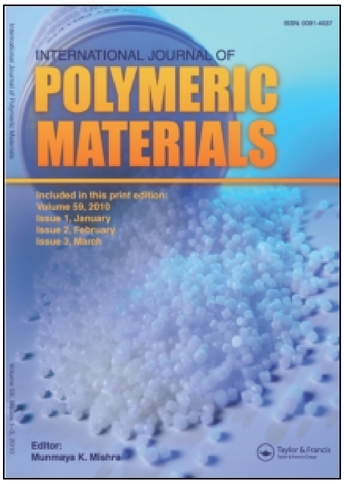

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SYNTHESIS OF UNSATURATED POLYESTER RESIN—EFFECT OF CHOICE OF REACTANTS AND THEIR RELATIVE PROPORTIONS

Benny Cherian[a]; Eby Thomas Thachil[a]
[a] Department of Polymer Science and Rubber Technology, Kochi, India

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SYNTHESIS OF UNSATURATED POLYESTER RESIN—EFFECT OF CHOICE OF REACTANTS AND THEIR RELATIVE PROPORTIONS

Benny Cherian
Eby Thomas Thachil
Department of Polymer Science and Rubber Technology,
Cochin University of Science and Technology, Kochi, India

Unsaturated polyesters are synthesized in the laboratory by the condensation of saturated and unsaturated anhydrides with glycols. The condensate obtained is mixed with styrene monomer to get an unsaturated polyester resin formulation. The properties of the polyester resin synthesized are affected by the synthesis parameters. In this study, the parameters investigated are the effect of choice of reactants and their relative proportions. Properties such as tensile strength, tensile modulus, elongation-at-break, toughness, impact strength, surface hardness, abrasion resistance, and water absorption were tested after curing the resin. Various combinations of (a) maleic anhydride and phthalic anhydride, (b) propylene glycol and ethylene glycol, and (c) propylene glycol and diethylene glycol were used to investigate the effect on the properties of the synthesized resin. The combinations of the anhydrides and glycols that give optimum properties are identified. The results show that most of the properties are maximum at 60% maleic anhydride composition in a mixture of maleic anhydride and phthalic anhydride. Similarly, a better balance of properties is obtained when propylene glycol is mixed with 30% ethylene glycol or 20% diethylene glycol.

Keywords: unsaturated polyester resin, maleic anhydride, phthalic anhydride, propylene glycol, ethylene glycol, diethylene glycol

INTRODUCTION

Unsaturated polyester resins (UP resins) are a class of thermosets widely used in the fiber-reinforced plastic (FRP) industry. The widespread use of these resins is due to their low cost, ease of processing,

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Address correspondence to Eby Thomas Thachil, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, 682 022, India. E-mail: ethachil@cusat.ac.in

ease of combination with reinforcements, rapid cure without any volatile products, excellent dimensional stability, and the wide variety of grades available. Carothers was the first to prepare polyester with well-defined polymeric structures [1]. Carleton Ellis discovered that the rate of cure of UP resin can be increased more than 30 times by the addition of unsaturated monomers [2]. UP resins are prepared by blending the polycondensate of unsaturated and saturated dicarboxylic acids with diols, with an unsaturated co-reactant diluent like styrene. The unsaturated acid provides sites for crosslinking at the curing stage. When the crosslinking is initiated with the help of a catalyst and an accelerator, styrene facilitates crosslinking at the sites of unsaturation in the polyester chains [3]. Styrene forms linear polystyrene chains at the site of unsaturation in the polyester chain and extends to the site of unsaturation in another polyester chain. It has been estimated that the polystyrene crosslinks are two to three monomer units long [4]. The rate of polyesterification is influenced by the structure and stoichiometry of the glycol and dibasic acid components. The properties of the resin are influenced by the choice and proportion of the reactants and also the unsaturated co-reactant monomer. Properties of the cured resin also depend on the degree of crosslinking and the length of the crosslinks between the chains [5–6]. The general purpose (GP) grade resins are blends of styrene with the condensation product of 1,2 propylene glycol (PG) with a mixture of maleic anhydride (MA) and phthalic anhydride (PA).

UP resin was synthesized with different proportions of (a) phthalic anhydride and maleic anhydride to observe the effect of varying the proportion of saturated acid and unsaturated acid. Similarly, the resin was prepared with different proportions of (b) ethylene glycol (EG) and propylene glycol and (c) diethylene glycol (DEG) and propylene glycol and to study the effect on the properties of resin. The optimum concentrations of anhydrides and glycols were determined. The properties were compared with those of commercial GP grade resin.

EXPERIMENTAL

Materials

GP grade UP resin (Bakelite Hylam resin HSR 8113M), styrene, catalyst methyl ethyl ketone peroxide (MEKP), and accelerator cobalt napthenate were supplied by Sharon Engineering Enterprises, Cochin. 1,2 propylene glycol, ethylene glycol, diethylene glycol, maleic anhydride, phthalic anhydride, xylene, hydroquinone, and triphenyl phosphate were supplied by E. Merck India Ltd, Bombay.

