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UTILIZATION OF POLYETHYLENE TEREPHTHALATE (PET) WASTE IN THE PREPARATION OF NEW RESINOUS MATERIALS

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Various reactions of phenol and formaldehyde have been investigated under acidic conditions and in the presence of polyethylene terephthalate waste. These reactions led to the formation of new resinous materials, which were used to prepare different moulding powders under various parameters. A variety of articles were prepared from these moulding powders using compression mould press, some of which were free from blisters and indicated good finish. Moreover, their hardness, resistance to chemical corrosion and moisture penetration etc., suggest that some of the products thus prepared have good potential for use as caps and closures for pharmaceutical and other containers. Possible course of reactions leading to the formation of new resinous materials has also been briefly described.

Key words: Polyethylene terephthalate, Waste utilization, New resinous materials.

Introduction

Undoubtedly, the containers have great importance in the pharmaceutical and other industries. In this connection, phenol formaldehyde resins are used to produce moulded articles such as caps and closures for pharmaceutical containers [1], and electrical, radio and television parts [2]. They find uses in varnishes [3,4], electrical insulation including other protective insulators [5] and wood products [6]. Many phenolic resins and foams have excellent elasticity, thermal insulation, adhesion and fire resistance [7]. They have numerous other applications [8].

Polyethylene terephthalate finds particular uses where primarily strength, toughness, flexlife and resistance to abrasion and micro-organism are required. Thus, these excellent physical, electrical and mechanical properties coupled with good thermal stability, allow the material to be used for protective covers for glass replacement and in a number of special packaging outlets [9]. In an attempt to improve the quality of such materials the reactions of phenol and formaldehyde have been investigated under acidic conditions in the presence of polyethylene terephthalate waste. Products obtained from such reactions have been used to prepare different articles using compression moulding. Comparison of their characteristics has been made and their potential for use in pharmaceutical and other containers described in this manuscript.

Materials and Methods

Solvents used (acetone, ethyl alcohol etc.) were of commercial grade, but were purified before use following standard procedure. Phenol (95% w/v) [10] and paraformaldehyde (containing 88% of formaldehyde) [11] were of technical

grade. Polyethylene terephthalate waste was obtained from the Imperial Chemical Industries, Punjab. In addition hexamethylenetetramine (hexa), high alumina clay, lime, calcium stearate and stearic acid were also of technical grade. Wood flour used as filler was obtained from furniture makers using Shishum or Acacia wood.

Method for the preparation of phenol-formaldehyde resins and polyethylene terephthalate modified Resins. The samples of the resins labelled as A,B,C,D,E & F were prepared by using phenol (47 gm), paraformaldehyde (12 gm), oxalic acid (1 gm), water 20.5 cm³ containing 0, 2, 4, 6, 8 and 10 gm, of polyethylene terephthalate (PET) respectively. PET was dissolved in phenol and the reaction mixture was heated to 80° and then cooled to room temperature. This solution was added to a flask, which already contained other reactants (paraformaldehyde, oxalic acid and water) in amounts as indicated above. The contents in the flask were heated on a water-bath at 95° for 4.5 hrs followed by heating on an oil-bath at about 150° for only 10 mins.

Determination of various characteristics of the resins.

(i). Unreacted formaldehyde was determined by a known method [12]. (ii). Unreacted phenol was determined by the method advanced by Fleck [13]. (iii). Acid value resin (1 gm) dissolved in warm ethanol (20 cm³) was taken in conical flask (100 cm³) and 1% phenolphthalein solution (0.5 cm³) was added to serve as an indicator. The mixture was titrated against alcoholic potassium hydroxide (0.1 N) till the solution acquired a pink colour. The acid value was then calculated in accordance with the method described by Martin [14]. (iv) Viscosity. It was also measured by a reported procedure [13].

Preparation of moulding powders and moulded articles.

