

Preparation and Characterization of Water-Extended Polyester Based on Recycled Poly(ethylene terephthalate)

M. E. Tawfik

Department of Polymers and Pigments, National Research Center, Dokki, Cairo, Egypt

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ABSTRACT: An unsaturated polyester resin was prepared that was based on the reaction of oligomers obtained from the depolymerization of poly(ethylene terephthalate) waste products, with both maleic anhydride and sebacic acid. The structure of the produced polyester was compared with that prepared from the reaction of dimethyl terephthalate with both maleic anhydride and sebacic acid with IR and NMR spectroscopy. Water-extended polyester resins were prepared from these two polyesters through curing with styrene in the presence of various amounts of water with benzoyl peroxide as an initiator. The mechanical prop-

erties of the prepared water-extended polyesters, as well as scanning electron microscopy, were investigated. The use of water-extended polyesters based on recycled poly(ethylene terephthalate) waste for the preparation of decorative art objects and statues was investigated. Therefore, three pharaonic statues representing Tutankhamen, Nefertiti, and a black head of a cat were prepared. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3693–3699, 2003

Key words: waste; recycling; oligomers; polyesters; composites

INTRODUCTION

The low cost and versatility of unsaturated polyesters (UPs) have further been expanded through the use of water as an extender or filler.^{1–3} The preparation of water-containing resins through polymerization in an inverted emulsion, that is, in a water-in-oil (W/O) emulsion, was first reported by Bartl and Von Bonin.⁴ UPs are copolymerized with styrene monomer to form W/O-type emulsions in the presence of various basic compounds, which act as very effective W/O emulsifiers for the UP prepolymer.^{5–7} The mechanism of polymerization in an inverted emulsion is not very different from that of ordinary radical polymerization; the most important factor in producing water-containing polymers is obtaining stable emulsions with suitable emulsifiers.^{8,9} The hardening of a water-containing polyester prepolymer was carried out with a radical type of initiator, and the result was a hard, water-containing solid resembling fine-grained plaster.

A wide variation in the properties of water-extended polyester (WEP) composites can readily be achieved by changes in the water level, catalyst, and additives in either the resinous or aqueous phases. It has been reported that a compressive strength approaching that of concrete is obtainable at a 50–60% water content.² The tensile and flexural strengths correspond to those of wood, and materials of a related construction can also be achieved.²

The use of water as an extender offers important advantages, such as lower cost, lower density, reduced flammability, moderation of the exothermic cure temperature, and ease of mixing and dispensing liquid ingredients.¹ Ikladios et al.¹⁰ examined two types of WEPs as an alternate method of cementing for the immobilization of aqueous radioactive wastes. The mechanical properties, radiation stability, and mechanical resistance appeared to be good.

Moreover, some work has been done on the production of polyols and UP resins based on poly(ethylene terephthalate) (PET).^{11–19} PET wastes are a potential source for recycling applications. PET wastes are typically found in scrap textile and beverage bottles that are collected after use in many locations and recycled in applications not requiring contact with food.^{20,21}

This work reports the synthesis, characterization, and application of WEPs from UPs based on PET bottle waste for the production of water composites. The emulsion stability of WEPs with different concentrations of triethanol amine (TEA) as an emulsifier was studied. The mechanical properties of the water composites were also investigated. The polyester prepared from PET wastes was compared with styrenated polyester made from virgin materials based on bis(2-hydroxy propyl terephthalate) (BHPT).

EXPERIMENTAL

Materials

The PET used was a waste product of a PET bottle factory. Dimethyl terephthalate (DMT), propylene glycol (PG), maleic anhydride (MA), sebacic acid (SA), sty-

Correspondence to: M. E. Tawfik (magdaemileta@hotmail.com).

