

Alkyd resins derived from glycolized waste poly(ethylene terephthalate)

George P. Karayannidis ^{*}, Dimitris S. Achilias,
Irini D. Sideridou, Dimitris N. Bikaris

Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Macedonia, Greece

Received 3 September 2004; received in revised form 28 September 2004; accepted 1 October 2004

Abstract

In this investigation the production of secondary value-added products, such as alkyd resins, derived from the glycolysis of poly(ethylene terephthalate) (PET) is examined as an effective way for its recycling. PET was taken from common soft-drink bottles and diethylene glycol (DEG) was used for the depolymerization at several initial molar ratios. The oligomers obtained were analyzed according to their average molecular weights. Furthermore, the glycolized PET products (oligomers) were reacted with maleic anhydride, phthalic anhydride and propylene glycol to form unsaturated polyester resins. These were subsequently mixed with styrene and cured using the benzoyl peroxide/amine initiator system to carry out the reaction in ambient temperature. The curing characteristics of the resins produced were investigated with respect to the initial molar ratio of DEG/PET as well as the initial initiator concentration. Finally, the mechanical properties (tensile strength and elongation at the break point) of the resins were compared with the conventional general purpose resin and were found to be comparable.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Recycling; Alkyd resins; Curing of unsaturated polyesters; Glycolysis; Poly(ethylene terephthalate)

1. Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester showing excellent thermal and mechanical properties. Although its main application was by far the textile industry, tremendous quantities of this mate-

rial are consumed in the manufacture of video and audio tapes, X-ray films, food packaging and especially of soft-drink bottles.

PET recycling represents one of the most successful and widespread examples of polymer recycling. PET bottle collection in Europe (European Union member states plus Norway, Iceland, Switzerland, and all EU candidate countries) is growing steadily. In 2001 344,000 ton were collected, a 20% increase in comparison with 2000. By 2006, it is forecast that European PET collection will increase to 700,000 ton [1]. The main driving force responsible for this extremely increased recycling

^{*} Corresponding author. Tel.: +30 2310 997814; fax: +30 2310 997769.

E-mail address: karayan@chem.auth.gr (G.P. Karayannidis).

of post-consumer PET is its widespread use, particularly in the beverage industry. A very important feature of PET, decisive in the choice of its wide application in the manufacture of packaging for the food industry is that it does not have any side effects on the human organism. It should be pointed out, that PET does not create a direct hazard to the environment but, due to its substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents, it is seen as a noxious material [2]. Therefore, the recycling of PET does not only serve as a partial solution to the solid waste problem but also contribute to the conservation of raw petrochemical products and energy.

Among the different recycling techniques, the only one acceptable according to the principles of "Sustainable Development" is the chemical recycling, since it leads to the formation of the raw materials from which the polymer is made of, as well as of other secondary value-added products [3]. A successful recycling program does not only depend on post-consumer waste collection, it also depends on whether the products made out of collected, reclaimed and recycled material respond to consumers' needs, in other words if recycled products are actually bought. This is the reason why the PET industry constantly researches for reclaimed material new applications. Recently, a growing interest has been observed in the use of PET wastes for the production of specialized products such as unsaturated polyester, polyurethane foams and polymer concrete.

In our previous publications [4,5], the alkaline and acid hydrolysis of PET was examined in order to take the pure monomer (terephthalic acid) from which the polymer is made of. This monomer was used as raw material for the reproduction of PET. As a step further, in this paper, glycolysis of PET is examined as a process for the production of raw materials used in coating resins. Vaidya and Nadkarni were among the first who systematically studied the formation of unsaturated polyester resins (UPR) from PET glycolysis [6,7]. Baliga and Wong [8] carried out the glycolysis of PET with ethylene glycol (EG) using various catalysts. They found that glycolized products had 1–3 repeating units depending on the catalyst used. Halacheva and Novakov [9] have investigated the chemical structure of the oligoesters produced from PET glycolysis with diethylene glycol (DEG). Furthermore, Suh et al. [10] examined the properties of unsaturated polyesters produced from glycolized PET with various combinations of the glycols DEG/propylene glycol (PG). Farahat and Nikles [11,12] provided results on the glycolysis of PET and the production of novel binder systems for solventless magnetic tape manufacturing. Farahat et al. also synthesized modified UPR from PET glycolysis using different DEG/PET molar ratios [13,14]. The production of fiber-reinforced thermosetting composites using the product of PET glycolysis has been investi-

gated by Aslan et al. [15]. In the same process of glass-fiber-reinforced plastics manufacturing, Radenkov et al. [16] investigated the possibility of direct using products from PET glycolysis. Glycolysis of recycled PET was also investigated by Chen et al. [17] and Mansour and Ikladious [18]. Finally, the mechanical properties and the characteristics of UPR produced from post-consumer PET bottles was investigated by Pimpan et al. [19] and the synthesis of coating resins from recycled PET was investigated recently by Kawamura et al. [20].

The aim of this research was to use the unsaturated oligoester diols produced from PET recycling as potential raw materials for the production of alkyd resins used as enamel paints or coatings. In order to fulfill this goal three steps were distinguished. The first step includes the depolymerization of PET using various diethylene glycol/PET ratios and the identification of the oligomers produced. In the second step the curing behavior of unsaturated polyester resins used for the production of alkyd resins for ambient temperature coatings was investigated by manipulating the amounts of the initiators used. In the final step, the glycolized products (glycolyates) taken from PET recycling replace the diols used for the conventional production of the alkyd resins and the final mechanical properties of the resins were compared.

