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Physiochemical properties of polymer mortar composites using resins derived from post-consumer PET bottles

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Abstract

In this study, post consumer polyethylene terephthalate (PET) waste bottles were used, to produce unsaturated polyester resin by depolymerization through glycolysis reaction with diethylene glycol. The glycolysis was optimized by varying temperature, amount of catalyst, and the glycolysis time. The glycolysis product bis-2-hydroxy ethylene terephthalate (BHET) monomers were converted into unsaturated polyesters, which were diluted with styrene to produce the unsaturated polyester resin. These resins were used to produce polymer mortar and cured using benzoyl peroxide as an initiator and *N*,*N*-diethyl aniline as promoter. These polymer mortar composites were analyzed for physiochemical properties using carbon, hydrogen and nitrogen (CHN) elemental analysis, Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis–differential thermal analysis (TGA–DTA). The polymer mortar so produced has a compressive strength of about 10 MPa and may be used in applications such as pavements, median barriers, sewer pipes, etc. Its tensile strength at 45 days of age is 18–23% of its compressive strength at the same age.

Keywords: Glycolysis of poly(ethylene terephthalate); Unsaturated polyester resin; Curing behavior; Polymer mortar composite; Tensile strength; Compressive strength

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1. Introduction

Plastics have become an indispensable part of modern life. No aspect of human life is untouched by plastics, which are used in cars, computers, telephones, clothing, packaging, etc. The packaging industry is the biggest consumer of plastics. Of various plastics that are being used in the packaging industry, polyethylene terephthalate (PET), a thermoplastic polyester is widely used [1]. Soft drink and mineral water bottles are all made of PET and constitute the third largest food packaging that is being regularly consumed after packaged tea and biscuits. The estimated production of soft drink bottles alone as per the Ministry of Food Processing Industry of India was about 6600 million in 2001–2003. If mineral water bottles are also included then this figure may well reach about 20,000 million bottles in 2005–2006 in India.

The production of such a large amount of PET bottles has created an environmental problem of gigantic proportions, since these bottles are not reused by the manufacturers and therefore are left as plastic waste, which do not decompose readily in nature [2,3]. The effective solution to solve this problem is to recycle these post consumer PET bottles.

In the present research work the recycling of the PET bottles was done by glycolysis and the product was converted into unsaturated polyester resin (UPER). These resins were used in preparing the polymer mortar composites by mixing with river sand mechanically. The prepared material was cast in cubes and briquettes for testing under compression and tension respectively. The mortar produced is

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observed to have sufficient strength and can be used in many precast applications such as pavements, median barriers, sewer pipes, etc. The use of unsaturated polyester resin as a binder is important for the construction industry [4] and also helps in the long-term utilization of PET waste in an effective and economical manner [5].

2. Experiments

2.1. Materials

The PET was obtained from post consumer soft drinking and water bottles, which were cut into small pieces for producing PET flakes. The diethylene glycol is used for glycolysis and subsequent depolymerization of PET, whereas zinc acetate is used as catalyst. Maleic anhydride and phthaleic anhydride are used to carry out non-catalyzed melt polyesterification reaction. For the preparation of cured resin benzoyl peroxide is used as initiator and *N*,*N*-diethyl aniline as promoter. These materials were obtained from CDH (India). The styrene monomer obtained from GSC (India) was used to reduce the viscosity of the resin and to allow the cross linking of the chains. All chemicals and reagents were of analytical reagent grade.

Standard sand (fineness modulus = 2.6) obtained from Madras, India, was used for the preparation of the polymer mortar composites to study the mechanical properties. The standard sand as obtained from the supplier was oven dried for a minimum of 24 h at 60 °C to reduce the moisture content to less than 0.5% by weight, thus ensuring good bond between the polymer matrix and the inorganic aggregates.