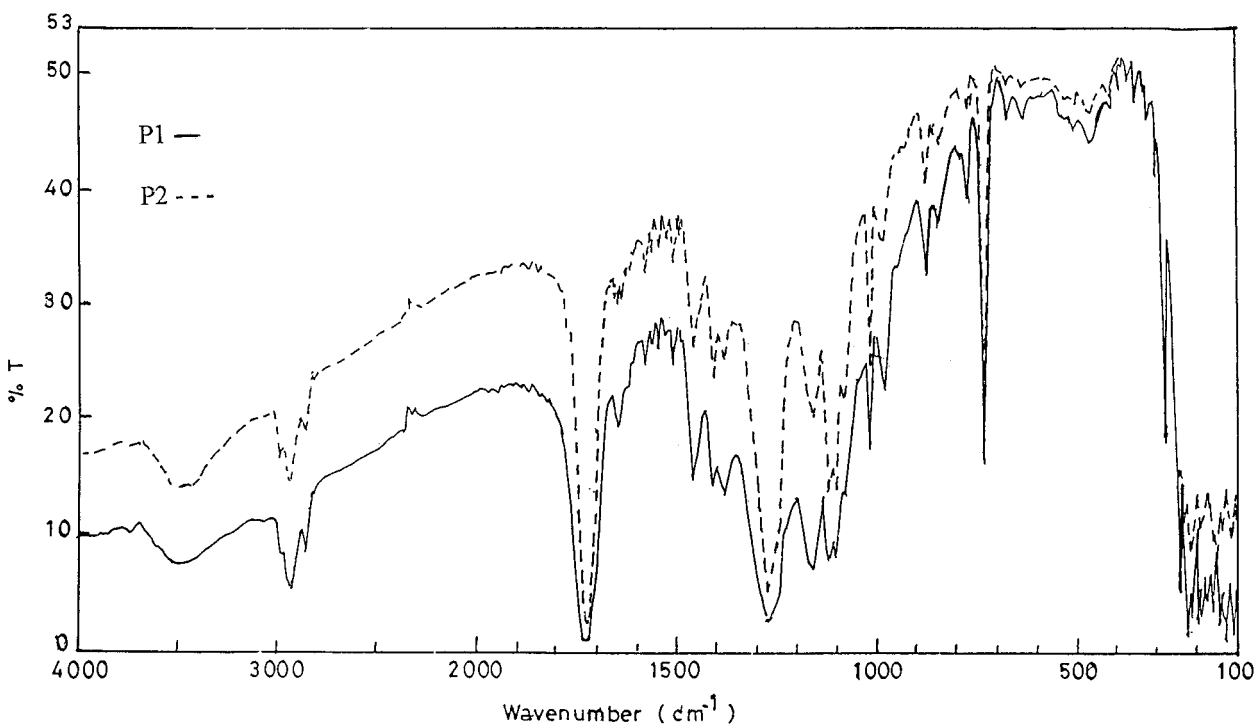


Figure 1 IR spectra of polyesters P1 and P2.

rene, and TEA, all reagent-grade, were obtained from Merck (Germany) and were used without further purification. Benzoyl peroxide (Bz_2O_2) was obtained from Fluka Co. (Switzerland) and was purified by dissolution in chloroform and precipitation by the addition of methyl alcohol in excess.

Methods of preparation

Preparation of the UP resin (P1) based on PET bottle wastes

The glycolysis of PET bottle wastes was carried out with PG (50 wt %) in the presence of zinc acetate (0.5% by weight of PET) as a catalyst to obtain PET oligomers with a hydroxyl value of 727 mg of KOH/g according to a method previously described.²⁰ The temperature was raised to 200°C under reflux for 10 h under a nitrogen atmosphere. The UP resin was prepared from the produced hydroxy-terminated oligomers at a ratio of 1.1/1 (mol/mol) hydroxyl/carboxyl. The hydroxyl number of the glycolyzed products was used to determine the amount of acid required.^{22,23} Therefore, a mixture of the produced PET oligomers with both MA and SA in a molar ratio of 1.1/0.5/0.5 was heated in an oil bath, and the temperature was raised to 150°C and then increased at a rate of 10°C/h up to 210°C until the acid number reached 35 ± 2 mg of KOH/g.

Preparation of the UP resin (P2) based on DMT

BHPT was prepared according to a method detailed previously.²⁴ UP P2 was obtained from the reaction of

BHPT with MA and SA in a molar ratio of 1.1/0.5/0.5 according to a method used previously for the preparation of polyester P1 and used as a reference resin. The acid number of the produced polyester (P2) was 39 ± 2 mg of KOH/g.