Synthesis of UP Resin

The UP resin was prepared by a one-stage process where the anhydrides and glycols were taken in a 1-litre three-necked RB flask, equipped with a mechanical stirrer, CO_2 inlet, and a reflux condenser. A slight excess (10%) of glycol was provided to allow for evaporation losses. The reaction was conducted in an inert blanket of CO_2 and 0.05% triphenyl phosphate was added, to obtain good color and to prevent premature gelation. The reaction mixture was heated at 210°C in a temperature-controlled heating mantle for several hours with continuous monitoring of the acid value. The reaction temperature was kept constant at 210°C, the optimum temperature at which MA in the cis configuration was isomerized to less strained and more planar trans fumaric acid, especially in presence of branched secondary glycols like PG [7]. Fumaric acid is more reactive than MA and the resin shows superior properties [8]. About 10 ml xylene was used to remove water of hydration azeotrophically. The acid value was monitored every two hours as per ASTM D 4662-87. When the acid value became 50, vacuum was applied to bring the value below 30 by removing unreacted reactants and residual water of condensation. At this stage heating was discontinued. When the temperature of the reaction mixture cooled down to 100°C, 0.02 wt% hydroquinone [9], 0.25 wt% paraffin wax, and 40 wt% styrene were added and thoroughly mixed. Paraffin wax was added to prevent inhibition of the crosslinking reaction by the oxygen of the air [10]. The blend was cooled to room temperature and stored in containers.

Variation of Anhydride Composition

In order to study the effect of anhydride composition, polyester resin was synthesised by taking (a) MA and PA at different proportions, that is, MA/PA – 20/80, 30/70, 40/60, 50/50, 60/40, 80/20. Propylene glycol was used as the diol. Resin made purely of PA and PG was not prepared as it offers no crosslinking sites. Casting of the resin, prepared using MA alone, was impossible because of instantaneous gelling on addition of catalyst and accelerator. An optimal composition was determined and this resin was compared with a commercial GP grade resin.

Variation of Glycol Composition

UP resins were synthesized using different proportions of (b) ethylene glycol and propylene glycol as well as (c) diethylene glycol and propylene glycol. In this study, the following proportions of EG/PG and DEG/PG: 0/100, 20/80, 30/70, 40/60, 50/50, 60/40, 80/20, 100/0 were selected. MA and PA were taken in equimolar proportions for these studies. The optimal composition was determined and the properties were compared with those of a commercial GP grade resin.

Curing

UP resins were first cured at room temperature by the catalyst MEKP (60% solution in dimethyl phthalate) and the accelerator cobalt napthenate (4% solution in styrene) [11]. These were used in concentrations of 0.5% and 1% of the weight of the resin, respectively, to obtain a reasonable gel time (10–20 min). The resin was then poured into the tensile mold with dumbbell-shaped cavities coated with a releasing agent. Samples for impact test, abrasion resistance, and water absorption were cast separately in appropriate molds. Curing was done at room temperature for 24 h followed by post curing at 80°C for 3 h.

Testing

The samples after post curing were tested for tensile strength, toughness, elongation at break, modulus, impact strength, water absorption, and hardness, taking six trials in each case. The tensile properties were tested on a Schimadzu Autograph universal testing machine (ASTM D 638-89) and Izod impact strength was measured on a Zwick impact tester as per ASTM D 256 specifications. Abrasion resistance was tested on a Zwick DL 100 machine as per DIN 55516. A shore D Durometer was employed for measuring surface hardness (ASTM D 2240-86). Water absorption was tested as per ASTM D 570. The quality of the resin was tested by determining specific gravity, viscosity, reaction time, $\overline{\mathrm{Mn}}$, gel time, and peak exothermic temperature. The viscosity of the resin was measured on a Brookfield viscometer as per DIN 53015. The gel time and peak exothermic temperature of the resin were determined as per ASTM D 2471-99.

RESULTS AND DISCUSSION

Effect of Variation of Reactant Composition

Properties of Cured UP Resin

Tensile properties. Figure 1a shows the variation of tensile strength of unsaturated polyester resin with different proportions of anhydrides. The tensile strength increased with MA composition up to