2.2. Glycolysis experiment

The conversion of polyethylene terephthalate (PET) in presence of glycol is known as alcoholysis or glycolysis in the presence of a catalyst. A one-litre three-necked round bottom flask (reactor) was used for all glycolysis experiments. In order to ensure that the water content in the reactor was as low as possible, the reactor was heated to 110 °C and held at that temperature for at least 2 min. The reactor was equipped with a thermometer and a reflux condenser. A magnetic stirrer was put in the reactor to ensure proper mixing. The ratio of diethylene glycol to PET used in the glycolysis experiment was 4:1 by weight. The weights of diethylelene glycol and PET flakes were 84 and 21 g, respectively. In order to realize the influence of glycolysis temperature, glycolysis time and amount of the catalyst on the depolymerization of PET flakes, three groups of glycolysis experiments were conducted:

1. Glycolysis temperature was set at 190 °C and glycolysis time was 2 h. The amount of zinc acetate (catalyst) was varied from 0.25% to 1.75% by weight of PET (Table 1).
2. The glycolysis temperature was set at 190 °C and the amount of the catalyst was 0.25% by weight of PET. The glycolysis time was varied from 2 to 10 h in steps of one hour (Table 2).
3. The glycolysis time was 8 h and 0.25% of zinc acetate was used. The glycolysis temperature was varied from 140 to 210 °C (Table 3).

Table 1
Influence of the amount of catalyst on the glycolysis conversion of the recycled PET

S. no.	Catalyst (%)	Glycolysis conversion (%)
1	0	0
2	0.25	98.7
3	0.50	97.3
4	0.75	97.0
5	1.00	96.9
6	1.25	96.6
7	1.50	96.0
8	1.75	94.0

PET:glycol::1:4, temperature = 190 °C, glycolysis time = 2 h.

After finishing each glycolysis experiment, the reactor was removed from the heating filament, and 200 ml of boiling water was slowly added into the reactor. The whole product mixture was quickly filtered using a copper screen of 0.5 × 0.5 mm pore size. The remaining polymerized PET flakes were collected, dried, weighed and labeled as the

Table 2
Influence of the glycolysis time on the glycolysis conversion of the recycled PET

S. no.	Time (h)	Glycolysis conversion (%)
1	2	25.31
2	3	52.92
3	4	61.32
4	5	89.43
5	6	91.89
6	7	95.89
7	8	99.28
8	9	99.30
9	10	99.35

PET:glycol::1:4, temperature = 190 °C, catalyst = 0.25%.

Table 3
Influence of the glycolysis temperature on the glycolysis conversion of the recycled PET

S. no	Temperature (°C)	Glycolysis conversion (%)
1	140	5.14
2	150	14.73
3	160	30.65
4	170	50.47
5	180	80.64
6	190	98.78
7	200	98.81
8	210	98.82

PET:glycol::1:4, catalyst = 0.25%, glycolysis time = 8 h.

PET fraction. The conversion for the glycolysis of recycled PET flakes is defined as below:

$$\text{Glycolysis conversion percentage} = \frac{A - B}{A} \times 100 \qquad (1)$$

where A is the weight of PET flakes before glycolysis and B is the weight of PET flakes after glycolysis.

2.3. Synthesis of unsaturated polyester resin

After glycolysis, the maleic and phthaleic anhydrides were added into the reactor for non-catalyzed melt polyesterification reaction. The reaction was carried out at 190 °C for 8 h, and 0.5% hydroquinone by weight of PET was added into hot resin to prevent the resin from curing before use. The resin was then allowed to cool at room temperature.

2.4. Preparation of polymer mortar specimen

The above-prepared unsaturated polyesters were then diluted with 33 ml of styrene monomer (a solvent monomer) to reduce viscosity and to allow for further curing and free radical initiator and promoter were added to the resin before mixing it with the inorganic aggregates. These polymer mortar composites were mixed manually for about 5 min to ensure the proper mixing.

2.5. Casting of polymer mortar test specimen

The compressive strength of the polymer mortar composites was determined by casting mortar cube of 70.7 mm size taking different percentages (10%, 15% and 20%) of resin by weight of aggregate. The unit weight of the resin was 1.1 gm/cc while that of polymer mortar was 1.78 gm/cc. Three cubes were tested for each set.

