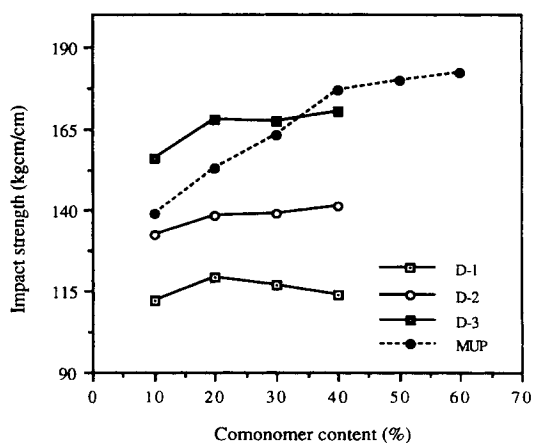
**Figure 6** Tensile strength of the composites vs. content of TMPTA comonomer.



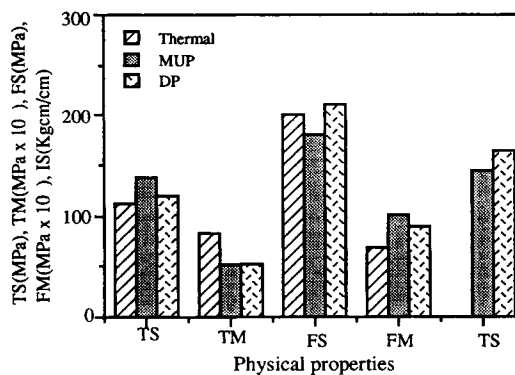
**Figure 7** Flexural strength of the composites vs. content of TMPTA comonomer.

the added comonomers are largely cured as a separate aliphatic phase of low strength surrounding the aromatic dendritic molecules. For the MUP system, the rate of photocrosslinking can be enhanced by the addition of TMPTA. It can be interpreted that comonomer TMPTA added is copolymerized first with acrylic double bonds at the chain ends of the MUP polyester and homopolymerized and then copolymerized with vinylene groups of MUP after an extra amount of comonomer is added, which largely improves the tensile properties of the cured composites.

The flexural strength of the UV-cured composites from D-1 and D-3 is increased by the addition of 10–30 wt % TMPTA, but with 20 wt % TMPTA added to the composite from D-2 (Fig. 7). There is a decrease at high addition, which means that flex-



**Figure 8** Impact strength of the composites vs. content of TMPTA comonomer.



**Figure 9** Comparison of mechanical properties of the cured dendritic polyester with thermally cured unsaturated polyester and UV-cured MUP composites. TS: tensile strength; TM: tensile modulus; FS: flexural strength; FM: flexural modulus; IS: impact strength.

ural strength in this case is largely related to the aromatic dendritic oligomer.

The same is true for the impact strength after addition of various amounts of the comonomer (Fig. 8). For the MUP resin, addition of the comonomer gives a considerable increase in impact strength, which can be explained by the same reason as to why the tensile strength changes with the comonomer added (Fig. 6).

### Comparison with Thermally Cured Unsaturated Polyester and UV-cured MUP Composites

The mechanical properties of composites with three kinds of cured oligomer resins are shown in Figure 9. “Thermal” refers to a maleate-based unsaturated polyester with styrene added (35 wt %) cured by heating to 80°C for 3 h and then to 40°C for 30 h.<sup>11</sup> “MUP” refers to maleate-based unsaturated polyester, modified with epoxy acrylate, cured by UV irradiation for 10 s in UV-CURE at room temperature.<sup>12</sup> “DP” refers to the dendritic polyester D-3, modified with epoxy acrylate and methacrylate anhydride, cured in a fusion system for 0.10 s at room temperature. To the resins “MUP” and “DP,” 3 wt % BDK was added. The three resins were cured as laminates with 35 wt % glass fiber mats added. It can be clearly observed that the recently developed dendritic polyester composite (DP) has the same level of mechanical properties as does the thermally cured and UV-cured unsaturated polyester composites. However, the dendritic polyester system was photocrosslinked at much higher speed than were the others, especially the thermally cured resin system.

## CONCLUSIONS

Dendritic methacrylated polyesters with a high number of functional groups on each molecule (about 8, 12, and 16) were photocrosslinked with UV light as glass fiber-reinforced composites (laminates) in a rapid process (0.02–0.10 s). The cured laminates from dendritic polyesters with 35 wt % glass fiber mats have excellent mechanical properties. Addition of 10–40 wt % comonomer (TMPTA) has only small effects on tensile modulus, flexural strength, and impact strength but decreases tensile strength by 15%.

The mechanical properties of the UV-cured composites with dendritic polyesters are comparable with the thermally cured UP and UV-cured MUP composites. Therefore, it has been shown that dendritic polyesters are promising for industrial applications as glass fiber-reinforced composites.

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## REFERENCES

1. I. R. Bellobono and L. Righetto, in *Radiation Curing in Polymer Science and Technology*, J. P. Fouassier and J. F. Rabek, Eds., Elsevier, London, New York, 1993, Vol. IV, p. 151.
2. S. Miyoshi, Jpn. Kokai Tokkyo Koho JP 6,273,939 (1987).
3. U. Koenig, Ger. Offen. 3,826,304 (1990).
4. D. A. O'Sullivan, *Chem. Eng. News*, **Aug. 16**, 20 (1993).
5. W. F. Shi and B. Rånby, *J. Appl. Polym. Sci.*, to appear.
6. W. F. Shi and B. Rånby, *J. Appl. Polym. Sci.*, to appear.
7. W. F. Shi and B. Rånby, *J. Appl. Polym. Sci.*, **51**, 1129 (1994).
8. R. Dowbenko, C. Friedlander, G. Gruber, P. Prucnal, and M. Wismer, *Prog. Org. Coat.*, **11**, 71 (1983).
9. Y. J. Huang and C. J. Chen, *J. Appl. Polym. Sci.*, **46**, 1573 (1992).
10. Y. J. Huang, J. D. Fan, and L. J. Lee, *Polym. Eng. Sci.*, **30**(11), 684 (1990).
11. A. F. Johnson, *Composites*, **17**(3), 233 (1986).
12. W. F. Shi, B. J. Qu, and B. Rånby, *Polym. Degrad. Stabil.*, **44**(2), 185 (1994).

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