(i) The moulding powder was prepared by homogenising the

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dry ingredients (filler, hardener, accelerator, lubricant etc.) and resin (20 gm) taken in methylated alcohol (100 cm³). The composition of various moulding powders thus prepared is shown in Table 2. All the lumps were broken and the mixture dried in an oven at 70-80°. The moulding powders so obtained were compressed in a compression moulding press at 140° under 2000 lb/in² to produce different house-hold articles. Their moulding characteristics have been noted in Table 3.

(ii) Five moulding powders (labelled as G₁—G₅) obtained from resin (30 gm), wood flour (25 gm), high alumina clay (3 gm), hexa (3.5 gm), lime (1.75 gm), stearic acid (3 gm)

and magnesium stearate (3 gm) were pressed in a moulding press for 90 sec. at 2000 lb/in² at temperatures varying from 80-150°. The physical characteristics of these moulded articles are shown in Table 4.

Results and Discussion

The resins of phenol and paraformaldehyde were prepared with and without addition of polyethylene terephthalate (PET). The characteristics of the pure phenolic and modified resins are shown in Table 1. It is obvious that the properties of resins containing PET (samples B to F) are considerably

TABLE 1. CHARACTERISTICS OF RESIN SAMPLES.

Samples	A	B	C	D	E	F
% Yield	62.2	61.5	60.9	60.1	60.5	60.2
% Free phenol	00.640	00.656	00.688	00.736	00.750	00.780
% Free formaldehyde	00.024	00.021	00.21	00.19	00.18	00.15
Acid value	55.3	56.0	55.9	55.1	55.1	55.4
Viscosity (cps)	3.00	3.67	4.11	4.46	4.97	5.88
Melting point	87.00	92.00	96.00	103.00	105.00	110.00
Colour	Slight yellow----- Light brown -----> Brown					
Hardness	----- Increases ----->					

TABLE 2. COMPOSITION OF MOULDING POWDERS.

Sample No.	Resin (gm.)	Wood floor ¹ (gm.)	High ² alumina clay (gm)	Hexa ³ (gm)	Lime ⁴ (gm)	Stearic ⁵ acid (gm)	Calcium ⁵ stearate (gm)
A ₁ -----A ₅	20	17,18,19,20,21	2.0	3.0	1.0	0.2	0.2
B ₁ -----B ₅	20	19	1,1.5,2.0 2, 5, 3.0	3.0	1.0	0.2	0.2
C ₁ -----C ₅	20	19	1.5	2.0,2.5,3.0 3.5,4.0	1.0	0.2	0.2
D ₁ -----D ₅	20	19	1.5	2.0	0.5,1.0,1.5 2.0,2.5	0.2	0.2
E ₁ -----E ₅	20	19	1.5	2.0	0.5	0.1,0.2,0.3 0.4,0.5	0.2
F ₁ -----F ₅	20	19	1.5	2.0	0.5	0.5	0.1,0.2,0.3 0.4,0.5

1. Filler; 2. Binder; 3. Hardener; 4. Accelerator; 5. Lubricant.

TABLE 3. CHARACTERISTICS OF COMPRESSION MOULDED POWDERS.

Mould powder Sample No.	Flow in mould	Delivery from mould	Finishing of articles produced	Useful samples*
A ₁ -----A ₅	E,E,E,NE,NE	NE,NE,E,E,FM	NG,NG,G,G,--	—
B ₁ -----B ₅	E,E, NE,NE,NE	NE,E,E,E,NE	G,G,G,NG,NG	B ₂
C ₁ -----C ₅	E,E,E,NE,NE	E,E,E,E,E	NG,G,G,G,G	C ₂ ,C ₃
D ₁ -----D ₅	E,E,E,E,E	E,E,E,E,FM	G,G,NG,NG,--	D ₁ ,D ₂
E ₁ -----E ₅	NE,E,E,E,E	NE,E,E,E,E	NG,G,G,G,G	E ₂ -----E ₅
F ₁ -----F ₅	E,E,E,E,E,	NE,E,E,E,E	NG,G,G,G,G	F ₂ -----F ₅

E=Easy; NE=Not easy; G=Good; NG=Not good; FM=Failed to mould; * Show good hardness.

different from the resins which were prepared without it (sample A). The pure phenolic resins were slightly yellow in colour, but gradually changed brownish. Their hardness, infusibility and resistance to chemical corrosion and moisture

TABLE 4. EFFECT OF TEMPERATURE ON MOULDING* OF VARIOUS RESIN SAMPLES.