The tensile strength of polymer mortar was determined by casting briquettes with different percentages of resins by weight of aggregate (10%, 15% and 20%). After casting, cubes and briquettes were left at room temperature for curing and setting.

2.6. Chemical composition

To determine the chemical composition of unsaturated polyester resin, carbon, hydrogen and nitrogen contents of the polymer mortar composite were determined by elemental analysis by using elemental analyzer (Carlo-Erba 1180).

2.7. Characterization of polymer mortar

The characterization of the polymer mortar composite material requires the determination of (i) thermal resistance of material, (ii) chemical structure, (iii) crystalline/amorphous nature and (iv) morphology of the material which are determined with the help of the following tests:

2.7.1. Thermogravimetric analysis–differential thermal analysis (TGA–DTA) studies

This test was carried out for determining the thermal resistance of the material at high temperature by using automatic thermal analyzer (V2.2A Du Pont 9900).

2.7.2. Fourier transform infrared spectroscopy (FTIR) studies

This test was carried out to verify the chemical structure of the three dimensional matrix of styrene supported polymer mortar composite by using FTIR spectrophotometer (Perkin–Elmer Spectrum-BX, USA).

2.7.3. X-ray studies

The X-ray diffraction pattern of the polymer mortar composite was recorded to ascertain the nature of the material, whether it is crystalline or amorphous by a Bruker AXS based X-ray diffractometer with Cu Kα radiation.

2.7.4. Scanning electron microscopy (SEM) studies

To study the morphology of the material SEM was performed on 1:3 cement sand mortar and polymer mortar composites by an electron microscope at magnification of 3.5 KX.

3. Results and discussion

3.1. Preparation and characterization of resin

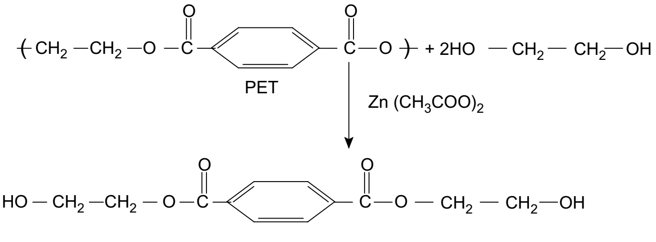
In the study of depolymerization of PET obtained from waste bottles by glycolysis, three groups of glycolysis experiments were conducted. In the first experiment, glycolysis temperature was set at 190 °C, glycolysis time was 2 h and the amount of catalyst was varied from 0.25% to 1.75% by weight of PET. It was observed that the glycolysis conversion increased with an increase in the amount of catalyst (zinc acetate). But after a critical amount of catalyst was reached, the glycolysis conversion decreased. The glycolysis conversion was found maximum when the zinc acetate was 0.25% by weight of PET (Table 1).

The influence of the variation of time on glycolysis conversion was studied by fixing the temperature at 190 °C and the amount of catalyst as 0.25% by weight of PET. The glycolysis time was varied from 2 to 10 h in steps of 1 h. It was observed that the glycolysis conversion increased with an increase in the glycolysis time and approached a steady state at about 8 h, it was 89% at 5 h and about 100% beyond 8 h (Table 2).

Table 3 shows the relationship between the glycolysis conversion of PET and glycolysis temperature. In this study, the glycolysis time was fixed at 8 h and catalyst at 0.25% by weight of PET. It was found that the glycolysis conversion was almost 0% at glycolysis temperature below 140 °C. The glycolysis conversion slowly increased after 140 °C and was about 50% at 170 °C and was 98% at 190 °C.