2. Experimental

2.1. Materials

PET flakes were prepared from post-consumer clear PET bottles, from which the polyethylene caps and the polypropylene label had been removed. The bottles were cut and fed to a rotary cutter with a max size of 6 mm. Diethylene glycol (DEG), 1,2-propylene glycol (PG), maleic anhydride (MA) and Styrene monomer were supplied by Fluka AG. Phthalic anhydride (PA) was obtained from Merck. Manganese acetate $[\text{Mn}(\text{CH}_3\text{COO})_2\text{H}_2\text{O}]$ with a purity of 99% was supplied from Aldrich. The initiators for the curing reaction of the synthesized unsaturated polyester resins were benzoyl peroxide (BPO) from Fluka AG and *N,N*-dimethyl-*p*-toluidine (DMT) from Aldrich. Tetrahydrofuran (THF) used as a solvent in gel permeation chromatography (GPC) was obtained from Riedel-de-Haen. All other chemicals used were reagent grade.

2.2. Glycolysis of PET

In the glycolysis of PET, 70 g (0.365 mol/repeating unit) of PET waste flakes were added into the reactor together with the diethylene glycol in three molar ratios [10]. The molar ratios of DEG/PET were 1.20 or 46.4 g, 1.60 or 61.9 g and 2.20 or 85.1 g of DEG for

experiments number 1, 2 and 3, respectively. Manganese acetate, 0.5 wt.% based on weight of PET, was added as transesterification catalyst. The reactor was immersed in an oil bath and heated for 4 h at 210 °C. The reaction was carried out under reflux in argon atmosphere. After the 4 h period, the reactor was allowed to cool at room temperature and the reaction product was filtered through a G3 glass filter. The filtrate was extracted with dichloromethane and the extract was finally washed with water in order to remove traces of DEG.

2.3. Synthesis of unsaturated polyester resin

Initially, a reference resin (blank) was synthesized using the following procedure. Into a three-necked resin kettle equipped with a mechanical stirrer, inlet to inert gas (argon), thermometer, condenser and calibrated distillate collector, 76.1 g (0.5 mol) of phthalic anhydride, 49.0 g (0.5 mol) of maleic anhydride, 41.0 g (0.43 mol) of diethylene glycol and 44.1 g (0.58 mol) of propylene glycol were introduced [21]. The reactor was purged with argon for 15 min before heating was switched on. Then the content was heated under argon atmosphere to 200 °C until approximately 15 ml of water were collected. This took approximately 9 h. The mixture was then cooled down to 90–100 °C and diluted with 125 ml of styrene. The amount of styrene was equal to 0.54 mol/mol of total initially added reactants (PA, MA, DEG and PG), or 35 wt.% 15 mg of hydroquinone were also added in order to inhibit initiation of the polymerization.

The above experiment was repeated but using the glycolyzates instead of diethylene glycol and exactly the same molar ratio for the rest of the reactants (i.e. PA, MA and PG). The amount of styrene added finally was also kept at exactly the same molar ratio as with the reference UPR.

2.4. Curing of the unsaturated polyester

In order to cure the resin in ambient temperature the redox system of peroxide–amine was used. Benzoyl peroxide (BPO) and *N,N*-dimethyl-*p*-toluidine were introduced into the mixture as the two coinitiators. The kinetics of the free-radical polymerization of the unsaturated resin were investigated using the DSC-Pyris 1 (Perkin-Elmer) equipped with the Pyris software for windows. Indium was used for the enthalpy and temperature calibration of the instrument. The molar ratio BPO:amine was kept constant at 1:1 and several initial BPO/resin weight percent were examined. Polymerizations were carried out at 23 °C. The reaction exotherm (in normalized values, W/g) at a constant temperature was recorded as a function of time. The rate of heat release ($d(\Delta H)/dt$) measured by the DSC was directly converted into the overall reaction rate (dx/dt) using the following formula:

$$\frac{dx}{dt} = \frac{1}{\Delta H_T} \frac{d(\Delta H)}{dt}$$

where ΔH_T denotes the total reaction enthalpy.

The polymerization enthalpy and conversion was calculated by integrating the area between the DSC thermograms and the baseline established by extrapolation from the trace produced after complete polymerization (no change in the heat produced during the reaction). The total reaction enthalpy was determined by heating the sample from the polymerization temperature to 180 °C at a rate of 10 °C/min. The sum of enthalpies of the isothermal plus the dynamic experiment was the total reaction enthalpy (approximately 300 J/g).

2.5. Measurements

The molecular weight distribution and the average molecular weights of the glycolized PET products were determined by gel permeation chromatography. The instrument used was from Polymer Laboratories and included a pump (Marathon III HPLC pump), an Evaporative Mass Detector (PL-EMD 950) and a Plgel 5 μ MIXED-D column. All samples were dissolved in THF at a constant concentration of 0.2 wt.%. After filtration of samples, 25 μl of each sample was injected into the chromatograph. The elution solvent was also THF at a constant flow rate of 1 ml/min. Calibration of GPC was carried out with standard polystyrene samples (Polymer Laboratories) by using the universal calibration technique.

