Synthesis and Characterization of Unsaturated Polyesters Based on the Aminolysis of Poly(ethylene terephthalate)

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ABSTRACT: The depolymerization of poly(ethylene terephthalate) via an aminolysis process was studied. An excess of ethanol amine in the presence of sodium acetate as a catalyst was used to produce bis(2-hydroxyl ethylene) terephthalamide (BHETA). Unsaturated polyester (UP) resins were obtained by the reaction of BHETA with different long-chain dibasic acids such as decanedioic acid, tetradecanoic acid, and octadecanoic acid in conjunction with maleic anhydride as a source of unsaturation. The chemical structure of the UP resins was confirmed by ^{1}H-NMR. The vinyl ester resins were used as crosslinking agents for UP. The curing behavior and mechanical properties of the UP resins with vinyl ester were evaluated at different temperatures ranging from 25 to 55°C. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3327–3336, 2009

Key words: curing of polymers; polyamides; polyesters; recycling; resins

INTRODUCTION

Poly(ethylene terephthalate) (PET) has been known for many years simply as a textile-fiber-forming material. The main growth now observed in the PET market is due to films, bottles, sheets, and coating products, which came into existence in the 1970s.[1] PET was first prepared by Whinfield and Dickson[2] in 1946 and was commercially introduced in 1953 as a textile fiber. It has become one of the most important thermoplastics in world production because of its excellent mechanical properties, good thermal properties, and cost. PET is a semicrystalline saturated polyester produced from terephthalic acid and ethylene glycol.[2] PET products are characterized by high strength, transparency, and safety. However, because it is difficult to dispose of PET bottles in nature, the disposal of a large number of PET bottles has caused serious environmental problems.[3,4] Since the green revolution movement was established in the 1980s, researchers have begun to focus on the recycling and management of plastic wastes.[5,6]

The chemical recycling of PET has been the subject of keen interest as a valuable feedstock for different chemical processes. During chemical recycling, PET can be depolymerized into monomers and oligomers by methanolysis,[7–9] glycolysis,[10,11] hydrolysis,[12–16] and ammonolysis.[17] Aminolysis is another method used for the chemical degradation of PET and has been little explored in comparison with other techniques. The depolymerization of PET waste using different amines such as allylamine,[18] morpholine and hydrazine,[19] and polyamine[20] has been investigated.

Today, PET bottles are among the most valuable and successfully recyclable materials for producing useful products with several applications, such as foam insulation and reinforced unsaturated polyester (UP). Previous investigations[21–25] have studied the production of curable resins based on the glycolysis of PET, which would also help to alleviate an environmental problem.

UP resins are some of the most common matrix resins for composite applications. They possess a wide range of properties and are used in automotive, construction, sport, and furniture applications.[26] Although UP has been used as a coating, it suffers from rigidity, low acid and alkali resistance, and low adhesion. Improvements in resin flexibility can be obtained by the incorporation of long-chain aliphatic compounds into the chemical structure of UP resins. The first part of this work deals with the use of ethanol amine (EA) for the aminolytic degradation of PET to produce curable resins. The second part of this work concerns the blending of the prepared UP with vinyl ester (VE) resins to influence their curing behavior and mechanical properties. To this end, we designed UP resins based on long-chain aliphatic dibasic acids to impart flexibility to the cured resins.

EXPERIMENTAL

Materials

PET waste was collected from beverage bottles. It was crushed into small pieces after being washed

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with soap and methanol to remove any surface finish and dirt present in it. The intrinsic viscosity of PET in *m*-chlorophenol at 25°C was found to be equal to 0.015 dm^3/kg. The weight-average molecular weight, determined by gel permeation chromatography (GPC), was close to 63,200 g/mol. EA was used as supplied. Sodium acetate was used as a transesterification catalyst for the aminolysis of PET. *p*-Toluenesulfonic acid monohydrate was used as a catalyst for the esterification process. Decanedioic acid (DA), tetradecanedioic acid (TDA), octadecanedioic acid (ODA), and maleic anhydride (MA) were used without further purification. Ethylene glycol diacrylate (EGD), trimethylol propane triacrylate (TMPTA), and bisphenol A dimethacrylate (BAD) were used as linear, branched, and aromatic cross-linker VEs, respectively. Methyl ethyl ketone peroxide (MEKP) and cobalt octoate (Co) were used as the initiator and activator, respectively. MEKP was supplied as a 50% paste in dimethylphthalate. Co was a 10% solution in styrene. High-purity-grade toluene, ethanol, acetone, and methylene chloride (purchased from Aldrich Chemical Co., Germany) were used as received. Aldrich Chemical supplied all chemicals.