Preparation of WEPs

Each of the prepared UPs (P1 and P2) was mixed with styrene (70/30). WEPs (WEP1 prepared from polyester P1 and WEP2 from P2) were prepared by the dispersal of 50 wt % water and various concentrations of TEA as an emulsifier (0.05–1 mmol/g) and the subsequent thorough stirring of the mixture. The emulsion stability was estimated from the rates of phase separation of the emulsions. Separation curves were obtained from the changes in the height of the interface between the separated phases in a test tube kept in a thermostat over a period of 24 h. The measurements were carried out at 30°C. The complete curing of each polyester prepolymer (containing 0.2 mmol/g TEA) was obtained by the addition of 2 wt % Bz_2O_2 as an initiator. The curing occurred in a test tube at room temperature and resulted in a white, dry, tough, cylindrical rod of solid composite.

Testing and measurements

IR spectra were performed with a Jasco FTIR 300 E Fourier transform infrared spectrometer (Tokyo, Japan). Thin films of the polyester samples, approximately 1 mm thick, were used for the transmission IR

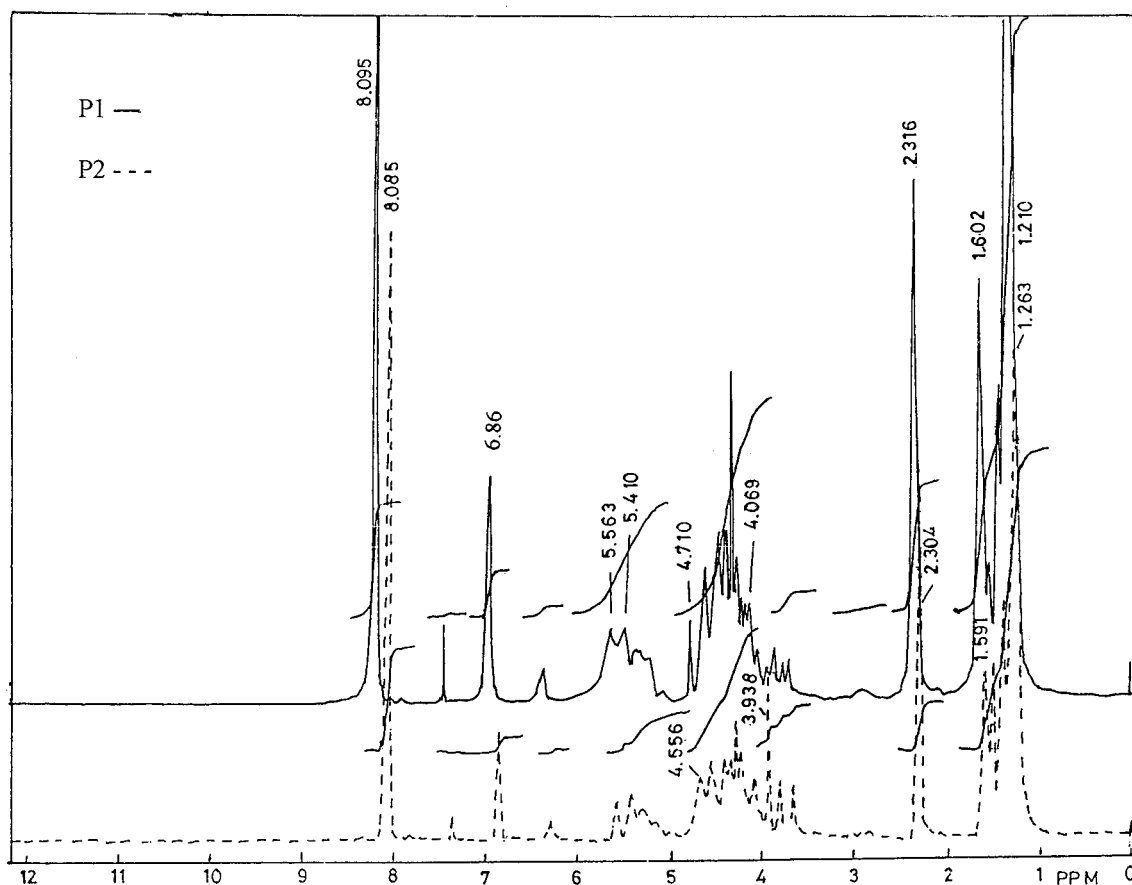


Figure 2 NMR spectra of polyesters P1 and P2.

measurements. NMR spectra were recorded with a Bruker AC-400 spectrometer (Germany) with deuterated chloroform as a solvent.