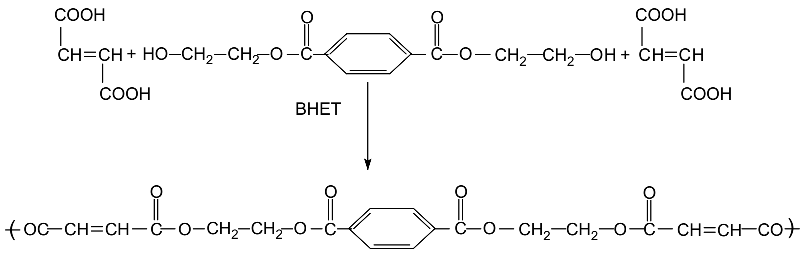
There may be other combinations of variables at which glycolysis is possible but since the primary purpose of the present study was to obtain a condition at which the PET bottles are depolymerized completely and this objective was satisfactorily achieved at above mentioned combination of parameters, therefore other possible combinations were not tried.

Thus, the depolymerization of PET accomplished by esterification reaction using zinc acetate as an esterification catalyst, produced bis-2-hydroxy ethylene terephthalate (BHET) monomers and oligomers. The chemical reaction involved in the depolymerization of PET is given as:



Bis-2 hydroxy ethylene terephthlate (BHET)

The BHET fractions of glycolyzed product of PET as prepared by optimal glycolysis conditions as given above, i.e. amount of the catalyst as 0.25% by weight of PET, glycolysis temperature 190 °C, glycolysis time 8 h and (1:4) (PET:glycol) ratio were used for the preparation of unsaturated polyester resin by polycondensation with maleic/phthaleic anhydrides. A segment of polyester obtained from polycondensation of glycolyzed product i.e. BHET might have the following structure:

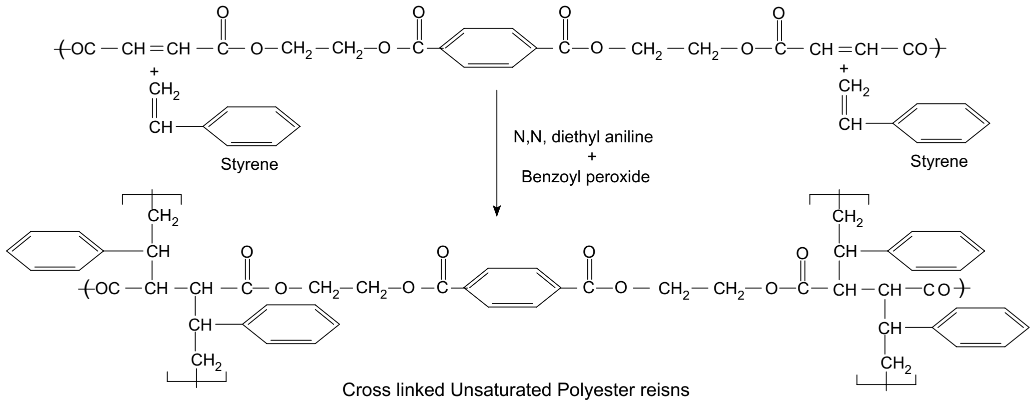


Unsaturated Polyester (UPE)

Appreciable *cis–trans* isomerization generally occurs during polyesterification of unsaturated anhydrides. Such isomerization is marked particularly with the maleic anhydride, which becomes incorporated into the polymer chains mostly as fumerate groups. At these unsaturated sites the cross linking occurs with styrene.

3.2. Structural and physiochemical properties of polymer mortar

The polymer mortar composite was prepared by the cross linking between the styrene and unsaturated polyester resin as derived above. The reaction is initiated by addition of free radical organic peroxide, i.e. benzoyl peroxide as initiator and *N*, *N*-diethyl aniline as promoter which were taken as 0.5% and 1% of UPER respectively. Curing of unsaturated polyester resin took place because the styrene combined with reactive double bond of unsaturated polyester chains, which are activated by the free radical initiator and promoter. Thus, bonds can be formed between styrene and the unsaturated polyester resin, giving the three-dimensional matrix of styrene supported UPER as:



Cross linked Unsaturated Polyester reisns

The styrene supported unsaturated polyester resin can be cured with different types of aggregates, to produce polymer mortar composite. Polymer mortar composite derived from styrene supported unsaturated polyester resin have carbon, hydrogen nitrogen ($\mathrm{C} = 2.38\%$, $\mathrm{H} = 0.08\%$, $\mathrm{N} = 0.07\%$). These results support the chemical structure of unsaturated polyester resin.