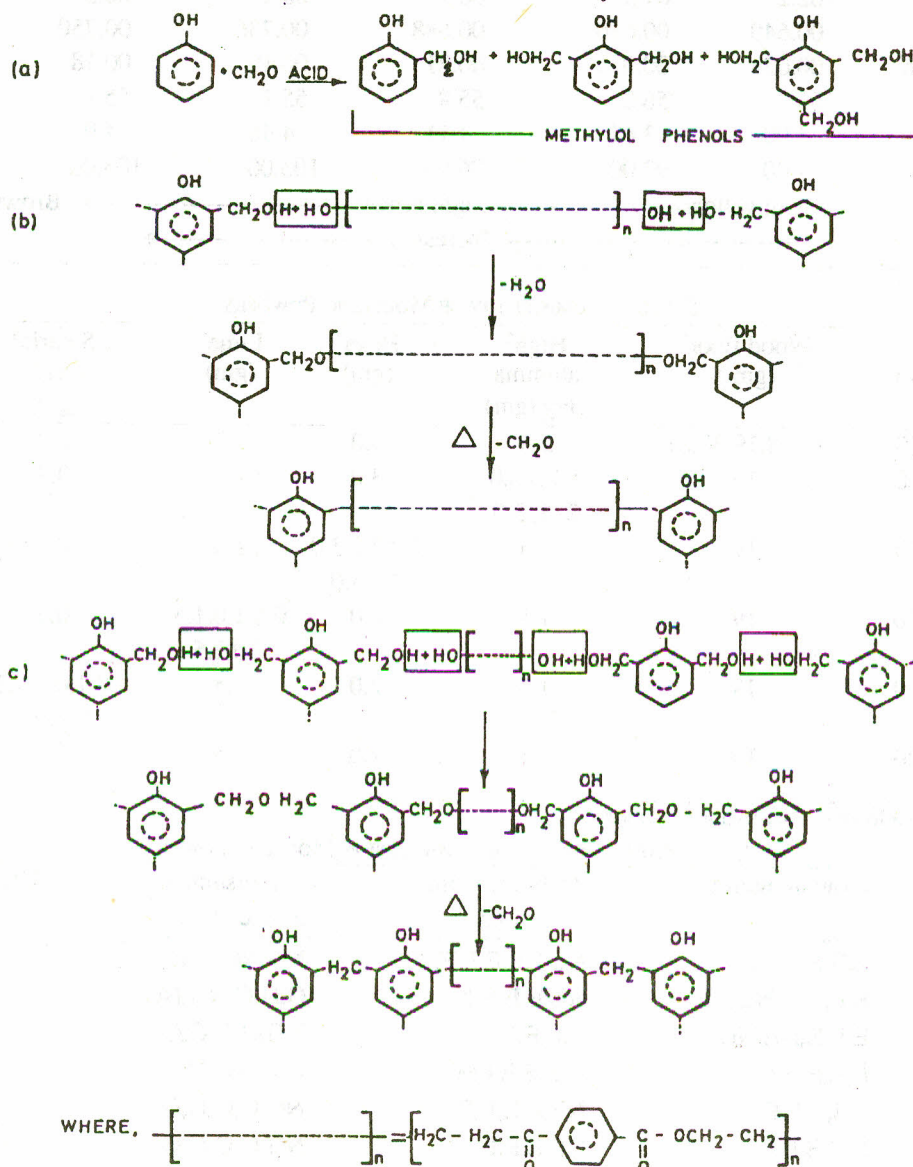
Sample No.	Temp. °C	Gas evolved	Delivery from mould	Hardness
G ₁	80	No	FM**	No
G ₂	120	Yes	Easy	Breakable
G ₃	130	Yes	V.easy	Breakable
G ₄	140	No	V.easy	Very hard
G ₅	140	No	N.easy	No hardness

* Moulding time is 90 Sec., FM**=Failed to mould.

penetration appeared to vary according to the amount of the polyester added from samples A to F.