Techniques

Aminolysis of PET

EA was used for the aminolysis of PET waste materials with a PET/EA molar ratio of 1 : 6 under reflux in the presence of 0.1 wt % sodium acetate (with respect to the weight of PET) for various time periods up to 8 h. At the end of the reaction, distilled water was added handily in excess to the reaction mixture with vigorous agitation to precipitate out the product, bis(2-hydroxyl ethylene) terephthalamide (BHETA). The filtrate contained mainly unreacted EA and small quantities of a few water-soluble PET degradation products. The obtained precipitate was filtered and dissolved in distilled water by boiling for about 30 min; the filtrate was concentrated first by boiling and then by chilling, and a white, crystalline powder of BHETA was obtained. It was further purified by recrystallization in water. It was then dried in an oven at 80°C and weighed at time intervals until the weight of the yield was constant.[27]

Synthesis of the UP resins

The UP resins were prepared by the reaction of 1.1 mol of BHETA with 0.5 mol of MA and 0.5 mol of saturated aliphatic dibasic acids such as DA, TDA, and ODA. UPs with different chemical structures were obtained and were designated UP1, UP2, and UP3, respectively. The reactions were carried out in an esterification reactor equipped with a stirrer, a thermometer, a Dean–Stark side arm, and a nitrogen inlet. The reactants were heated from room temperature to 180°C in a nitrogen atmosphere for 1.5 h and held at this temperature for 4 h. Finally, the temperature was raised and kept at 200°C for 1 h. The extent of the reaction was determined by monitoring of the water volume. Then, the reaction product was permitted to cool to 60°C, and hydroquinone (0.1 wt %) was added as an inhibitor to avoid the polymerization of the product.

The UP resin was dissolved in an adequate amount of CH$_2$Cl$_2$, and then an equal volume of distilled water was added to the reaction products. The organic layer was separated, and the solvent was evaporated. The polyester was a viscous, dark yellow to pale brown liquid, and it was diluted with a sufficient quantity of styrene monomer to produce a 60% solution of the polyester.

Measurements

The melting point of the purified monomer, BHETA, was determined in an open capillary. Elemental analysis was carried out with a Heraus combustion apparatus (Perkin-Elmer, Germany). The prepared UP and BHETA were dissolved in CDCl$_3$ and analyzed with a Varian model JNM-EX (300-MHz) ^{1}H-NMR spectrometer for determining their chemical structures. In addition, the prepared BHETA was characterized by Fourier transform infrared spectroscopy with a Mattson Infinity Bench Top 961 Fourier transform infrared spectrophotometer. Their molecular weights were measured with a Water model 600E gel permeation chromatograph.

The curing exotherms of the UP resins were measured with MEKP as the initiator and Co as the activator, as described in our previous work.[25] The UP was dissolved in 40% (w/w) styrene monomer and mixed with various weight percentages of EGD, TMPTA, and BAD (0–20%). The curing exotherms were determined at different temperatures ranging from 25 to 55°C with a Digitron type K model 3202 digital differential thermometer with a resolution of 0.1°C, as described in our previous study.[28,29] The concentrations of MEKP and Co were 2 and 0.2% (w/w) with respect to the total weight of the cured resins.[25]

Mechanical properties of the cured UP/VE resins

The following section is concerned with the measurement of the comparative properties of the prepared polyesters in the form of test specimens of a standard shape. The cured rods were immersed in an acetone solution for 24 h to extract soluble

materials. Then, the rods were dried in an oven at curing temperatures of 25, 35, 45, and 55°C.

The mechanical characteristics of the cured polyesters under investigation, represented by Young's modulus and the compressive strength, were measured with a Shimadzu universal testing machine (series UH-A model 2000 KN computer-controlled hydraulic servo system). Testing of the mechanical properties was carried out according to ASTM D 695-44T.

RESULTS AND DISCUSSION

Aminolysis of PET

Recycling is feasible when the process and product of recycling are ecofriendly and cost-effective. In chemical recycling, PET is depolymerized with various solvents to get different products such as terephthalic acid, the ester, and bis(2-hydroxyl ethylene) terephthalate.[11] Bis(2-hydroxyl ethylene) terephthalate shows the potential for further chemical reactions.

Zahn and Pfeifer[30] carried out the aminolysis of PET with solutions of hydrazine, benzyl amine, ethylenediamine, hexamethylene diamine, piperidine, and aniline. They obtained different reaction products such as the diamides of terephthalic acid, which do not possess any potential for further chemical reactions.

According to Popoola,[31] the basicity of an amine with respect to water as well as its steric hindrance due to size decides the rate of degradation of PET. During the aminolysis of PET with methylamine, methyl terephthalamide is obtained, which is not reactive enough for recycling into any useful product through further reactions.