Tensile tests were performed using an Instron 1122 dynamometer, in accordance to the ASTM D638 method at room temperature. Prior to measurements the samples were conditioned at $50 \pm 5\%$ relative humidity for 36 h, placed in a closed chamber containing a saturated $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution in distilled water (ASTM E-104). Tensile tests were performed under the condition that the crosshead speed of tensile tester was set at 5 mm/min and the initial gauge length was fixed at 22 mm. Five measurements were conducted for each sample, and the results were averaged to obtain a mean value.

The specimens for the mechanical properties were prepared by mixing the resin with the two coinitiators and immediately spreading the product on a glass surface. Thin films were thus prepared from curing at room temperature.

The content of hydroxy end-groups (hydroxyl number, HN) of the oligoester diols obtained was determined by titration with 1 N KOH solution. About 1.6 g sample was accurately weighted and added to 10 ml acetylation solution, containing 10 vol.% acetic anhydride in pyridine, in a round-bottomed flask. The flask was fitted with a vertical reflux condenser and heated to 80 °C for 2 h. Afterwards 10 ml of water was added and the heating was continued for 5 min at 100 °C. The mixture

was then cooled at room temperature and 10 ml of methanol were added. The resulting solution was titrated against 1 N KOH standard using phenolphthalein as indicator. A blank run was also performed. The values obtained provide a means of the number average molecular weight.

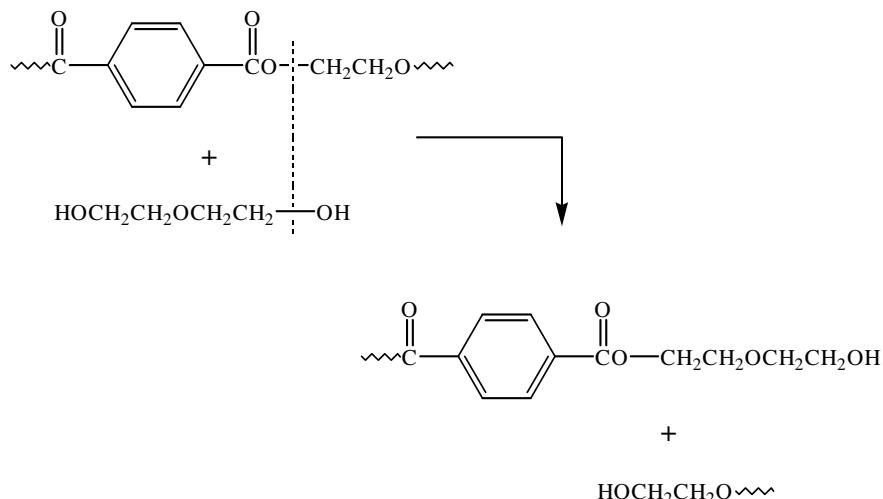
3. Results and discussion

3.1. Glycolysis of PET

The alcoholysis of PET with diethylene glycol proceeds according to the following reaction.

products, which in the next step of the polyesterification reaction produce two-phase unsaturated polyesters. One of these phases is incompatible with styrene, which is used in the curing reaction [15].

The glycolysis of PET in this study was carried out using three glycol compositions. The initial molar ratios of DEG/PET used were 1.20, 1.60 and 2.20 corresponding to glycolized products with sample codes GLY-1, GLY-2 and GLY-3, respectively. Results on the average molecular weights of the three glycolyzates are presented in Table 1. In this table results are included on the number average molecular weight (\bar{M}_n) of the polyester oligomers produced using the hydroxyl number or the GPC. Also, the weight average molecular weight (\bar{M}_w) and the



The alcoholysis consists of the transesterification of PET and the destruction of its polymer chain, resulting in the decrease of its molecular weight. Using glycols in the depolymerization of PET, the oligoesters obtained have two hydroxyl end groups, i.e. oligoester diols are formed. The choice of DEG to carry out the glycolysis is usually determined by the necessity of having well flexural properties in the UPR, since the long chains of the glycol improves flexibility. Use of other glycols such as propylene glycol or dipropylene glycol results in prod-

polydispersity of the molecular weight distribution of these samples obtained from GPC are included. As the amount of DEG is increased the depolymerization is carried out to a greater extent leading to oligoester diols with lower number average molecular weights. The same trend in the results observed by either end group analysis or GPC, while the results obtained from GPC were always higher than the corresponding from the hydroxyl number. The value of 454 measured for GLY-3 is very close to the value of 478 measured by Farahat and Ni-

Table 1

Average molecular weights of the glycolized PET products obtained from hydroxyl number and GPC

Glycolized product	Molar ratio (DEG/PET)	Hydroxyl number (HN)	\bar{M}_n from hydroxyl number	Data from gel permeation chromatography		
				\bar{M}_n	\bar{M}_w	Polydispersity
GLY-1	1.20	189	593	510	602	1.18
GLY-2	1.60	212	528	493	582	1.18
GLY-3	2.20	239	469	454	518	1.14