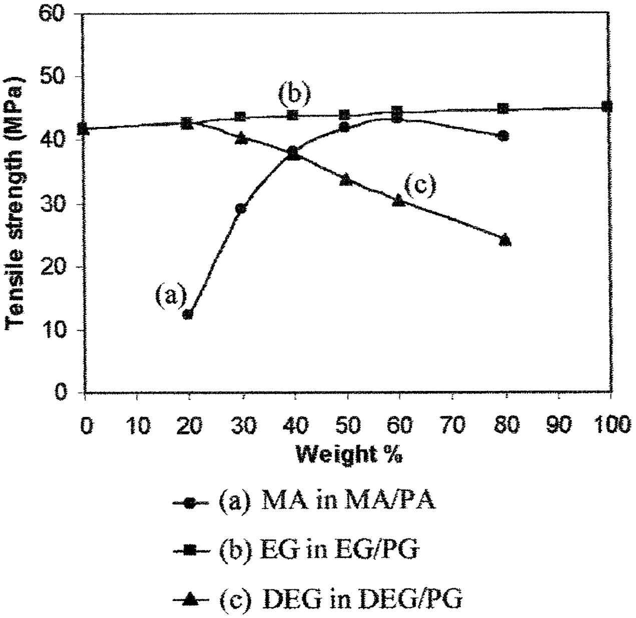

FIGURE 1 Tensile strength of UP resin as a function of relative proportions of reactants.

60% and a further increase lowered the tensile strength. The increase in tensile strength is due to an increase in the crosslink density resulting from higher amounts of unsaturated acid. At much lower concentration of MA, which is the source of unsaturation, polystyrene crosslinks will be far apart and thus the tensile strength decreases. In formulations with higher percentage of MA, molar amounts of maleate are relatively higher than that of styrene so that homopolymerization of fumarate groups becomes possible [12]. Again, at high concentrations, MA enters into side reactions with glycols, which reduce the unsaturation by about 10 to 20% [13]. Thus, resin of this type shows inferior properties.

The change in tensile strength with different EG and PG proportions is shown in Figure 1b. Tensile strength of pure ethylene glycol–based resin is slightly higher than propylene glycol–based resin. Shorter chain lengths of the diol give rise to higher tensile strengths. Due to the pendant methyl group polymeric chains based on propylene glycol are less compact and lead to a decrease in the tensile strength. Thus as propylene glycol content increases tensile strength decreases. The variation in tensile strength with different DEG and PG proportions is shown in Figure 1c. The addition of small proportions of DEG initially improves the tensile strength, but higher degrees of substitution reduce the tensile strength considerably because the isomerization of maleate to fumarate is only partially complete in presence of DEG [4].

The variation in modulus with anhydride composition is shown in Figure 2a. The tensile modulus shows a steady increase at higher percentages of MA until about 60%. In the range of 50 to 60%, the modulus is not very sensitive to the MA composition, but beyond 60%, the fall in modulus is rapid. This loss in modulus at high percentage of MA can again be attributed to the proliferation of double bonds and homopolymerization among the fumarate groups themselves. Figure 2b shows the change in modulus with EG/PG ratio. EG based resin has much higher stiffness than PG based resin. Modulus increases with increase in EG composition. The change in modulus on adding DEG is shown in Figure 2c. The modulus decreases sharply beyond 20% DEG. The flexibility of the polyester chains increases with higher proportions of DEG. As the chain length of the glycol increases, the flexibility of the copolymer increases due to the greater spacing of polar ester groups and acid components.

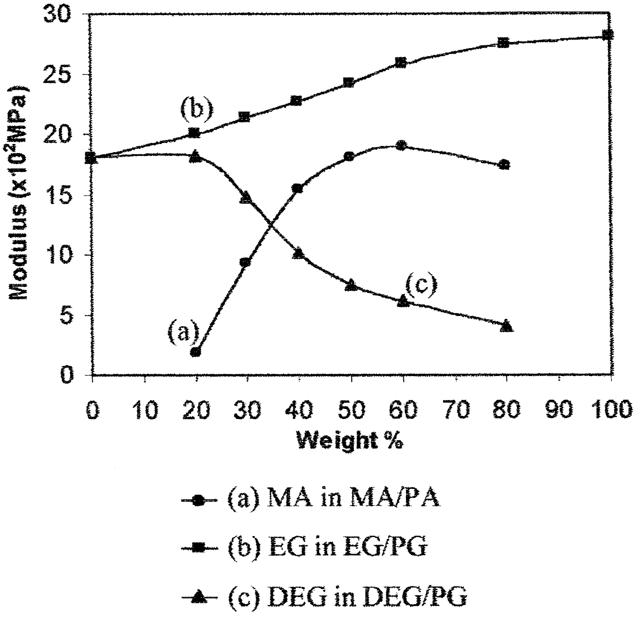

FIGURE 2 Modulus of UP resin as a function of relative proportions of reactants.

Figure 3a shows the variation of elongation at break with anhydride composition. Elongation at break falls rapidly with an increase in the MA composition in the range 20 to 50%. The samples are found to be flexible in this range of composition. The variation of elongation at break with EG percentage is shown in Figure 3b. There is a slight decrease in elongation at break with increasing EG composition due to the greater stiffness of EG-based resins. The variation in tensile elongation with different DEG and PG proportions is shown in Figure 3c. The elongation at break increases considerably due to the plasticization of the resin with higher proportions of DEG.