This work deals with aminolysis as a route to the depolymerization of PET with EA in the presence of a catalyst. The reaction has been shown to yield BHETA. In this reaction, EA has two nucleophilic centers. Nitrogen is more electronegative than oxygen, so the amine group of EA attacks C=O of PET, and BHETA is obtained, as shown in Figure 1. The catalyst that is used forms a complex with the carbonyl group[32,33] and increase its polarity. The optimized reaction time and concentration of the catalyst during the depolymerization of PET waste for obtaining the maximum yield of BHETA were found to be 8 h and 1% (w/w). Beyond 8 h and a 1% (w/w) catalyst concentration, the yield decreased, probably because of further degradation of the amide that formed.[27]

In our previous work,[25] glycolysis is reported to consist of the transesterification of PET and the destruction of its polymer chain, which results in the reduction of its molecular weight. With glycols used in the depolymerization of PET, the obtained oli-
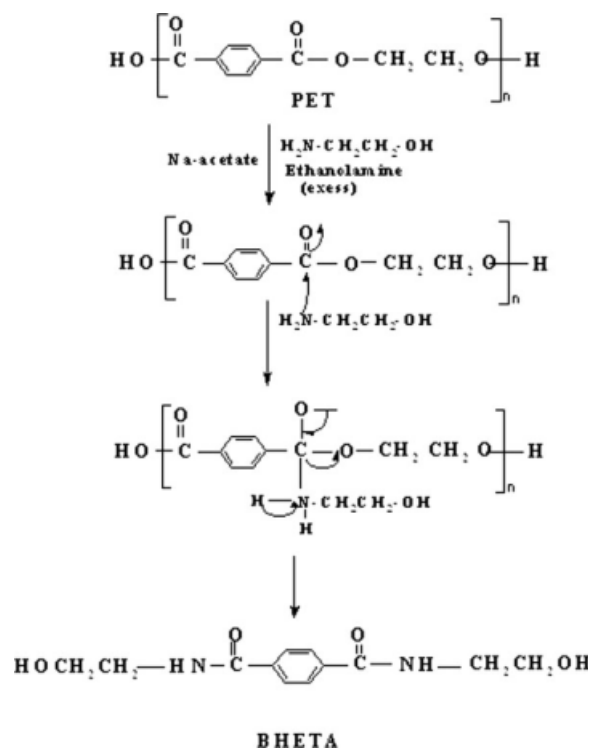

Figure 1 Mechanism for the aminolysis of PET.

goesters have two hydroxyl end groups; that is, oligoester diols are formed. The choice of diethylene glycol (DEG) and triethylene glycol (TEG) to carry out glycolysis is usually determined by the necessity of UP having good flexural properties because the long chains of the glycols improve flexibility.

The previous studies[34] have indicated that the best ratio of DEG or TEG to PET is 1 : 1 (w/w), which affords a better chance for dissolving the initially destroyed materials and hence enhances the reactivity between the solvent (DEG or TEG) and the dissolved glycolyzed product. This certainly leads to more and more destruction because of the increased probability of collisions between the reactants. It is well known that the use of a large excess of glycol in destroying PET leads to the formation of secondary OH groups in the formed oligoesters.[35] These secondary OH groups cause trouble (the formation of gel) during the conversion of the polyol into UP. In this study, the aminolysis of PET was performed with an excess of EA with respect to that required by the stoichiometric proportion for the reaction. The monomer BHETA, ending with a hydroxyl group, was obtained, and it possessed potential for further chemical reactions. In this way, UP based on PET was prepared from the condensation of BHETA with different long-chain dibasic acids (DA, TDA, and ODA) to enhance the flexibility of UP resins; this was due to the amide group, which imparted some rigidity to the compound in comparison with the carboxylic group.

TABLE I
Characterization of BHETA ($C_{12}H_{16}N_2O_4$)

	Elemental analysis (%)		Molecular weight		
	Calcd	Found	Calcd	Found	Melting point
C	57.14	55.38	252	260	227°C
H	6.34	6.15			
N	11.11	10.89			

Table I shows the elemental analysis, melting point, and molecular weight of the purified product, which confirm that the product of PET depolymerization is BHETA. More confirmation is given by ¹H-NMR and IR spectroscopy; the spectrum of BHETA is presented in Figure 2, and it can be observed that the peaks at $\delta = 8.5–9.4$ correspond to the amide (NHCO) group. This confirms the formation of BHETA.

Figure 3 displays the IR spectrum for the same compound; stretching bands at 1745 cm⁻¹ for the ester carbonyl (C=O) and a peak at 3450 cm⁻¹ for OH can be observed in the spectrum, indicating the presence of the terminal —OH group. The peak at 3350 cm⁻¹ is assigned to the secondary amide group and confirms the incorporation of the amide group into the PET backbone.