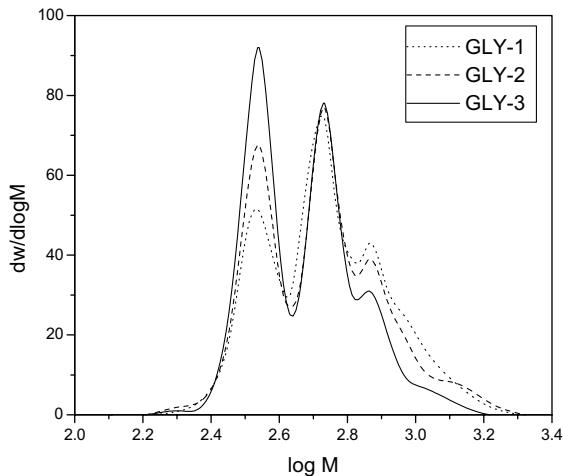
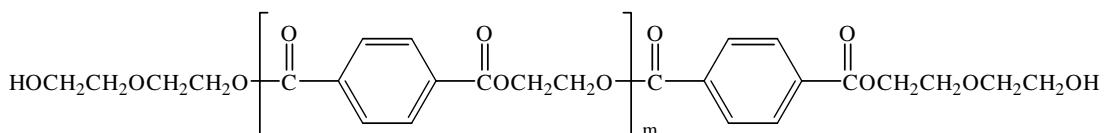


Fig. 1. Molecular weight distribution of the glycolized products with various DEG/PET molar fractions.

kles [11] using GPC and a DEG:PET molar ratio of 2.15:1. The polydispersity of the molecular weight distribution, which was always greater than 1, revealed that the distribution was not unimodal. Actually, in every sample three distinct peaks (trimodal shape) were identified. The full molecular weight distribution of the glycolized PET products obtained at the three different initial molar fractions appears in Fig. 1. The three peaks identified correspond to molecular weights of 350, 540 and 725. That means that PET glycolysis using DEG results mainly in three kinds of oligoesters. As the amount of DEG was increased the area under the peak corresponding to the lowest molecular weight was increased and respectively the area under the peak of the higher molecular weight was lowered. Hence, with increased amount of DEG a better depolymerization of PET was obtained.

On trying to identify the oligoester diols produced the following structure was proposed [9]:



where $m = 0-3$.

According to the above structure if one replaces m with 0, 1 and 2 the following molecular weights are obtained: 342, 534 and 726, respectively. By comparing these values with the values obtained by GPC, it can be concluded that the above structure is confirmed with $m = 0, 1$ and 2. Similar structures have been observed also in literature [11]. However, a definite identification

of the components of the glycolized PET products could be done for example by using ^{13}C NMR, or ^1H NMR.

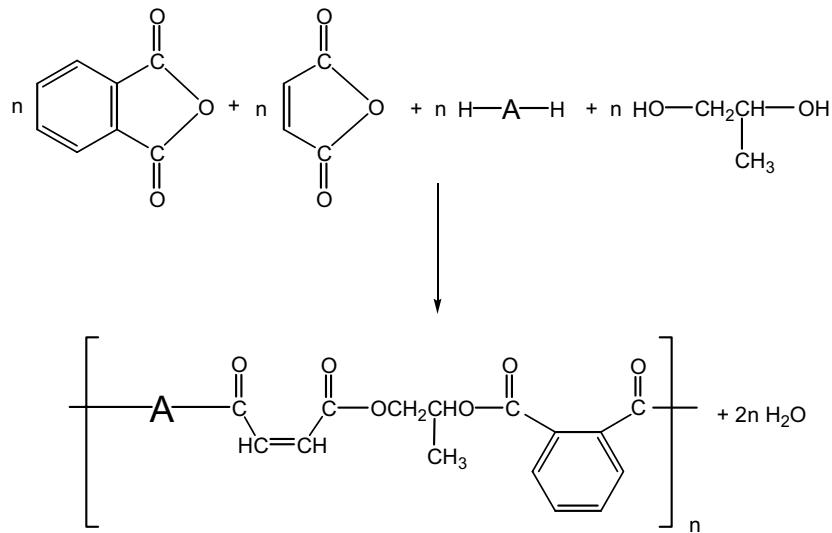
3.2. Synthesis of unsaturated polyester resin

Initially, a blank experiment was carried out, using the reactants that are usually used in the synthesis of alkyd resins. Afterwards the same experiment was repeated but using the oligoester diols obtained from PET glycolysis in place of diethylene glycol. Thus, it is possible to directly compare the results obtained when using the glycolized PET products instead of the conventional raw materials. The basic chemical reaction occurring in the production of alkyd resins from maleic anhydride, phthalic anhydride, diethylene glycol and propylene glycol is shown in Scheme 1. When the glycolyzates are used, then DEG is completely replaced by the oligoester diols. It is obvious that the molecular weight of the structural unit of the unsaturated polyester resin produced when using the glycolyzates is larger compared to the blank experiment. For this reason these products had always higher viscosity compared to the blank resin. The sample codes used for the UPR produced from the glycolized products were UPR-1, UPR-2 and UPR-3 in relation to the glycolized diols GLY-1, GLY-2 and GLY-3, used respectively.