The compressive and tensile strength of polymer mortar with varying percentages of resin (10%, 15% and 20%) by weight of sand was determined at 15, 30 and 45 days. The compressive strength was determined using cubes of 70.7 mm size and the tensile strength was determined with the help of briquette test. A briquette during tensile testing is shown in Fig. 1. The cubes tested in compression failed by the development of vertical cracks. The cracks do not pass through the aggregate; rather causes bond failure between aggregate and the resin. The failure of briquette in tension is also by bond failure.

The variation of compressive and tensile strength of polymer mortar with age is plotted in Fig. 2 for different percentages of resin. It is observed from the figure that the gain in compressive strength at 45 days over 15 days strength varies from 28% to 29% whereas gain in tensile strength at 45 days over 15 days varies from 49% to 77%. The 15 days tensile strength is about 16% of its compressive strength whereas 45 days tensile strength varies from 18% to 23% of its compressive strength.

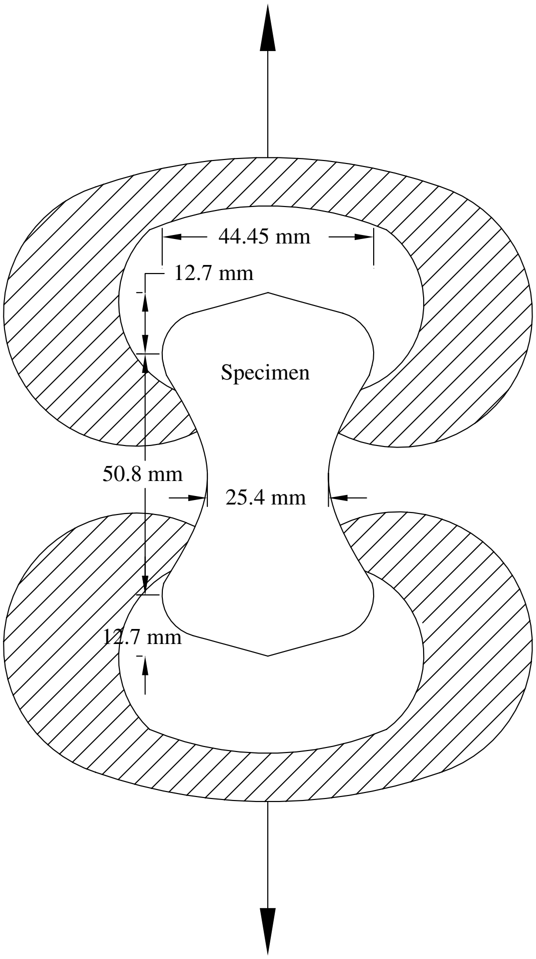


Fig. 1. Briquette of polymer mortar composite under tensile test.