The change in toughness with the anhydride composition is shown in Figure 4a. The toughness of the sample, as estimated from the area under the stress-strain curve shows a different behavior, being high at low percentage of MA. This is because crosslinks are few in number and the sample undergoes considerable elongation at break. The toughness readily decreases until 50%. After a minimum is reached, the energy absorption capacity shows only a slight improvement with higher concentration of MA. The change in toughness with the EG composition is shown in Figure 4b. There is a steady decrease in

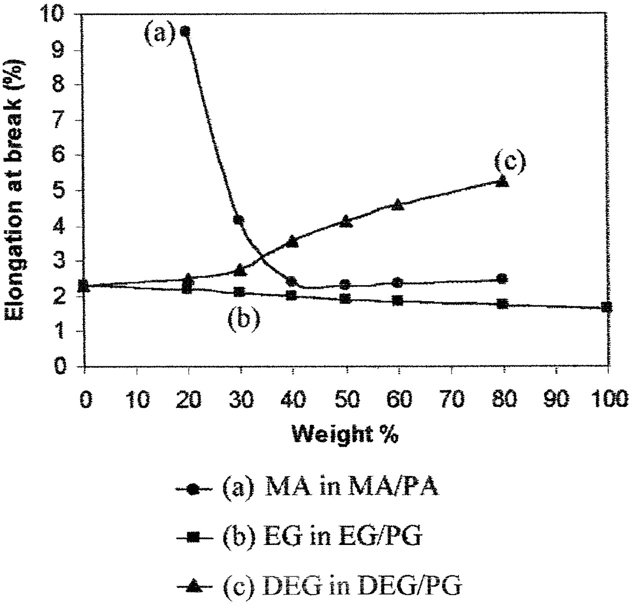

FIGURE 3 Elongation at break of UP resin as a function of relative proportions of reactants.

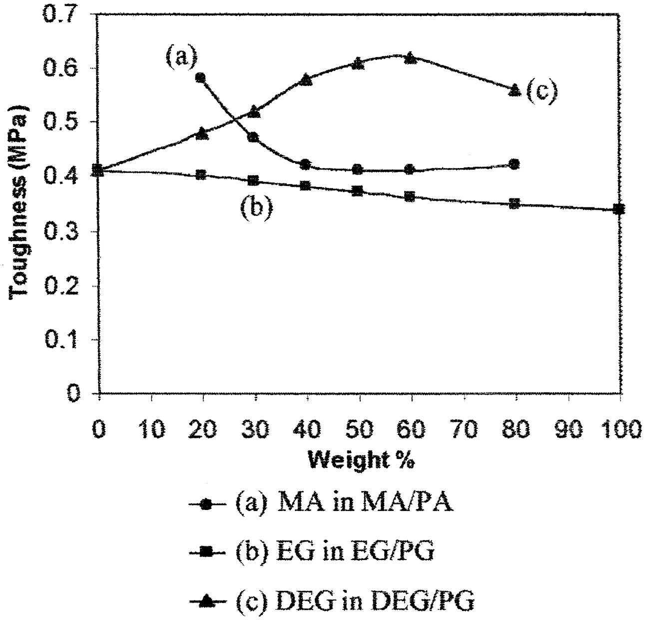

FIGURE 4 Toughness of UP resin as a function of relative proportions of reactants.

toughness of the resin as the percentage of EG content increases. The pendant methyl group in PG increases the flexibility of the resin presumably due to a less compact packing. The variation in toughness with different DEG and PG proportions is shown in Figure 4c. Toughness increases with increasing proportions of DEG. The ether linkage of DEG leads to higher flexibility and elongation at break.

Impact properties. Figure 5a shows the variation of the Izod impact strength with anhydride composition. Impact strength increases up to about 60% MA composition. After that, there is a rapid loss of impact strength. Initially, the crosslinks between the polyester chains provide protection against failure, but at higher percentages of MA the number of crosslinks multiplies and the crosslinked network becomes too rigid to absorb impact energy. Figure 5b shows the change in Izod impact strength with EG weight percentage. The pendant methyl group in PG increases the flexibility of the resin and pure PG based resins have higher impact strength. Impact strength is also related to toughness. The variation in impact strength with different DEG and PG proportions is shown in Figure 5c. Resin with high proportion of DEG has greater impact strength than pure PG based resin.

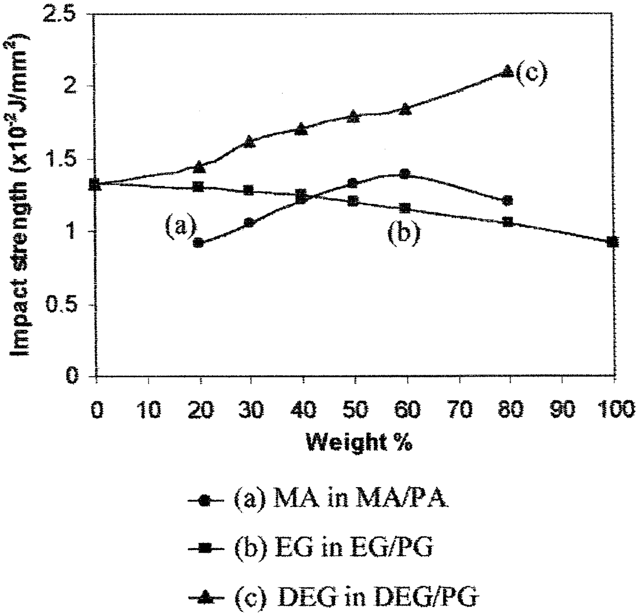

FIGURE 5 Impact strength of UP resin as a function of relative proportions of reactants.