3.3. Curing of the unsaturated polyester

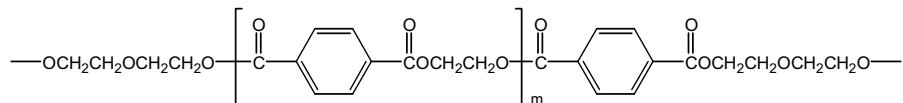
The unsaturated polyesters are long chain polymers containing a number of reactive double bonds. In order to form crosslinked networks, they are dissolved in a free-radical polymerizable monomer such as styrene. This polymerizable monomer, which also contains reactive double bonds ($\text{C}=\text{C}$), acts as a curing agent by bridging adjacent polyester molecules 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, we can have high

shrinkage on curing or a tendency not to cure fully, respectively. Vaidya and Nadkarni [6] proposed an effective range for the styrene percentage in a polyester resin from 30 to 40 wt.%. In this investigation a 35 wt.% for the blank resin was used, in accordance also to other literature sources [10]. The curing behavior of unsaturated polyester resins has been extensively studied in literature [22–28]. The polymerization is usually initiated using a



where \mathbf{A} in the case of the blank experiment is $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$

and in the case of the oligoester diols it takes the following form ($m=0,1,2$) :



Scheme 1. Synthesis of unsaturated polyester resins using either diethylene glycol, or the oligoesters diols derived from PET glycolysis. It should be noted that the places of the two diols in the UPR structural unit could be interchanged. The same holds for the place of the two anhydrites.

free radical initiator such as benzoyl peroxide. However, it requires elevated temperatures (50–90 °C) in order to decompose the initiator molecule and form the primary radicals needed. If the curing must be carried out in ambient temperature, then a peroxide/amine system is used to form the primary free radicals [21]. As such, we used the benzoyl peroxide/*N,N*-dimethyl-*p*-toluidine, already studied for the free-radical polymerization of MMA [29]. To prevent premature gelation and to inhibit the spontaneous polymerization of the resin, hydroquinone was added as an inhibitor [15].

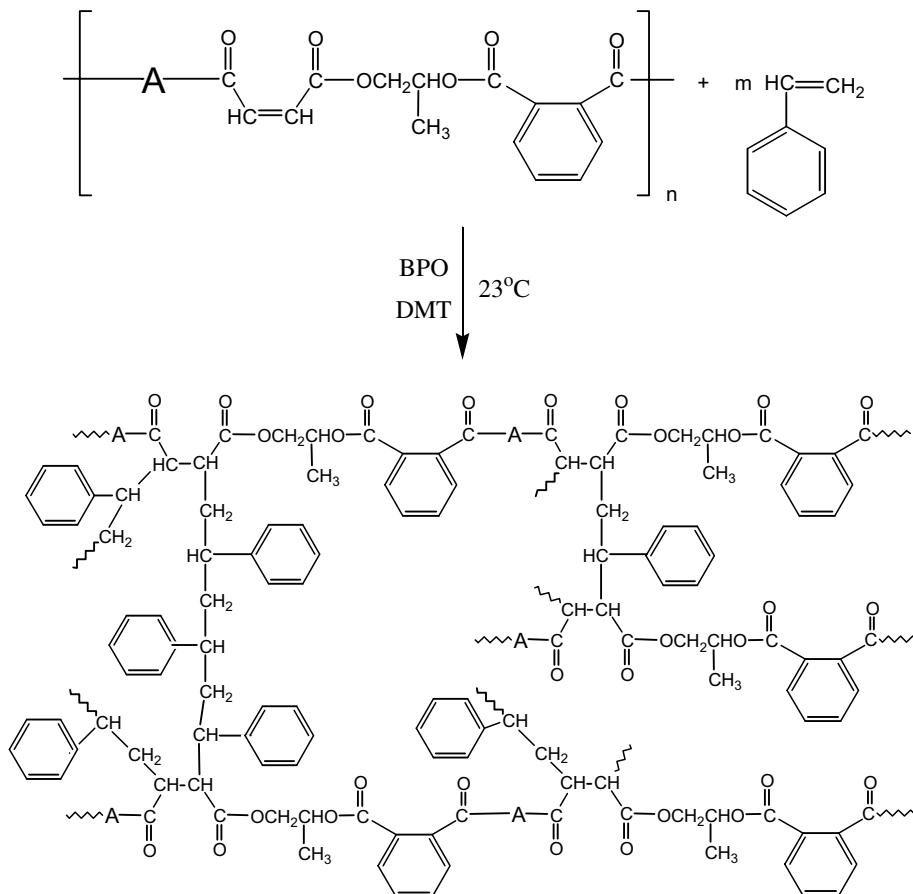
The free-radical polymerization reaction and the formation of the crosslinked network after the curing of the UPR with styrene is shown in Scheme 2.

In order to find the best initial weight fractions of the initiators, so that the polymerization to complete in a short time period, while long enough to be detected by DSC, several tests were carried out. Results on the time dependence of the reaction rate and double bond conversion at three initial initiator concentrations, appear in Fig. 2a and b. It should be pointed out that always the amine and the peroxide were in equimolar amounts.

As it was expected, an increase in the initial initiator concentration leads to higher reaction rates accompanied by shorter induction times, higher maximum polymerization rate and completion of the reaction at shorter times. According to the results of Fig. 2, a weight fraction of BPO 1% may be adequate in industrial use, when the curing must be completed fast. However, in laboratory scale experiments the low weight fraction of 0.5% is preferable in order to have enough time to process the material and produce films that are necessary for preparing the specimens that will be used in the mechanical properties testing.

The total heat of polymerization (i.e. the sum of the isothermal and the dynamic period) was approximately equal to 300 J/g, which is very close to corresponding literature values [15,22,25,27]. The ultimate total double bond conversion was not influenced much by the initial initiator concentration and it was approximately equal to 68%.