The microphotographs of the emulsions were obtained with a polarizing microscope from Nikon (Tokyo, Japan). A drop of the emulsion WEP1 was placed between two glass plates, and a plane-polarized light was used for the microphotographs.

The surface fracture of the cured WEP1 specimen was observed with a JEOL JSM-T20 scanning microscope (Germany). The sample was prepared by a small piece being cut with a sharp knife at room temperature. The surface of the sample was covered with gold for contrast.

The mechanical properties of the prepared WEPs were determined as follows. The compressive strength was determined according to ASTM D 695 on three to five 2.5-cm-long and 1.3-cm-diameter cylindrical rods with a no. 1 MaTest (Terzi di S. Agata, Italy). The tensile measurements were determined with a Zwick 1101 tensile testing machine (Tokyo, Japan). WEPs approximately 2 mm thick were cured and cut according to ASTM D 412.

RESULTS AND DISCUSSION

A UP resin based on the reaction of glycolized PET waste products was prepared with MA and SA. The

physical and chemical properties of the produced polyester were compared with those of the polyester based on DMT. The IR spectra of the two polyesters, P1 and P2, were quite similar (Fig. 1) and showed the following bands: a broad band at 3500 cm^{-1} characteristic of the stretching frequency of the OH groups and bands at $2860\text{--}2980\text{ cm}^{-1}$ that might stand for the CH stretching frequencies of CH_3 , CH_2 , aromatic, and olefinic groups. Also, Figure 1 shows a strong band at 1721 cm^{-1} due to the stretching frequency of the carbonyl group of aliphatic and aromatic acids and esters. The strong band at 980 cm^{-1} was due to the bending frequencies of trans-olefinic CH and might be an indication of the maleic-fumaric isomerization in the polyester backbone, and the bands at $730\text{--}880\text{ cm}^{-1}$ were quite indicative of the presence of cis-olefinic and aromatic residues in the polyester chain.

The $^1\text{H-NMR}$ spectra of the prepared polyesters, P1 and P2, were quite similar, as shown in Figure 2. The structure of the two polyesters, as well as the chemical shifts, is illustrated in Figure 3.

Emulsion stability

The prepared polyesters were used with styrene monomer in a ratio of 70/30 for the preparation of

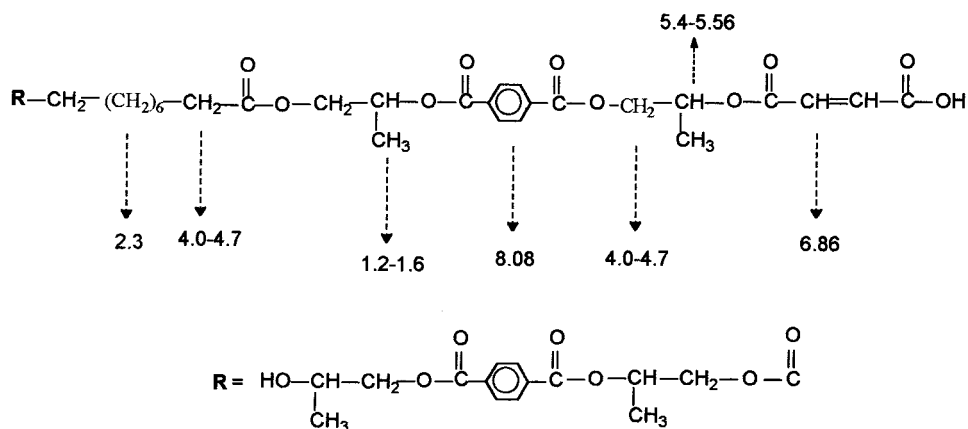


Figure 3 Chemical structures[with $^1\text{H-NMR}$ chemical shifts (ppm)] of polyesters P1 and P2.