Miscellaneous properties. The variation in surface hardness with anhydride composition is shown in Figure 6a. Hardness increases rapidly from 20 to 40% of MA and thereafter, the values are practically constant. Higher degree of crosslinking is seen to increase hardness only marginally. The variation in surface hardness with EG composition is shown in Figure 6b. As the proportion of ethylene glycol increases hardness increases. This is due to closer packing of EG-based polyester chains. The change in surface hardness with DEG weight percentage is shown in Figure 6c. The addition of DEG increases the flexibility of the resin and decreases hardness.

Figure 7a shows the change in abrasion loss with MA weight percentage. Abrasion loss decreases rapidly from 20 to 40% MA, but beyond 50% the fall in abrasion loss in gradual. In general, a higher degree of crosslinking is found to reduce abrasion loss. The change in abrasion loss with EG weight percentage is shown in Figure 7b. As the content of EG increases abrasion loss decreases. DEG leads to softer segments because of its ether structure. Thus the resin containing higher percentage of DEG is found to give higher abrasion loss as shown in Figure 7c.

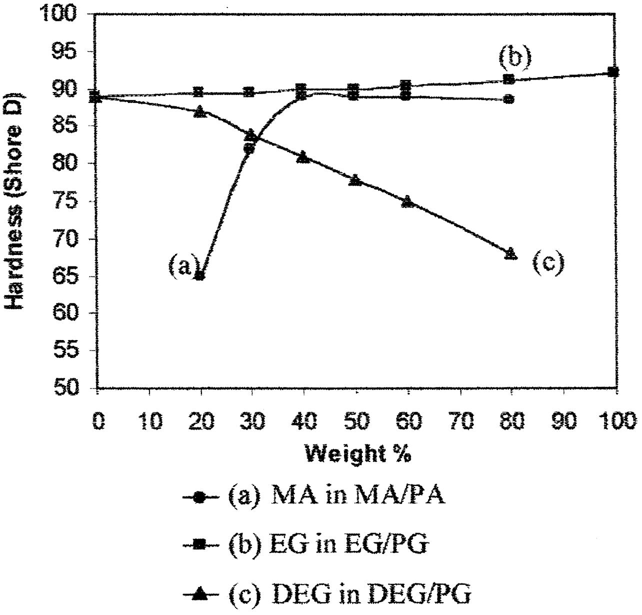

FIGURE 6 Surface hardness of UP resin as a function of relative proportions of reactants.

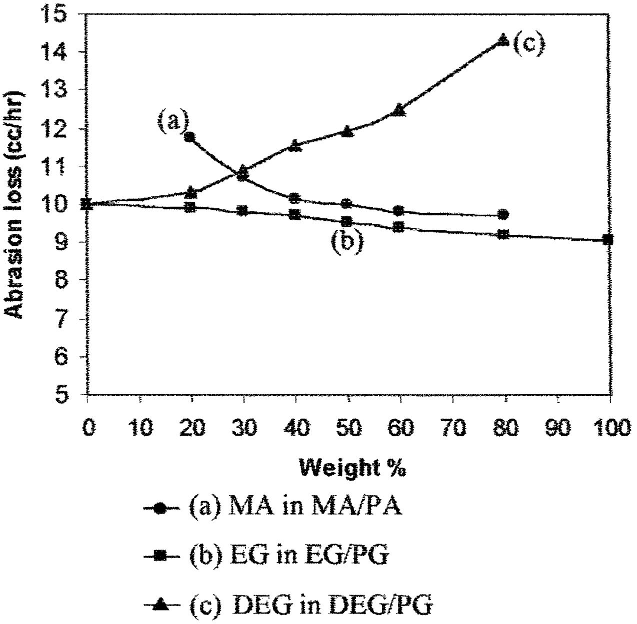

FIGURE 7 Abrasion loss of UP resin as a function of relative proportions of reactants.