Furthermore, the curing rate characteristics of the UPR-1, UPR-2 and UPR-3 alkyd resins produced from the glycolized PET products are compared to the blank



Scheme 2. Curing reaction of the UPR with styrene.

experiment in Figs. 3 and 4 for two different initial initiator concentrations 1 wt.% and 0.7 wt.%, respectively. A marked increase in the reaction rate is observed initially, which is caused by the strong influence of diffusional phenomena on the termination rate constant, together with the formation of the polymer network. At the peak of the reaction rate the network has become quite dense and thus the diffusion of small molecules, such as monomers, is hindered leading to a reduction in the reaction rate until it reaches a zero value. In every case the reaction ceases when the glass transition temperature of the reacting mixture equals to the polymerization temperature, though the monomers have not reacted completely. On comparing the reaction rate characteristics between the different resins obtained from the PET glycolysis diols to the blank experiment it can be noticed that in both initial initiator concentrations UPR-1 exhibits almost the same characteristics as the blank resin. The induction period is almost the same, as well as the value of the maximum in the reaction rate and the time at which it appears. A slight decrease in the induction time was observed at the initial BPO concentration of 1 wt.%. However, a much faster reaction rate has been observed

with UPR-2 compared to blank and UPR-1. In both initial initiator concentrations the start of the reaction was immediate without any induction time, the maximum in the curing rate occurred earlier and the peak was more pronounced. Compared to the blank resin, the greater reactivity of the UPR-2 can be attributed to a reduced steric hindrance of the reactive double bonds due to the longer chain of the repeated structural unit. UPR-1 with a slightly higher average chain length compared to UPR-2 exhibits a slightly slower reaction rate. However, this trend was not followed by UPR-3 since this resin exhibited a very high viscosity (due to a lower amount of styrene added as a diluent). Hence the maximum in the reaction rate was lowered compared to UPR-2 and the reaction lasted more than all the other cases. The maximum double bond conversion obtained with UPR-1 was around 70%, slightly higher than the corresponding of the blank resin.

3.4. Mechanical properties of the alkyd resins

Finally, the mechanical properties of the alkyd resins produced were studied in relation to the effect of the

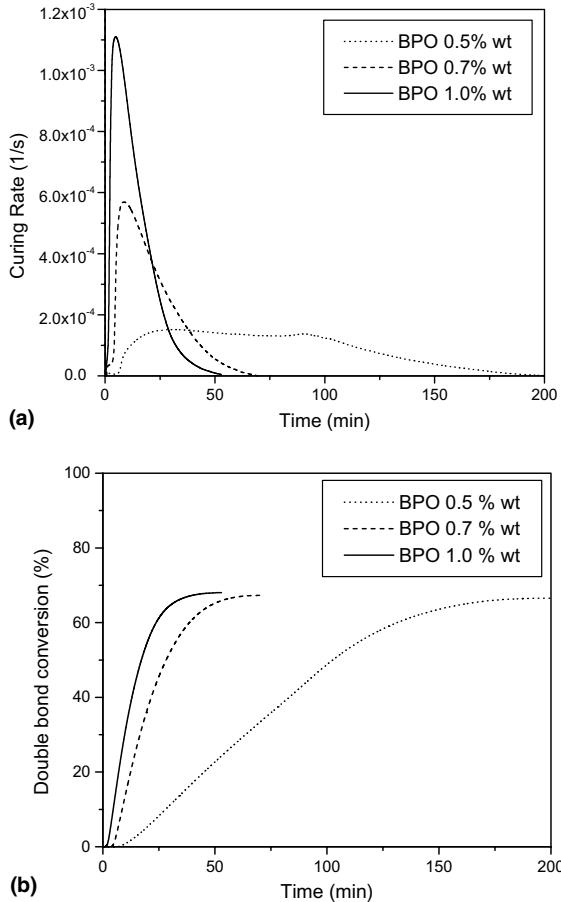


Fig. 2. Curing rate (a) and double bond conversion (b) versus time of the blank resin using different initial initiator (BPO) weight fractions. The amine/BPO molar fraction was always 1/1.

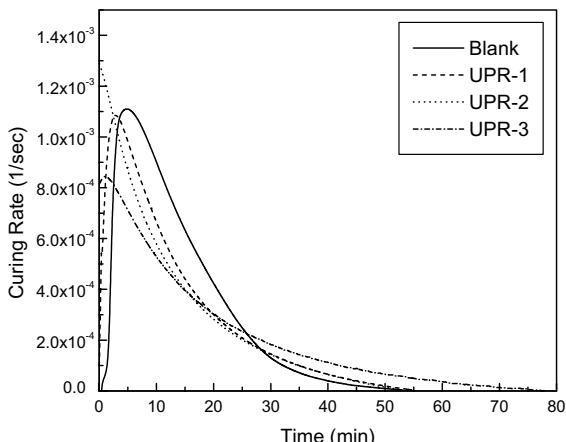


Fig. 3. Rate of curing as a function of time for the UPR produced from the glycolized oligoester diols and the blank resin. Initial BPO weight fraction 1%.