cured WEP composites. The various basic compounds acted as very effective W/O emulsifiers for the UP prepolymer. The basic compound reacted with the

free carboxyl groups of the polyester to form the polyester salts *in situ*, which stabilized the emulsion as a true emulsifying agent.⁵⁻⁷ For the formation of a

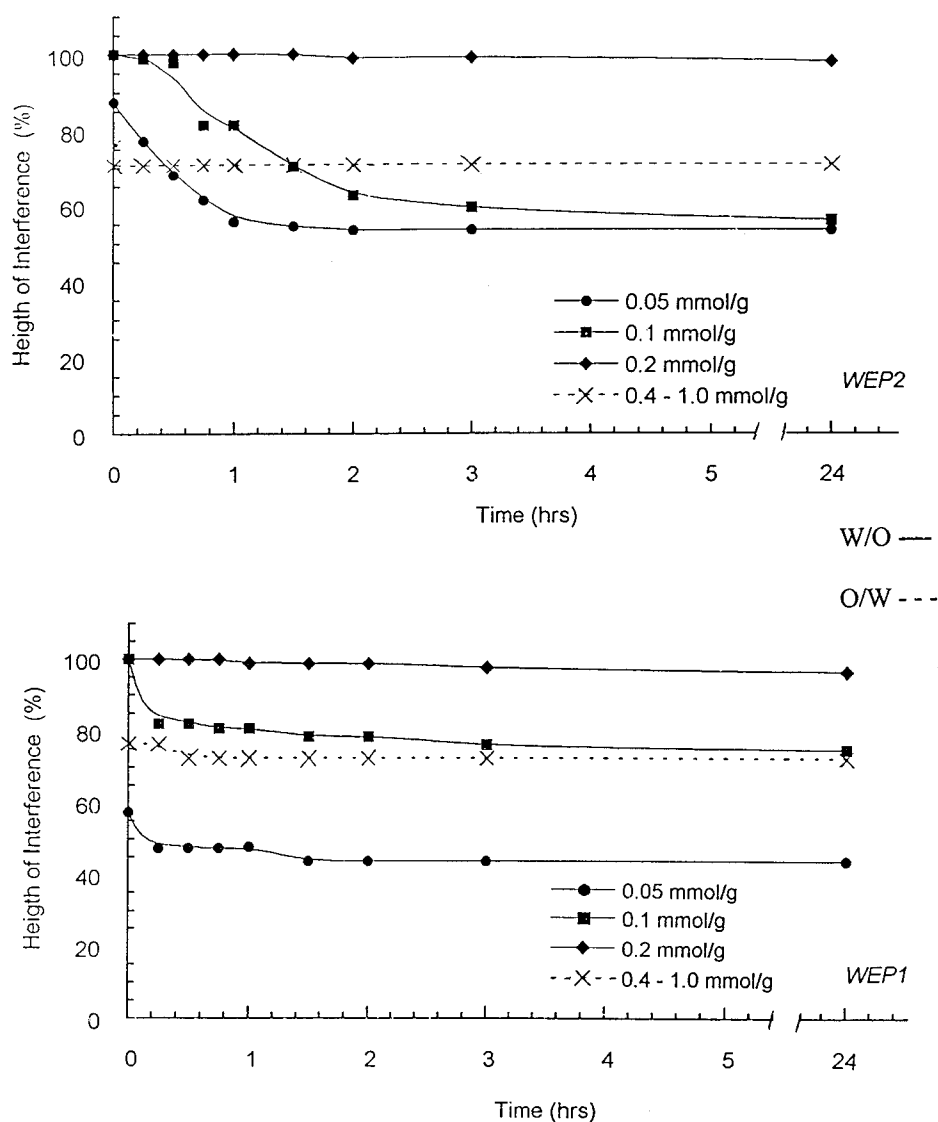


Figure 4 Separation curves of emulsions WEP1 and WEP2 at 30°C with various concentrations of TEA.



Figure 5 Microphotograph of a W/O emulsion of UP resin P1 (original magnification, 300 \times).