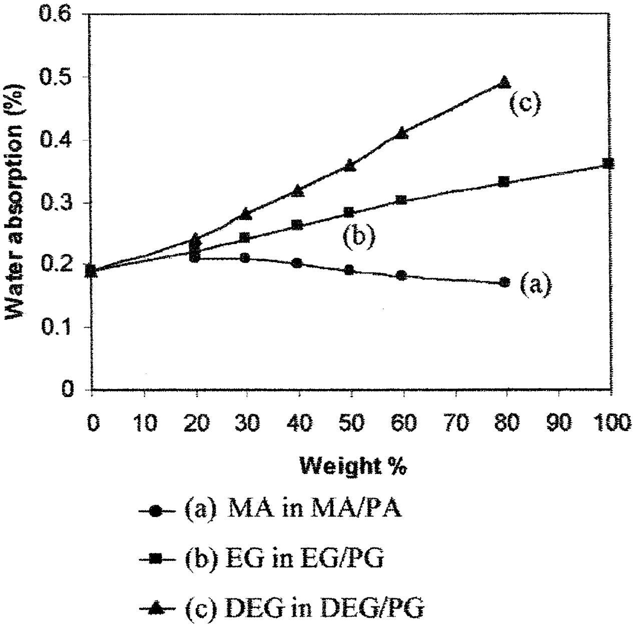

FIGURE 8 Water absorption of UP resin as a function of relative proportions of reactants.

The variation in water absorption with anhydride compositions is shown in Figure 8a. The amounts of water absorbed by the sample is smaller at higher percentages of MA. Closer packing of the polymer chain by extensive crosslinking may be the underlying reason for this. The increase in water absorption with EG content is shown in Figure 8b. EG and PA has the tendency to form low molecular weight oligomers having higher water absorption. The hydrophobicity of pendant methyl group in PG increases the water resistance of the cured resin. It has been reported that ester groups derived from glycols with primary hydroxyl groups have higher water absorption than glycols with secondary hydroxyl groups [4]. The change in water absorption with DEG weight percentage is shown in Figure 8c. The oxygen linkage in DEG increases the water absorption of the cured resin. Thus, higher proportions of DEG are not recommended for outdoor applications.

Properties of UP Resin

Figure 9a shows the variation in specific gravity with different proportions of MA. There is a marginal increase in specific gravity

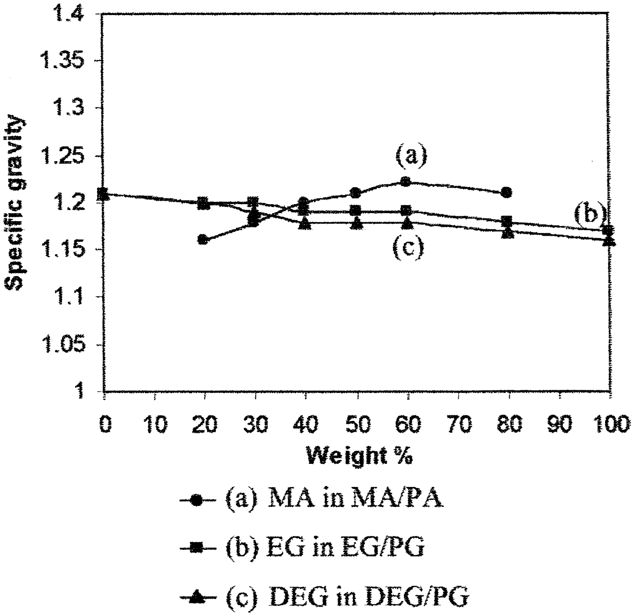

FIGURE 9 Specific gravity of UP resin as a function of relative proportions of reactants.

with increasing MA compositions. The variation in specific gravity with different proportions of glycols is shown in Figure 9b and c. There is a marginal decrease in specific gravity with increasing EG and DEG compositions.

The variation in viscosity with anhydride composition is shown in Figure 10a. Viscosity increases slightly with increase in MA compositions. The viscosity decreases marginally with increasing EG and DEG compositions as shown in Figure 10b and c.

As the MA concentration increases the peak exothermic temperature of the resin increases initially as shown in Figure 11a. It reaches a plateau at about 50%. Beyond that percentage, there is no substantial rise in temperature. This can be attributed to several reasons, for example, homopolymerization of fumarate groups, steric hindrance caused by already established styrene crosslinks, and competition among sites of unsaturation for styrene molecules. As the concentration of EG and DEG increases the peak exothermic temperature of the resin decreases as shown in Figure 11b and c, respectively. The isomerization of maleate to fumarate is only partial in the presence of primary glycols. The strained maleate esters are distorted slightly