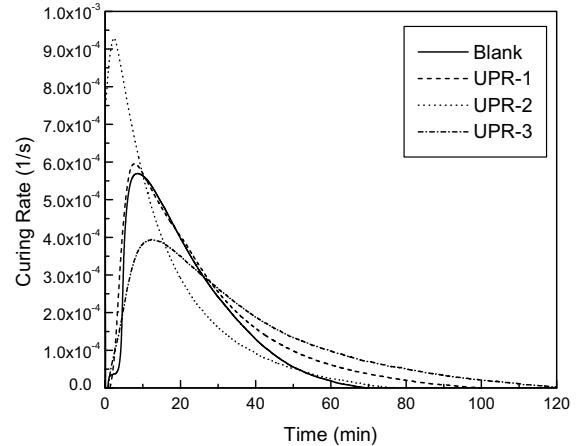


Fig. 4. Rate of curing as a function of time for the UPR produced from the glycolized oligoester diols and the blank resin. Initial BPO weight fraction 0.7%.

initial initiator concentration, as well as to the effect of the oligoester diols used. In all resin samples (containing MA, PA, PG and either DEG or the glycolyzates together with styrene) the mixture of the two initiators was added and thin films were prepared that were measured at different curing times from 1 day to 40 days. The effect of the curing time and of the initial initiator concentration on the elongation at the break point and the tensile strength of the blank resin is shown in Fig. 5a and b, respectively. As it can be seen the mechanical properties of the resins are time dependent and they seem to reach a steady value after approximately 20 days of curing period. Low curing rates cause a brittleness in the resins, which results in its low tensile strength. An increase in the initial initiator concentration leads to higher tensile strength and lower elongation at break. It seems that using a high initial initiator concentration the crosslinked network formed is denser. Thus, the chains are not able to move freely which makes the resin less flexible. Furthermore, at the same initial initiator concentration the effect of the resins produced from the oligoester diols on the tensile strength and elongation appear in Fig. 6a and b, respectively. Both alkyd resins produced from the glycolized PET products exhibit lower tensile strength and higher elongation at the break point, compared to the blank resin. This must be attributed to the longer distance between the reactive double bonds existing in the UPR derived from the glycolized products compared to that of the blank resin. This enables the cured resin to have a lower crosslinking density and thus to become more flexible. Comparing the resins UPR-1 and UPR-2, the tendency for the tensile strength is to become lower and for the elongation to become higher when the resin used has lower molecular weight. The reason to that can be attributed to the effect of the molecular weight of the repeating unit difference

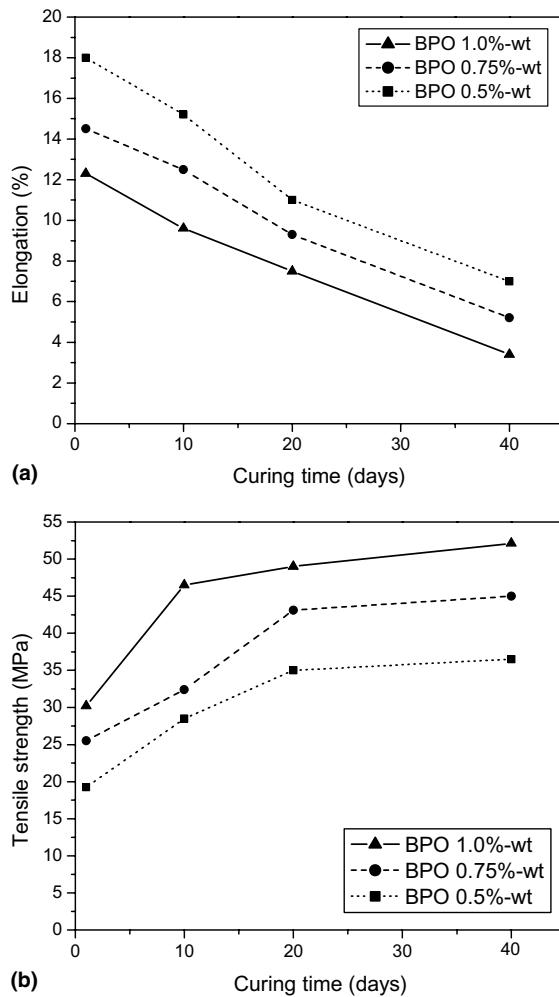


Fig. 5. Effect of the curing time on the elongation at the break point (a) and the tensile strength (b) of the blank resin cured using different initial initiator concentrations.

between resins UPR-1 and UPR-2. The former exhibits on average a higher molecular weight and thus it contains more terephthalate repeating units. The presence of more terephthalate repeating units between the cross-links results in the existence of harder domains and better separation between the crosslinks in the packed crosslinked structure and as a result the mechanical properties are improved [12]. Unfortunately, it was not possible to measure the mechanical properties of the UPR-3 resin since its high viscosity did not allow the production of thin films required for the analysis.

4. Conclusion

In this research, the glycolysis of recycled PET for the production of alkyd resins used as coatings was investi-