W/O-type emulsion, it was necessary that the lipophilic affinity of the emulsifier to the polyester be stronger than its hydrophilic affinity to water. It has been reported that the salts of a polyester formed by the reaction of the polyester itself with various bases are very effective as emulsifiers. The emulsion stability of WEP1 and WEP2 with different concentrations of TEA (mmol/g) as the basic emulsifier were studied, and the results are shown in Figure 4. Figure 4 shows the phase-separation curve at 30 $^{\circ}$ C for WEP1 and WEP2 emulsions with the same amount of water (50 wt %). The emulsion stability was studied semiquantitatively as a base in connection with the rate of polymerization of the prepolymer. The phase-separation curves show the effect of the TEA concentration on the emulsion stability. Unstable W/O emulsions were obtained with 0.05 and 0.1 mmol/g TEA. A stable and gel-like W/O emulsion was obtained only at 0.2 mmol/g TEA for WEP1 and WEP2. Unstable oil-in-water (O/W) emulsions were obtained with 0.4–1.0 mmol/g TEA, but the inversion of the O/W phase was not observed.

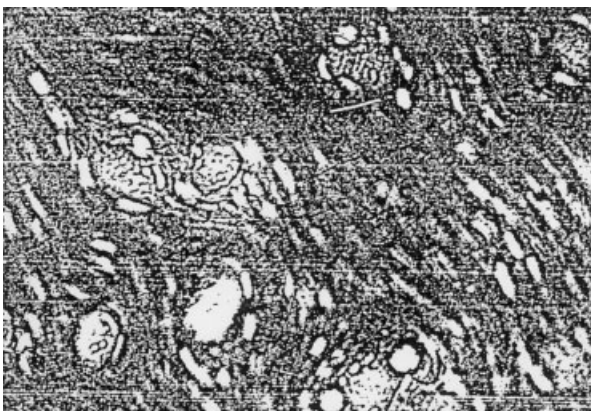


Figure 6 Microphotograph of an O/W emulsion of UP resin P1 (original magnification, 120 \times).

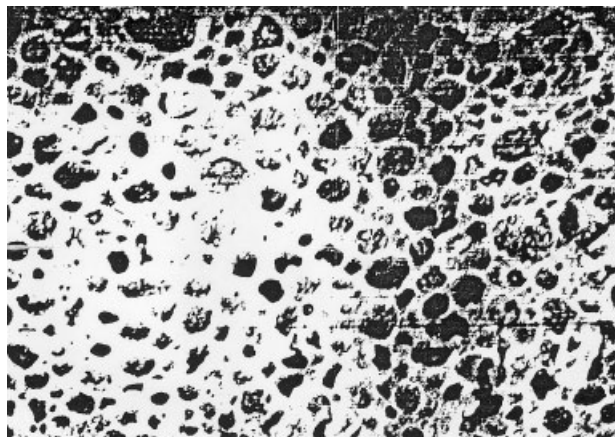


Figure 7 Scanning electron microscopy image of a section of cured WEP1 (original magnification, 1000 \times).

A microphotograph of the stable W/O emulsion with uncatalyzed P1 was prepared with 50 wt % water and 0.2 mmol/g TEA as an emulsifier, as shown in Figure 5. It is apparent from the micrograph that the polyester resin P1 was the continuous phase (dark background), and the water as small droplets was almost uniformly dispersed.^{6,25} If water is added too rapidly, an emulsion cannot be prepared at the desired water level, or a large-particle emulsion is formed. Large-particle emulsions produce composites with reduced strength.¹ With higher concentrations of TEA (\sim 0.8 mmol/g) with the same amount of water, an O/W-type emulsion was formed (Fig. 6). It is clear that the emulsion was an O/W type and that water was the continuous phase.

The stable emulsions obtained for the polyester resins P1 and P2 with 50 wt % water were cured by the addition of Bz_2O_2 as a radical initiator, and white, dry, and tough solid water composites with TEA as an emulsifier were obtained. Figure 7 shows the surface fracture of the cured WEP1 by scanning electron microscopy. The image indicates the shadow marks of the vaporized water droplets because the sample was heated in an oven at 100 $^{\circ}$ C during the deposition of the gold.