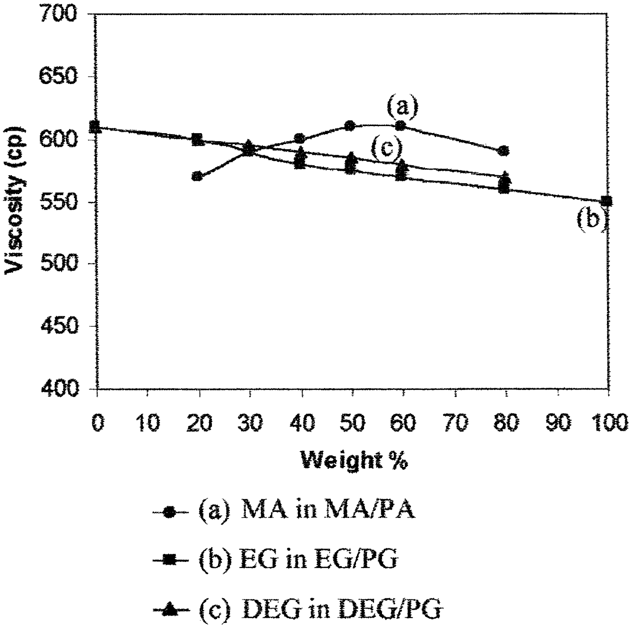

FIGURE 10 Viscosity of UP resin as a function of relative proportions of reactants.

from a planar configuration, which suppresses the ability to copolymerize with styrene monomer. Thus, maleate polymers form networks containing unreacted maleate groups and a higher distribution of styrene homopolymer blocks within the copolymer. These copolymers generate less exotherm and remain in a rubbery transition state [4].

Figure 12a shows the change in gel time with MA weight percentage. Gel time is directly affected by the peak exothermic temperature and the shape of the curve reflects this. As can be expected, a MA rich resin will be fast curing. The gel time increases slightly with EG and DEG compositions as shown in Figure 12b and c, respectively because of the low reactivity of maleate esters with styrene. The reactivity of fumarate esters is almost 20 times those of maleate esters in the copolymerization reaction with styrene [14].

Because MA is more reactive than PA, the reaction time decreases with increasing MA concentration as shown in Figure 13a. Similarly, the reaction time decreases slightly with increasing EG and DEG concentration as shown in Figure 13b and c, respectively. Because linear EG and DEG with primary hydroxyl groups are more reactive,

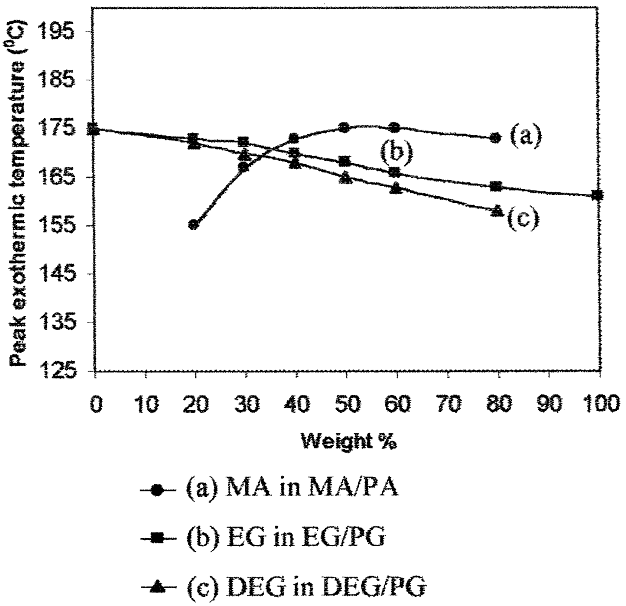

FIGURE 11 Peak exothermic temperature of UP resin as a function of relative proportions of reactants.

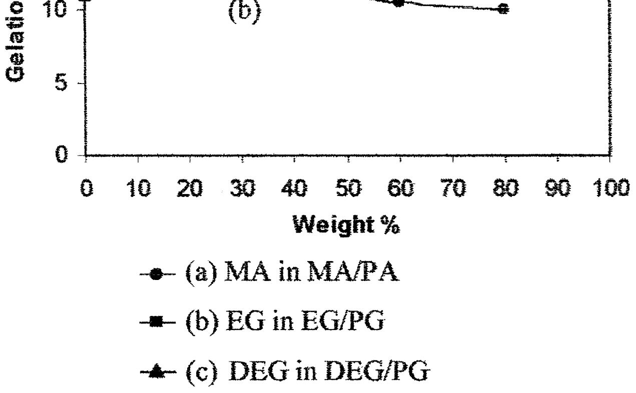

FIGURE 12 Gel time of UP resin as a function of relative proportions of reactants.

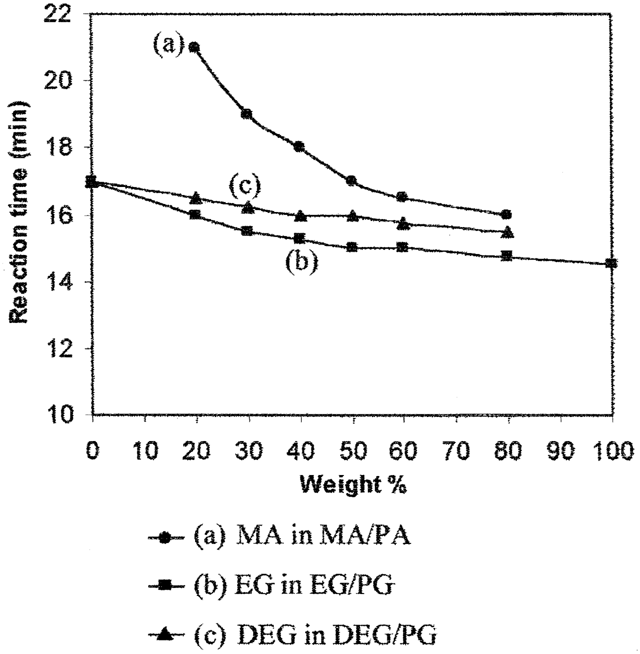

FIGURE 13 Reaction time of UP resin as a function of relative proportions of reactants.