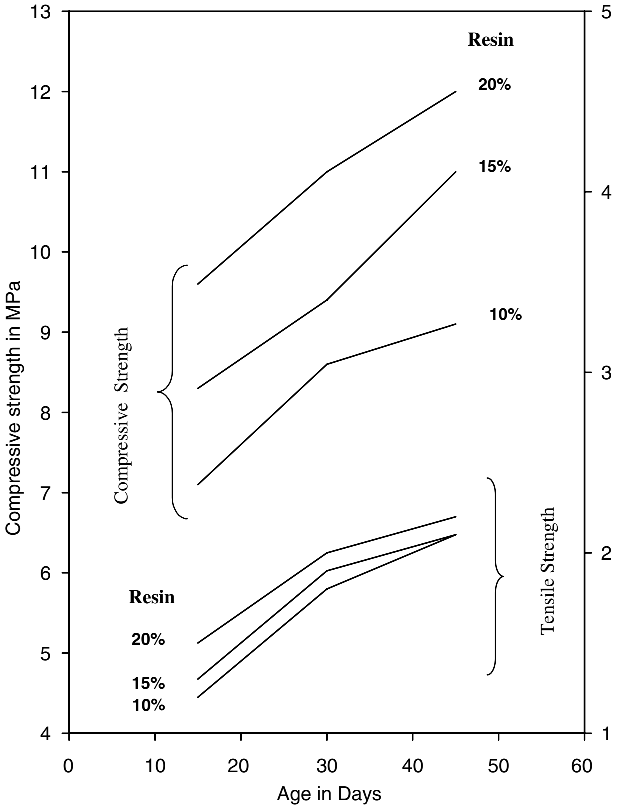


Fig. 2. Variation of compressive and tensile strength with age.

An indication of possible structure may be discussed in the light of the FTIR spectrum of the three-dimensional matrix of styrene-supported polymer mortar composite (Fig. 3). The twisting and wagging vibration frequencies of the methylene group $-\mathrm{CH}_2$ were in the region of 1300–1200 cm^{-1} [6]. These vibration frequencies are weaker than the scissoring and rocking vibration frequencies. The bands

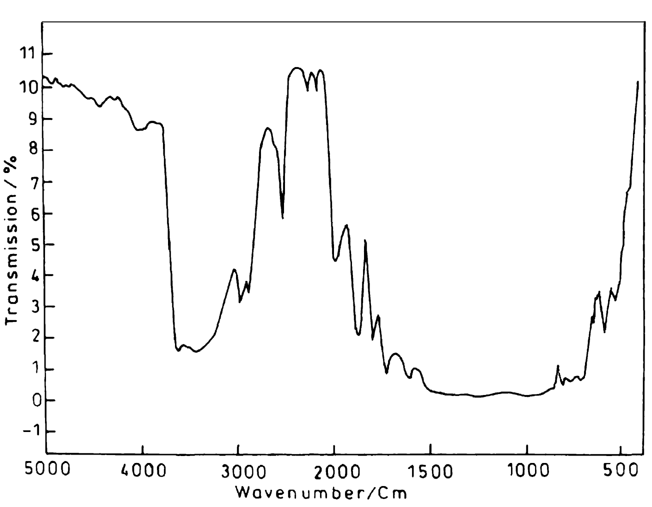


Fig. 3. FTIR spectra of polymer mortar composite.

near 1700 and 1500 $\mathrm{cm}^{-1}$are characteristics of the aromatic ring and also for carbonyl group itself [6]. Thus, a small sharp peak in the region of 1600 cm^{-1}may be due to the presence of carbonyl group of the resin. An intense absorption band around the region 3000 cm^{-1} may be due to the presence of –CH stretching vibration frequency of benzene ring in the plane. The –CH out of plane deformation vibration frequency of benzene ring was observed in the region around 593 cm^{-1} [6]. These peak positions justified the structure of styrene supported polyester resin present in polymer mortar composite.

The weight loss vs. temperature characteristics of the polymer mortar composite varied significantly as shown in Fig. 4, which also indicates the utility of TGA for providing relative thermal stability of this polymer mortar composite. The thermal degradation curve for this polymer mortar composite was fairly constant as the results indicate a continuous weight loss of mass of 1.18% up to 293 °C, which may be due to the removal of moisture content of