Their viscosity also increased with addition of the polyester in the reaction mixture. This increase in viscosity may be attributed solely to the inclusion of high molecular weight PET in the novolak or resole systems. Alternatively, it may partly be due to increase in the degree of polymerisation resulting in the enhancement of molecular mass of the new resins [2].

Moreover, as the reaction proceeded, the amount of free formaldehyde decreased with the increased addition of the polyester. In addition, pure phenolic resins were observed to be quite soluble in polar solvents like acetone, methyl acetate, methanol and methylated spirit, whereas the resins containing the polyester make only cloudy solution in such solvents, but were fairly soluble in nitrobenzene and benzyl alcohol.



Scheme 1. Mechanistic reaction scheme of polyethylene terephthalate with phenol and formaldehyde.

However, they were insoluble in benzene, ether and carbon tetrachloride, carbon disulphide, petroleum ether (b.p. 60-80°) and 2-butanone.

The m.p. of the modified resins also varied from 90° to 110° as amount of the polyester increased, and required comparatively less amounts of the hardener in the moulding composition. Moreover, no solid particles were left in the melts. Thus, addition of the polyester may be considered to be accompanied by a chemical change with phenol and formaldehyde. However, it is just possible that up to a certain limit the polyester may be combining chemically with phenol and formaldehyde to afford a polymeric product, which dissolved in the specific solvents like nitrobenzene and benzyl alcohol.

It may be noted that the modified resinous material (Sample F) has the highest m.p. (Table 1) and was selected for preparing thirty different moulding powders (Table 2). Out of these, thirteen moulding powders, varying in composition, were found to be satisfactory for use in compression moulding as shown in (Table 3). Moreover, five moulding powders were additionally prepared as described in the experimental section to study the effect of temperature on the moulded material. The physical characteristics of these moulded articles are described in Table 4. It was observed that no gas evolved during processing of sample G₄ at 140° and the articles were easily delivered from the mould. It was also noted that when the time of heating varied from 2-4 hr, the evolved formaldehyde caused blistering on the surface of the solid articles. However, the evolution of this gas was reduced by increasing the heating period during the formation of modified resins. Consequently, those samples of modified resins which were prepared by heating the reactants from 4.5-5 hr, did not evolve any gas during moulding. The moulded articles from such resinous materials had no blisters and indicated good finish. Moreover, their hardness, resistance to chemical corrosion and moisture penetration etc., suggest that some of them have good potential for use as caps and closures for pharmaceutical containers. The cost of the articles thus prepared is likely to be competitive since the modified resin makes use of the polyester waste, which is available at a throw-away price.

Mechanism. After discussing the properties associated with these new resinous materials, it is equally important to keep in mind the mode of condensation of phenol and formaldehyde in the acidic medium initially forming dihydroxydiphenyl methane and/or other methylol phenols. The latter being very reactive are likely to undergo normal condensation. Especially in the acidic medium, however, they may also react further with the terminal hydroxy groups of PET either through the methylene or through ether linkages [15], as shown in the reaction Scheme 1.

The products containing ether linkages are proposed to lose formaldehyde upon heating and afford stable polymeric materials. The proposed mechanism also explains the evolution of formaldehyde gas during moulding of certain moulding compositions. However, it is premature to describe the exact nature of these new polymeric products and further exhaustive investigations are required to determine their structural details and other physical properties.

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