Synthesis of the UP resins

Depolymerization of this polyester has been studied in the presence of a variety of catalysts and glycols to obtain dimethyl terephthalate or oligomeric polyester.[36–40] Vaidya and Nadkarni[10,41] were among the first to systematically study the formation of UP resins from PET glycolysis. Baliga and Wong[42] carried out the glycolysis of PET with ethylene glycol and various catalysts. Suh et al.[43] examined the properties of UPs
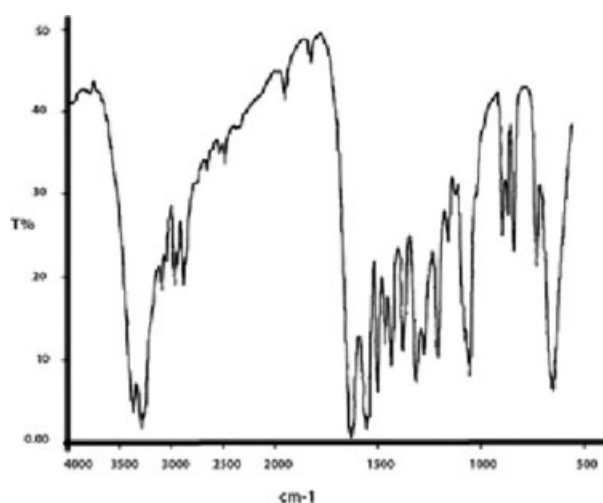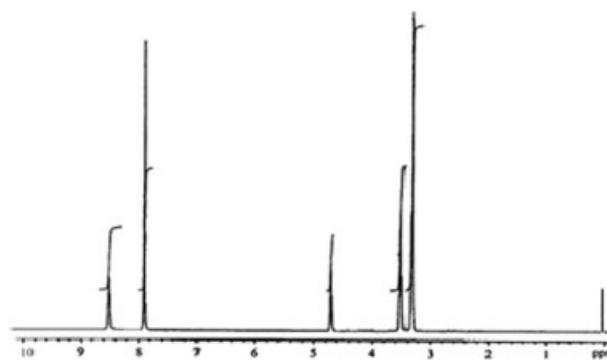

Figure 3 ¹H-NMR spectrum of BHETA.

produced from glycolyzed PET with various combinations of the glycols DEG and propylene glycol.

Farahat and coworkers[44,45] synthesized modified UP by PET glycolysis with different DEG/PET molar ratios. The production of UP from recycled PET is reported in previous works.[46]

The molecular weight of the monomer BHETA was determined to estimate the amount of dibasic acids required for the completion of the esterification reactions. After complete esterification, the polyester was a viscous, dark yellow to pale brown liquid diluted with a sufficient quantity of styrene monomer to yield a 60% UP solution (UP1, UP2, and UP3). The molecular weights of the prepared UP resins were determined with GPC as described in the Experimental section. Preliminary tests have shown that UP resins based on PET and maleic acid are often crosslinked in the presence of 40% styrene, which can dissolve the polyester.

The chemical structure of the UP resins was confirmed by ¹H-NMR analysis. To this end, the spectrum of UPI is presented in Figure 4. The bands at $\delta = 7–8$ are assigned to phenyl ring protons, those at

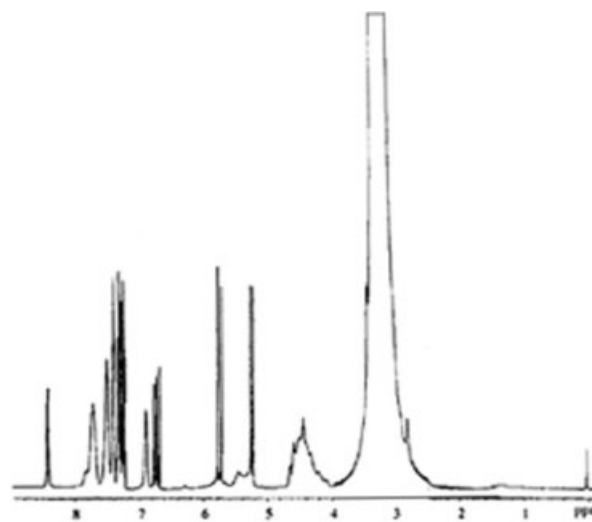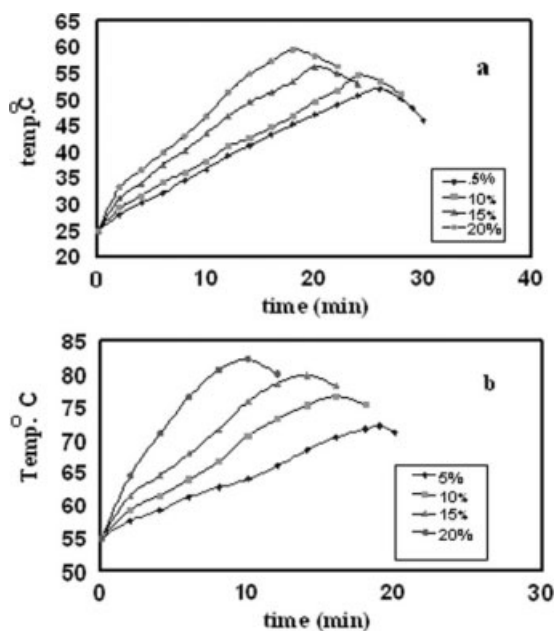**Figure 2** IR spectrum of BHETA.