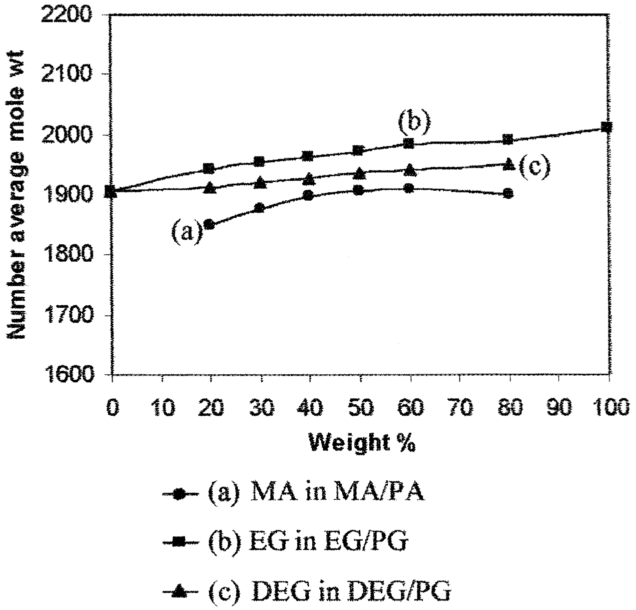

FIGURE 14 Number of average molecular weight of UP resin as a function of relative proportions of reactants.

the condensation reaction proceeds rapidly at lower temperature and the reaction time decreases.

The number average molecular weight ($\overline{Mn}$) was calculated as 56000/acid value [15]. $\overline{Mn}$ shows only marginal variation on changing the relative proportions of reactants (Figure 14).

From the earlier results, the optimal composition of anhydride is found to be in the range of 60% MA, which gives the highest tensile strength, modulus, and impact strength to the cured resin. The optimal composition of EG/PG is in the range of 30/70. The optimal composition of DEG/PG is found to be in the range of 20/80. The properties of synthesized UP resin with optimal compositions are compared with a commerical UP resin [16] as shown in Table 1. The synthesized resin is found to be superior to commercial resin in most properties.

TABLE 1 Summary of the Properties of Commerical Resin and Resin Synthesized by Varying Reactant Composition

		Synthesised UP resin		
Property	Commerical UP resin	60/40 MA/PA (100%PG)	30/70 EG/PG (50/50 MA/PA)	20/80 DEG/PG (50/50 MA/PA)
Tensile strength (MPa)	38	43.35	43.5	42.58
Elongation at break (%)	2.4	2.35	2.1	2.5
Modulus ($\times 10^2$ MPa)	14.10	18.9	21.3	18.25
Toughness (MPa)	0.4	0.41	0.39	0.48
Impact strength ($\times 10^{-2}$ J/mm^2)	1.2	1.38	1.28	1.45
Surface hardness (Shore D)	88	89	89.5	87
Abrasion loss (cc/hr)	10.09	9.82	9.81	10.35
Water absorption (%)	0.21	0.22	0.23	0.25
Specific gravity	1.21	1.22	1.2	1.2
Viscosity (cp)	590	610	590	600
Peak exothermic temperature (°C)	172	175	176.5	173
Gelation time (min)	12	10.5	10.4	12
Reaction time (hr)	—	16	15.5	16.5
$\overline{Mn}$	—	1910	1953	1911

Initiator system: cobalt napthenate, 0.5%; MEKP, 1%.

CONCLUSIONS

It is concluded that the composition of 60/40 MA/PA with pure PG shows optimum properties and its properties are better than those of the commercial resin. But tough and flexible resins can be prepared by using higher proportions of PA.

Although UP resin based on ethylene glycol has slightly better tensile strength and modulus, it becomes hazy and crystallizes upon standing [16]. But propylene glycol–based resins are tough, flexible, less crystalline, compatible with styrene, and water resistant. A resin composition of 30% EG in a mixture of EG and PG containing equimolar amounts of MA and PA is found to have optimum properties.

DEG increases the toughness, impact strength, and flexibility of the UP resin. Optimal properties are observed in the case of 20/80 (DEG/PG) resin containing equimolar amounts of MA and PA. This resin is found to have slightly higher toughness and impact strength compared to the resin containing 30% EG referred earlier. But it lacks water resistance, tensile strength, and modulus at higher proportions of DEG.

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