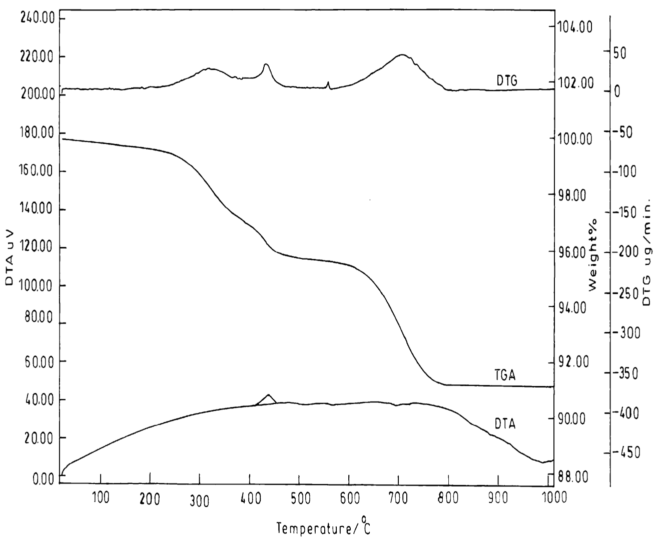


Fig. 4. TGA–DTA curves of polymer mortar composite.

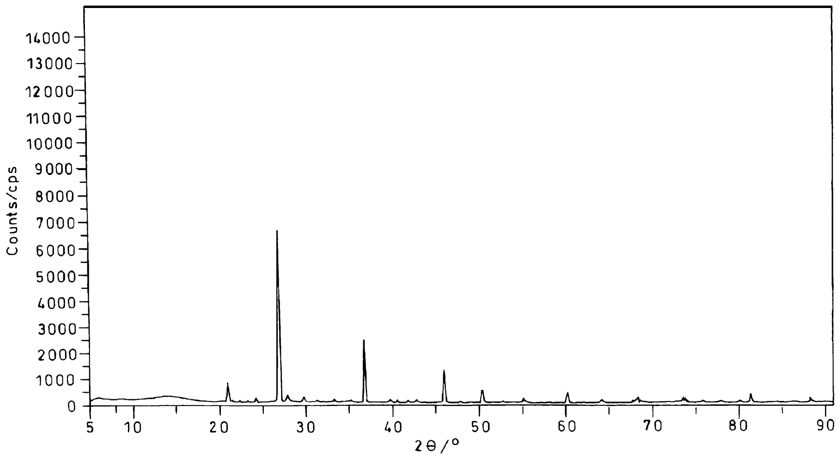


Fig. 5. Powder X-ray diffraction pattern of polymer mortar composite.

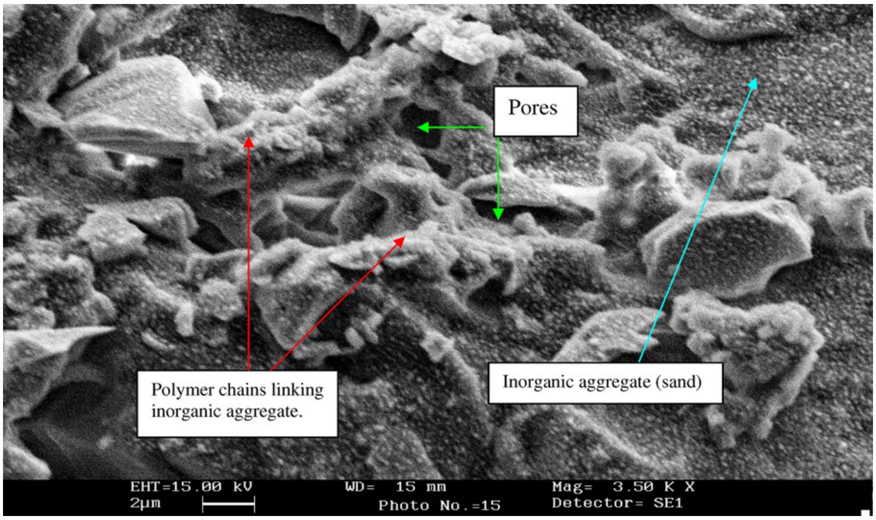


Fig. 6. Scanning electron microphotographs (SEM) of polymer mortar composite at the magnification of 3.50 KX.