Figure 4 ¹H-NMR spectrum of UP1.

Figure 5 Curing exotherms of UP1 with EGD at (a) 25 and (b) 55°C.

δ = 8.59 are assigned to the —NHCO group, and those at δ = 4.2–5.0 are assigned to —OH of the terminal alcohol. The signals at δ = 2.25–3.85 correspond to the —CH$_2$ ester aliphatic protons and NH—CH$_2$ proton, and those at δ = 5.3–6.0 are assigned to the unsaturation system (HC=CH). These bands were observed in all spectra of UP2 and UP3.

Curing exotherms

The curing stage is the second step in the preparation of thermoset polymers. The choice of the resin and curing agent depends on the application and on the handling characteristics.

The UPs are long-chain polymers containing a number of reactive double bonds. To form crosslinked networks, they are dissolved in a free-radical-polymerizable monomer such as styrene. This polymerizable monomer, which also contains reactive double bonds (C=C), acts as a curing agent by bridging adjacent polyester chains at their unsaturation positions. The content of styrene in the final resin is important to ensure good processability. Moreover, if its content is very high or very low, there can be high shrinkage on curing or a tendency to not cure fully, respectively.[41]

In this investigation, the curing exotherms of mixtures of UP and VE diluted with styrene were obtained through the plotting of the curing temperature as a function of time at different temperatures (25, 35, 45, and 55°C). For brevity, the curing exotherm curves of UP1 at 25 and 55°C are illustrated in Figure 5(a,b), respectively. Because the amount of

heat that evolves upon curing depends on the sample size, it is desirable to consider this parameter. For this reason, it was very important to use glass bottles of the same volume in all measurements to achieve repeatability of the measurements and to afford legitimate comparative study. The formulas are based on UP and styrene in the presence of 5, 10, 15, or 20% VE (based on the total weight of UP and styrene). The cure of this reaction proceeds via free-radical bulk copolymerization. The following section concerns the possibility of modifying the curing behavior of UP resins through changes in the amounts and types of VE (EGD, TMPTA, and BAD) with constant concentrations of MEKP and Co of 2 and 0.2%, respectively.[47] The effect of temperature on the curing exotherms is discussed. The curing exotherms were determined at temperatures of 25, 35, 45, and 55°C. In this system, Co and MEKP are the produced radicals. These radicals initiate the exothermic precautions with UP, and the temperature rises when the number of radicals is sufficient to make the rate of heat generation larger than the heat dissipation. For this reason, the temperature of the reaction of the proposed system was varied from 25 to 55°C. The data of curing at these temperatures are listed in Tables II–IV. As the curing temperature increases, the time required for the complete curing reaction (t_{max}) decreases. This can be attributed to the increase in the reaction temperature, which reduces the viscosity of the reactants and consequently affects the diffusion and reactivity ratios between the reactants.

The effects of the UP and crosslinker structure are also discussed. The values of the maximum temperature (T_{max}), which is inversely related to t_{max}, are shown in Tables II–IV. The data listed in these tables indicate that, in all cases, the curing time decreases with the content of each crosslinker increasing. This can be attributed to an increase in the number of polymerizable double bonds and enhanced diffusion of the styrene monomer toward the unreacted double bonds embedded in the three-dimensional network. On the other hand, the type of VE affects the reaction rate and curing time. This is indicated by the data listed in Tables II–IV, which show that the curing behavior of the branched crosslinker (TMPTA) is different from that of the linear crosslinker (EGD). This can be attributed to the fact that the branched crosslinker (TMPTA) is shorter and more compatible with styrene because it has more polymerizable double bonds than the linear crosslinker (EGD). On the basis of compatibility with styrene, the aromatic crosslinker (BAD) is expected to be the most compatible one. This explains the maximum heat that evolves during its curing reaction. This finding agrees with Martin's results.[48] He observed that the increased compatibility between

TABLE II
Curing Parameters of UP1 with EGD, TMPTA, and BAD at Different Temperatures

	25°C		35°C		45°C		55°C	
	t_{max}	T_{max}	t_{max}	T_{max}	t_{max}	T_{max}	t_{max}	T_{max}
EGD (wt %)								
0	29	50.1	27	59.1	24	62.3	22	68.3
5	26	52.3	25	61.2	21	65.8	19	72.1
10	24	54.6	22	64.0	18	68.2	16	76.6
15	21	56.2	20	67.2	16	71.2	14	79.8
20	19	59.0	17	69.4	15	73.0	11	82.2
TMPTA (wt %)								
0	29	50.1	27	59.1	24	62.3	22	68.3
5	20	55.4	18	63.3	16	69.5	15	74.2
10	19	56.3	15	66.0	13	72.0	11	78.0
15	17	58.0	13	69.1	11	78.2	9	82.8
20	15	61.3	11	71.2	9	77.1	8	85.3
BAD (wt %)								
0	29	50.1	27	59.1	24	62.3	22	68.3
5	18	58.2	16	66.5	15	70.3	12	78.5
10	17	60.1	15	69.5	12	75.4	10	82.0
15	15	63.1	12	71.0	11	80.5	9	84.1
20	13	66.1	11	74.3	9	83.4	7	88.3

the monomer solvent and the unsaturated molecule to be polymerized leads to a faster curing reaction and higher heat generation.