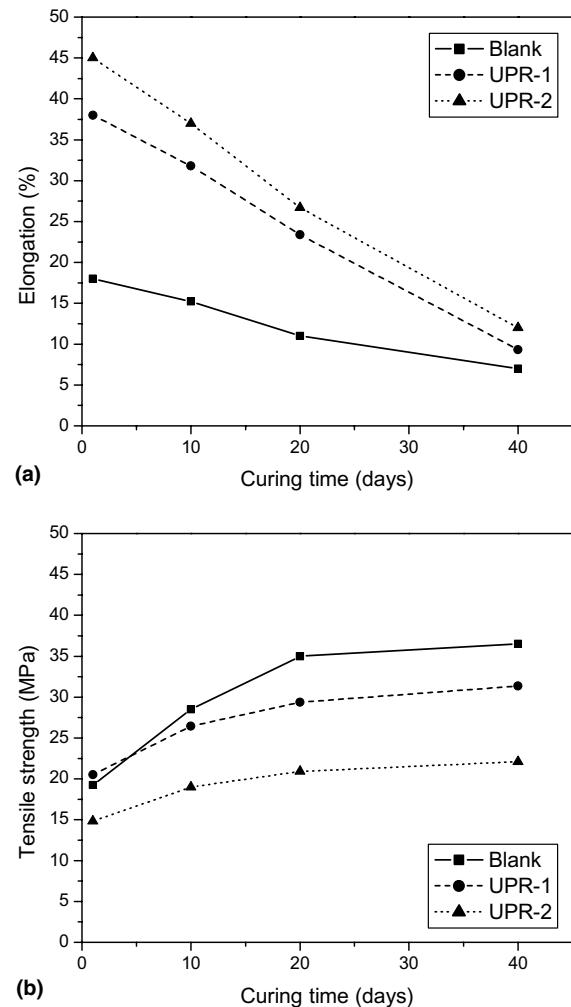


Fig. 6. Effect of the curing time on the elongation at the break point (a) and the tensile strength (b) of the blank resin and the resins produced for the glycolized PET diols cured at 0.5 wt.% initial BPO concentration.

gated. The oligoester diols produced from the reaction of DEG with PET consisted mainly of three oligomers. An increase in the molar ratio of DEG:PET led to better depolymerization and to an increase in the amount of the oligomer with the lower molecular weight. The oligoester diols produced were mixed with maleic anhydride, phthalic anhydride and propylene glycol to form unsaturated polyester resins. These were subsequently diluted with styrene and cured at ambient temperature using the benzoyl peroxide/*N,N*-dimethyl-*p*-toluidine system. The curing kinetics of this system was investigated and the results obtained from the glycolized products were compared to corresponding of a typical alkyd resin recipe. The replacement of DEG with the glycolized PET products gave higher curing rates completed in shorter

time periods. However, the elongation at the break point of the resin was higher and the tensile strength lower.

References

- [1] PETCORE Report 2002, 4(4). Available in www.Petcore.com.
- [2] Scheirs J. Polymer recycling. Sussex: J. Wiley & Sons; 1998.
- [3] Achilias DS, Karayannidis GP. Proceedings of the international conference “Protection and restoration of the environment VI”, Skiathos, 1–5 July 2002. p. 925–36.
- [4] Kosmidis VA, Achilias DS, Karayannidis GP. *Macromol Mater Eng* 2001;286:640.
- [5] Karayannidis GP, Chatzivgoustis A, Achilias DS. *Adv Polym Technol* 2002;21:250.
- [6] Vaidya UR, Nadkarni VM. *Ind Eng Chem Res* 1987;26: 194.
- [7] Vaidya UR, Nadkarni VM. *J Appl Polym Sci* 1989;38: 1179.
- [8] Baliga S, Wong WT. *J Polym Sci Part A: Polym Chem* 1989;27:2071.
- [9] Halacheva N, Novakov P. *Polymer* 1995;36:867.
- [10] Suh DJ, Park OO, Yoon KH. *Polymer* 2000;41:461.
- [11] Farahat MS, Nikles DE. *Macromol Mater Eng* 2001;286: 695.
- [12] Farahat MS, Nikles DE. *Macromol Mater Eng* 2002;287: 353.
- [13] Farahat MS, Abdel-Azim A-AA, Abdel-Raowf ME. *Macromol Mater Eng* 2000;283:1.
- [14] Farahat MS. *Polym Int* 2002;51:183.
- [15] Aslan S, Immirzi B, Laurienzo P, Malinconico M, Martuscelli E, Volpe MG, et al. *J Mater Sci* 1997;32: 2329.
- [16] Radenkov Ph, Radenkov M, Grancharov G, Troev K. *Eur Polym J* 2003;39:1223.
- [17] Chen C-H, Chen C-Y, Lo U-W, Mao C-F, Liao W-T. *J. Appl. Polym. Sci.* 2001;80:943.
- [18] Mansour SH, Ikladious NE. *Polym Test* 2002;21:497.
- [19] Pimpan V, Sirisook R, Chuayjuljit S. *J Appl Polym Sci* 2003;88:788.
- [20] Kawamura C, Ito K, Nishida R, Yoshihara I, Numa N. *Prog Org Coat* 2002;45:185.
- [21] Duliban J. *Macromol Mater Eng* 2001;286:624.
- [22] Lucas JC, Borrajo J, Williams RJ. *Polymer* 1993;34:3216.
- [23] Lee DS, Lee SH, Kim JH. *Polym Int* 1997;44:143.
- [24] Eisenberg P, Lucas JC, Williams RJ. *J Appl Polym Sci* 1997;65:755.
- [25] Delahaye N, Marais S, Saiter JM, Metayer M. *J Appl Polym Sci* 1998;67:695.
- [26] Vilas J, Laza JM, Garay MT, Rodriguez M, Leon LM. *J. Appl. Polym. Sci.* 2001;79:447.
- [27] Lu M, Kim S. *J Appl Polym Sci* 2001;80:1052.
- [28] Simitzis J, Zoumpoulakis L, Soulis S. *Polym Int* 2002;51:308.
- [29] Achilias DS, Sideridou ID. *J Macromol Sci-Part A: Pure Appl Chem* 2002;A39:1435.