Mechanical properties

The effect of the polyester/styrene ratio on the mechanical properties of the prepared cured WEPs was

TABLE I
Effect of the Styrene Ratio on the Compressive Strength of WEP Composites

Polyester/styrene ratio	Compressive strength (kg/cm ²)	
	WEP1	WEP2
60/40	150	122
70/30	160	156

With 50 wt % water and 2 wt % Bz_2O_2 as an initiator.

TABLE II
Effect of the Concentration of Bz_2O_2 Initiator on the Mechanical Properties of WEP Composites

Bz_2O_2 (wt %)	WEP1			WEP2
	Compressive strength (kg/cm ²)	Tensile strength (kg/cm ²)	Elongation (%)	Compressive strength (kg/cm ²)
0.5	95	—	—	94
1	107	9	12	135
1.5	134	12	15	148
2	161	23	16	156
3	118	20	12	96

With 50 wt % water and 30 wt % styrene.

studied. Table I shows that a cured WEP with a polyester/styrene ratio of 70/30 gave a higher compressive strength, and this agreed with the results obtained in earlier studies.⁵⁻⁷

Also, the effect of the initiator concentration (Bz_2O_2) on the mechanical properties of the WEP composites was studied, and the results are given in Table II. There was an increase in the compressive strength with an increasing initiator concentration. The highest values were obtained at a 2 wt % Bz_2O_2 concentration for WEP1 and WEP2. The tensile strength and elongation at rupture followed the same trend.

The effect of the water content on the compressive strength of the cured composites is shown in Table III. The highest values for the compressive strength were obtained with composites with the lowest water percentage (20 wt %). It has been reported previously⁸⁻¹⁰ that the properties of cured polyester composites vary with the water content.

Applications

WEP composites are economically and technologically attractive candidates for commercial decorative art objects (wall plaques, figurines, statues, drawer fronts, pictures, mirror frames, and cinema decorations). A WEP based on recycled PET bottle wastes (WEP1) was used for making some statues. Figures 8–10 show illustrations of commercial art figurines produced from WEP1. The statues were obtained by the mixing of P1 with styrene (70/30), different amounts of water,

0.2 mmol/g TEA as an emulsifier, and 2 wt % Bz_2O_2 as an initiator. The mixture was poured in a silicon rubber mold and was left to cure at room temperature for 1 h. The statues were easy to make and showed nice luster; this could be considered a starting material with great potential for this field.

Figure 8 presents a photograph of the death mask of Tutankhamen. The Living Image of Amon (1336–1327 BC) was one of the kings of the 18th dynasty. His tomb was discovered in 1922. The treasure of his tomb occupies a great portion of the second floor of the Egyptian Museum. The Tutankhamen statue was prepared from WEP1 with 20 wt % water.

Figure 9 presents a photograph the famous head of Nefertiti, a member of the royal family of the 18th dynasty. It was discovered between 1904 and 1914. The head of Nefertiti is now in the Berlin Museum. The Nefertiti statue was prepared from WEP1 with 30 wt % water.

Figure 10 presents a photograph of a black cat figurine prepared from WEP1 with 40 wt % water and 6 wt % carbon black.

TABLE III
Effect of Water Content on the Compressive Strength of WEP Composites

Water (%)	WEP1		WEP2
	Compressive strength (kg/cm ²)	Tensile strength (kg/cm ²)	Compressive strength (kg/cm ²)
20	243	62	222
30	211	30	180
40	181	25	170
50	161	23	156

With 30 wt % styrene and 2 wt % Bz_2O_2 as an initiator.



Figure 8 Death mask of Tutankhamen statue prepared from WEP1 with 20 wt % water (original magnification, 1 \times).



Figure 9 Head of Nefertiti statue prepared from WEPI with 30 wt % water (original magnification, 1 \times).

CONCLUSIONS

The process of recycling PET bottle wastes is commercially important because it converts a waste material into useful value-added products. The appearance and density of WEP composites based on recycled PET bottle wastes are favorable for many consumer products. WEPs prepared from PET wastes are a potential source of valuable materials with fairly good mechanical integrity and could be used for many practical applications. One of these applications is the production of art figures.

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Figure 10 Black cat figurine prepared from WEPI with 40 wt % water and 6 wt % carbon black (original magnification, 1 \times).