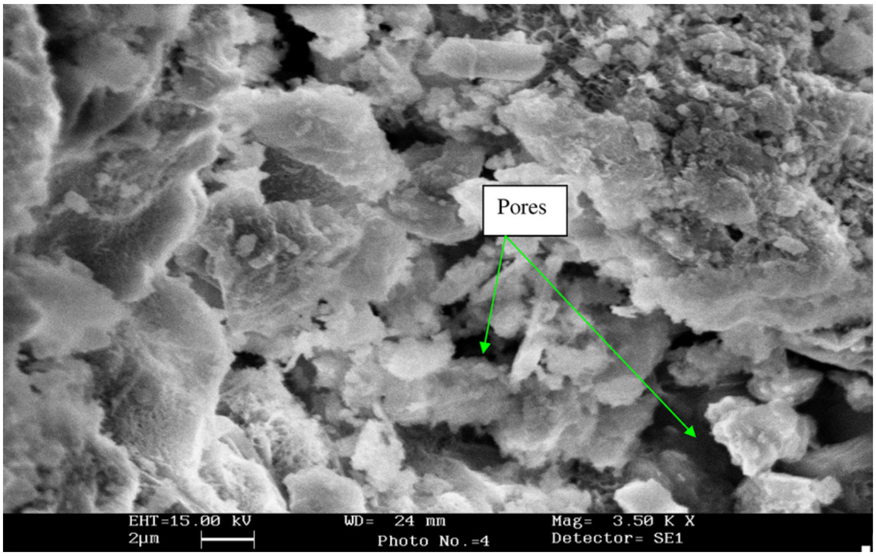


Fig. 7. Scanning electron microphotographs (SEM) of cement mortar composite at the magnification of 3.50 KX.

polymer mortar composite. A slow weight loss of mass of about 8.85% at 787 °C may be due to a partial decomposition of organic part of polymer mortar composite.

Studies of thermal degradation of polymeric materials in polymer mortar composites are important on two accounts: the practical and scientific. On the practical side TGA studies not only explain the behavior of polymer exposed to high temperature [7], but also help in establishing criteria for the selection of materials for specific use [7]. The TGA analysis indicates that the polymer resins obtained after recycling of PET bottles have high thermal resistance and can be used in various civil engineering applications as a binder.

The X-ray diffraction pattern of this composite material shows large peaks of 2θ values. The analysis of these sharp signal peaks indicates the crystalline nature of the material as shown in Fig. 5. This crystalline nature can help to understand the physical properties.

Scanning electron microscope (SEM) photograph of polymer mortar composite is presented at a magnification of 3.50 KX (Fig. 6), which indicates the binding of inorganic aggregates with the styrene supported recycled polyester resin. The SEM picture also represents the porosity in the polymer mortar matrix and shows that it has a very low porosity in comparison to the cement mortar as given in Fig. 7. Thus, this material can be utilized for a variety of applications.

4. Conclusions

The plastic waste may be used after recycling to produce polymer mortar by proper glycolysis of PET. The optimum conditions for the glycolysis of PET were observed at 190 °C temperature, 8 h of glycolysis time and 0.25% catalyst by weight of PET. The thermogravimetric analysis of polymer mortar composite indicates that the material is stable at high temperature (up to 800 °C) and X-ray study shows that it is crystalline in nature. The FTIR spectrum shows the possible chemical composition of the crossed linked styrene supported polyester resin. The SEM picture of the polymer mortar matrix shows that it has a very low porosity in comparison to the cement mortar of even rich grade.

The polymer composite has compressive strength of about 10 MPa grade, and may be used in applications such as pavements, median barriers, sewer pipes, etc. The tensile strength of mortar at 45 days of age is 18–23% of its compressive strength at the same age. The 15 days compressive strength is about 60% of its 45 days strength, therefore, striping time for polymer composite may be taken as 15 days. The gain in strength after 45 days was studied for 10% resin and was found to be only nominal but for other percentages of resin, there may be increase in strength beyond 45 days, which needs to be studied.

Acknowledgement

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