As mentioned before, variations in the types and amounts of the individual components allow a lot of variety in the design of resin formulas. The types of saturated acids used in the preparation of UP resins have a profound influence on their curing behavior. It has been reported that the amount of fumarates in a UP resin affects its rate of cure.[49] Horie et al.[50] studied the effect of the structure of UP resins on their curing behavior and reported that the final degree of cure under isothermal conditions decreases markedly with an increase in the amount of fumarates in the resins. In our study, DA, TDA, and ODA were used to control the amount of fumarates in the UP resins.

This study used three UP formulas with different chemical structures. The prepared UP is based on PET, which includes long chains having both

TABLE III
Curing Parameters of UP2 with EGD, TMPTA, and BAD at Different Temperatures

	25°C		35°C		45°C		55°C	
	t_{max}	T_{max}	t_{max}	T_{max}	t_{max}	T_{max}	t_{max}	T_{max}
EGD (wt %)								
0	31	43.2	30	46.2	27	50.2	24	55.2
5	30	45.1	28	49.3	24	54.3	21	58.2
10	28	48.2	26	51.6	22	59.3	19	61.3
15	26	49.9	23	54.2	20	61.2	17	64.5
20	24	51.5	21	59.0	18	64.2	15	69.8
TMPTA (wt %)								
0	31	43.2	30	46.2	27	50.2	24	55.2
5	27	49.8	23	54.8	22	60.1	20	66.2
10	25	53.6	20	60.2	18	65.3	17	70.2
15	22	58.9	18	66.8	17	68.0	14	75.2
20	20	61.5	16	70.1	15	72.5	12	77.6
BAD (wt %)								
0	31	43.2	30	46.2	27	50.2	24	55.2
5	24	52.6	21	59.1	17	63.5	16	69.5
10	22	58.9	19	63.2	16	66.6	13	73.2
15	21	64.2	17	67.8	14	71.5	11	78.5
20	19	68.3	14	72.3	11	75.3	9	80.3

TABLE IV
Curing Parameters of UP3 with EGD, TMPTA, and BAD at Different Temperatures

	Curing parameters							
	25°C		35°C		45°C		55°C	
	t_{max}	T_{max}	t_{max}	T_{max}	t_{max}	T_{max}	t_{max}	T_{max}
EGD (wt %)								
0	40	39.5	39	42.1	37	46.3	34	50.1
5	38	42.9	36	45.6	35	50.1	33	55.3
10	37	44.0	34	47.6	32	52.4	30	59.6
15	35	48.0	31	50.3	28	56.3	27	63.2
20	32	50.1	29	52.6	25	59.6	24	66.0
TMPTA (wt %)								
0	40	39.5	39	42.1	37	46.3	34	50.1
5	35	45.2	33	49.2	30	54.2	26	58.3
10	32	48.6	30	53.2	27	58.2	23	61.8
15	30	50.3	28	57.6	24	60.3	20	64.8
20	27	53.3	25	61.5	21	64.3	18	69.5
BAD (wt %)								
0	40	39.5	39	42.1	37	46.3	34	50.1
5	31	49.5	29	51.6	26	58.9	23	61.5
10	28	51.2	27	56.3	24	62.3	20	63.5
15	26	54.2	25	60.2	21	65.3	17	66.8
20	23	58.3	22	64.0	19	68.2	15	70.5

aromatic moieties and aliphatic moieties. On the other hand, the length of the dibasic acid moieties affects the molecular weight of UP and the number of polymerizable double bonds of the MA group in the UP structure. Accordingly, it is legitimate to state that the curing time is reversibly proportional to the chain length of the dibasic acids. In addition, it can be stated that an increase in the chain length leads to a decrease in the efficiency of the VE cross-linker. Therefore, the curing time of UP1 should be lower than that of UP2 and UP3 (Tables II–IV).

Mechanical properties

It is interesting to measure the mechanical properties of cured resins to determine their potential applications. The mechanical properties are quantified easily because the test methods are standardized and are easily related. The derived values of Young's modulus (GPa) and the maximum compressive strength (MPa) for cured UP1, UP2, and UP3 are given in Tables V–VII. The values of Young's modulus (GPa) and the compressive strength (MPa) were derived from the stress–strain curves for different

TABLE V
Mechanical Parameters of Cured UP1 with EGD, TMPTA, and BAD at Different Temperatures

	Curing parameters							
	Maximum compressive strength (MPa)				Young's modulus (GPa)			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
EGD (wt %)								
0	130.201	133.251	146.769	155.214	22.210	24.440	27.264	30.325
5	137.214	144.582	153.247	159.358	18.254	20.247	23.254	26.587
10	157.651	161.254	170.289	178.327	17.214	19.687	21.478	24.369
15	166.325	170.247	177.321	182.314	15.257	17.258	19.689	21.357
20	172.641	180.254	196.124	215.217	13.247	16.897	17.257	20.012
TMPTA (wt %)								
0	130.201	133.251	146.769	155.214	22.210	24.440	27.264	30.325
5	142.231	150.234	158.105	164.147	19.321	21.200	24.501	26.111
10	161.985	170.953	179.125	186.345	18.625	20.213	22.921	25.123
15	170.602	177.097	184.113	190.323	16.153	19.201	20.983	22.478
20	180.531	190.981	203.114	233.152	14.824	17.565	18.238	20.730
BAD (wt %)								
0	130.201	133.251	146.769	155.214	22.210	24.440	27.264	30.325
5	155.312	166.236	175.245	188.987	21.214	22.354	24.561	27.523
10	169.248	179.278	189.324	196.247	20.147	21.658	23.587	26.358
15	177.389	186.257	192.354	215.274	18.564	20.587	22.214	24.546
20	188.254	196.378	241.257	267.147	16.321	18.587	21.566	23.874

TABLE VI
Mechanical Parameters of Cured UP2 with EGD, TMPTA, and BAD at Different Temperatures

	Curing parameters							
	Maximum compressive strength (MPa)				Young's modulus (GPa)			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
EGD (wt %)								
0	130.201	133.251	146.769	155.214	22.210	24.440	27.264	30.325
5	135.245	140.214	150.214	156.247	18.247	19.698	21.214	23.587
10	144.287	158.214	162.478	165.258	17.258	18.958	23.654	25.684
15	158.247	163.540	170.012	173.247	15.687	17.321	19.574	21.202
20	164.214	171.247	179.897	186.247	11.235	13.241	15.021	17.025
TMPTA (wt %)								
0	130.201	133.251	146.769	155.214	22.210	24.440	27.264	30.325
5	139.012	148.651	153.654	160.278	17.214	19.320	21.547	24.657
10	157.541	160.214	168.247	177.584	16.358	18.214	20.021	22.657
15	167.147	168.587	176.358	186.874	15.278	15.871	18.687	21.000
20	177.894	180.247	189.251	199.231	13.257	14.354	16.021	19.541
BAD (wt %)								
0	130.201	133.251	146.769	155.214	22.210	24.440	27.264	30.325
5	149.687	155.201	162.021	170.584	19.214	21.254	23.547	26.540
10	165.324	167.251	181.278	190.210	18.254	20.254	22.941	24.210
15	172.021	178.589	189.987	200.001	16.234	18.254	20.980	22.005
20	183.210	191.587	207.014	236.958	14.258	16.874	18.600	21.014

cured resins. Accordingly, UP resins designed from recycled PET may be used for making polymer concrete. The following sections discuss the effects of the chemical structures of both UP and VE on the mechanical properties of the cured resins. On the other hand, the effect of the VE concentration and reaction temperature are discussed afterward.

The effect of the structure of the resin on its mechanical and curing behavior has been investigated. The molecular weights of the prepared polymers were determined by GPC analysis. In this study, the resultant molecular weight of UP1 is 3310 g/mol, whereas the molecular weights of UP2 and UP3 are 5720 and 7236 g/mol, respectively. This can be attributed to the effect of the molecular weight of the repeating unit, the difference in the initial initiator concentration, and the effect of the oligoester diols for UP1, UP2, and UP3. The presence of the amide group in all the structures of the UP resins provides some rigidity in comparison with the carboxylic group, so the choice of the saturated acid (aliphatic) offers great latitude in the design of

TABLE VII
Mechanical Parameters of Cured UP3 with EGD, TMPTA, and BAD at Different Temperatures

	Curing parameters							
	Maximum compressive strength (MPa)				Young's modulus (GPa)			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
EGD (wt %)								
0	130.201	133.251	146.769	155.214	22.210	24.440	27.264	30.325
5	133.020	138.541	149.541	153.274	16.241	17.014	18.564	20.140
10	142.258	147.587	154.287	160.021	15.120	16.258	18.014	19.002
15	152.784	158.274	166.387	170.001	12.054	14.257	16.254	18.574
20	160.325	166.321	171.258	179.998	10.001	11.354	12.540	14.257
TMPTA (wt %)								
0	130.201	133.251	146.769	155.214	22.210	24.440	27.264	30.325
5	137.251	145.612	151.247	159.87	17.204	18.214	20.541	22.584
10	140.257	158.204	163.047	172.471	15.214	17.002	20.214	23.514
15	148.012	164.026	171.245	182.471	13.654	15.354	18.541	19.201
20	156.010	177.025	180.147	191.589	10.214	12.547	14.021	16.541
BAD (wt %)								
0	130.201	133.251	146.769	155.214	22.210	24.440	27.264	30.325
5	147.580	153.470	158.584	166.984	18.024	19.568	22.214	24.687
10	159.998	165.801	177.589	188.657	16.254	17.987	19.028	24.580
15	164.580	170.002	182.695	197.845	14.025	16.541	17.854	20.561
20	173.258	183.287	198.998	225.001	13.024	15.258	15.254	17.254

polymer backbones. The crosslinking density of the cured product depends on the type and percentage of the unsaturated dibasic acid used in constructing the resin. In this respect, the UP1 backbone is based on DA, whereas UP2 and UP3 are based on TDA and ODA, respectively. The structures of UP2 and UP3 are more flexible than that of UP1. The flexibility of this resin may be attributed to the effect of the chain length of the dibasic acid molecules used in constructing the UP resin. The increase in the length of the dibasic acid molecules certainly leads to an increase in the length of the polymer segments. This in turn reflects the intramolecular and intermolecular interactions and yields lower energy barriers for rotation, which enhances the flexibility of the resin. Accordingly, increasing the molecular weight of the dibasic acid causes a decrease in the crosslinking density. Consequently, the mobility of the polymer segment increases, and hence an increase in the flexibility is detected as a reduction in Young's modulus. The reduction in Young's modulus can be attributed to an increase in the length of the polymer segments. Recalling data listed in Tables V–VII, we find that the compressive strength of formulas based on UP2 and UP3 is lower than that of formulas based on UP1. This can be attributed to the chain length of the dibasic acid. This affords some flexibility to the resin. This finding is supported by the previous work.[51]

The mechanical properties of the UP resins produced were studied with respect to the effects of the type and percentage of VE. Different mechanical data were observed when EGD, TMPTA, and BAD were used as crosslinkers. The compressive strength values increased with the VE content increasing from 0 to 20%. This indicates that the flexibility of the resins decreased with the incorporation of VE into the network structure. The increase in the maximum compressive strength with increasing VE content can be attributed to the increased content of curable double bonds, which greatly increased the crosslink density. This resulted in the cured UP/VE resins being harder and more resistant to deformation upon the application of external stresses. The net effect was that the mechanical strength was significantly improved as a result of the more chemically bonded structures.

Tables V–VII show the different mechanical properties when EGD, TMPTA, and BAD were used as crosslinkers for UP. The compressive strength increased with increasing concentrations of VE. This can be explained by the fact that VE is more reactive with UP than UP is with styrene. We can conclude that the formulations composed of BAD and UP resins possess the maximum compressive strength. This can be attributed to the incorporation of the aromatic ring, which affords greater rigidity to the cured

resin.[52] The compressive strength of the linear crosslinker (EGD) is lower than that of the other crosslinkers. This is due to the similarity of the spacing between the double bonds available to form the final network structure in the curing reaction. As these double bonds become separated from one another, the resins become less rigid than if these double bonds were close.[53] The compressive strength of the resins containing the branched crosslinker (TMPTA) lies between the compressive strengths of those with the linear crosslinker and those with the aromatic crosslinker. Young's modulus decreases with the homopolymerization of the monomer.[54] Therefore, it is possible that the homopolymerization of styrene occurs at high crosslinking concentrations. It is obvious that this finding agrees with these results. This speculation agrees with the data listed in Tables V–VII, which indicate that Young's modulus decreases upon the incorporation of VE into a network of crosslinked UP.

The data show that the value of Young's modulus increases as the temperature of the reaction increases. This is due to a decrease in the molecular weight with an increase in the polymerization temperature. Because of an increase in the rate of termination and chain transfer and an increase in the relative amount of polymer chain ends, the mechanical properties of the polymers are affected. Accordingly, an increase in the reaction temperature leads to a denser network of the cured polymers and reduces the average molecular weight between crosslinks.[55] Therefore, increasing the polymerization temperature results in increases in both the maximum compressive strength and Young's modulus.

CONCLUSIONS

- The synthesis of BHETA through the aminolysis of PET has a high yield and a shorter reaction time.
- BHETA has the potential for being recycled into useful products through various chemical reactions.
- New UP ester resins based on recycled PET through aminolysis were prepared.
- The curing exotherms of UP3 had greater t_{max} values and lower T_{max} values than those of UP2 and UP1 when they were cured with a VE crosslinker at different temperatures. This can be related to the effect of the molecular weight of saturated dibasic acids.
- The increase in the curing temperatures of all the prepared UPs with VE from 25 to 55°C reduced t_{max} of curing.
- The curing of the VE resins with UP resins in the presence of styrene indicated that the curing

times were reduced and the cure exothermic temperatures were increased by the incorporation of VE into the crosslinked networks.

- VE (BAD) showed a superior curing time and gave some rigidity to all UPs.
- The compression strength of the cured resins was improved by the incorporation of VE resins.

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