Abstract—Recycling of the polyethylene terphthalate (PET) waste does not only serve as a partial solution to the solid waste but also contributes to the conservation of raw materials and energy. In our study, depolymerization process of post consumer PET beverage bottles was carried out by glycolysis using cis-2-butene-1,4-diol (2BD). The PET glycolysis products (GP) were incorporated as a compatibilizer in 50/50 styrene butadiene rubber/ethylene propylene diene monomer (SBR/EPDM) blends in different concentrations. The feasibility of the use GP as a compatibilizer was assessed by calculating the heat of mixing, strain energy of the SBR/EPDM compounds. Swelling measurements were carried out to evaluate the compatibilizer-rubber blend interaction and to calculate the molecular weight between two crosslink’s and crosslink density. Differential scanning calorimetry (DSC) experiments were used to examine the compatibilizer efficiency by detecting the glass transition temperature (Tg) of the SBR/EPDM compounds. Scanning electron microscope (SEM) was used to study the effect of the compatibilizer on the morphology rubber blends. Moreover the effect of high abrasion carbon black (HAF) and paraffinic oil on the compatibilizer efficiency were also studied.

Index Terms—compatibilizer, crosslink density, glycolysis, heat of mixing, mechanical properties, polyethylene terphthalate waste, rubber blend, strain energy.

I. INTRODUCTION

Poly (ethylene terphthalate), more commonly known as PET in the packaging industry and generally referred to as ‘polyester’in the textile industry. It is considered one of the easiest materials to recycle, and is second only to aluminum in terms of the scrap values for recycled materials. Although PET does not create a direct hazard to the environment, it has substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents [1]. Thus, PET recycling has been one of the most successful and widespread among polymer recycling [2], [3]. The recycling PET can be carried out in many ways. Four main approaches have been proposed which are primary or ‘in-plant’, secondary or mechanical, tertiary or chemical, quaternary involving energy recovery [4],[5]. Chemical-recycling processes for PET are divided as follows: (i) hydrolysis, (ii) glycolysis, (iii) methanolysis and (iv) other processes such as aminolysis and ammonolysis. The main depolymerization processes that have reached commercial maturity are glycolysis and methanolysis. [1], [3]. In literature, glycolysis reactions involved the insertion of ethylene glycol, diethylene glycol, propylene glycol, (1, 4)-butane diol, (1, 2)-butane diol, cis -2-butene-1,4-diol, or mixtures of diols [6]-[11]. The main disadvantage is that the glycolysis reaction products are not discrete chemicals but come along with higher oligomers, which are difficult to purify with conventional techniques. However, the end products produced from the glycolysis of PET waste were used as a new raw material for preparing other polymers such as epoxy resin, polyurethane, alkyd resins used as enamel paints or coatings, unsaturated polyester used for the production of polymer composite, and water extended polyester for manufacture of art figures [9],[12]-[14].

Polymer blends have always been considered to be interesting combinations for obtaining new high-performance polymeric materials without synthesizing fully new polymers especially when the properties of two or more polymers are synergistically combined. Unfortunately, most polymers are immiscible. Hence, their blends show poor mechanical properties and unstable morphology. These problems can be overcome by using various kinds of compatibilizers. [15]
Ethylene propylene diene terpolymer (EPDM) is one of the most widely used and fastest growing synthetic rubbers. It has general purpose applications, which usually imparts good aging characteristics, good weathering oxidation, little moisture adsorption, good electrical properties and chemical resistance. Styrene–butadiene rubber (SBR) has good mechanical properties; it does not break down easily. Also, it has good abrasion resistance, greater ozone and weathering resistance, but its oil resistance is very poor [16]. EPDM like SBR can be vulcanized with sulfur cure systems. However, the differences in the solubility of sulfur and the level of unsaturation in both elastomers result in incompatibility in blends of these elastomers [17].

The goal of our present study is to use the recycling process of PET wastes; not only as a partial solution to the solid-waste problem but also to conserve raw materials and energy. This will be achieved by depolymerization of post-consumer PET by glycolysis. The reaction products (GP) will be used as a compatibilizer for EPDM/SBR blends. The compatibilizing effect of these compounds will be evaluated via various measurements and techniques.

## II. METHODOLOGY

### A. Materials

Post-consumer soft-drink clear bottles were used as a source for PET. The caps and bottom parts as well as the labels and the adhesives had been removed. The bottles were cut into flakes at a maximum size 2-3 mm, cleaned thoroughly by washing with water and soap and then with distilled water. The clean flakes of PET wastes were dried at 80°C to constant weight.

Chemicals used for glycolysis are: cis-2-buten-1, 4-diol, (2-BD) a liquid with a boiling point of 234°C and a density of 1.07 g/cm³ from Aldrich; zinc acetate from Merck was candidate as catalyst for the proposed PET recycling process.

Styrene butadiene rubber (SBR 1502) with a specific gravity of 0.945, styrene content of 23.5% and Mooney viscosity ML (1 + 4) at 100°C is 48–58. Ethylene-propylene-diene monomer (EPDM) with density 0.86 g/cm³, ethylene weight content of 70%, an unsaturated ratio NB/100, 8 and 22% propylene and Mooney viscosity ML (1 + 4) at 100°C is 85. SBR and EPDM were purchased from Transportation & Engineering Company (TRENCO) – Alexandria, Egypt.

Chemicals used for rubber compounding: stearic acid with specific gravity 0.9–0.97 is 15°C; zinc oxide (ZnO) with specific gravity = 5.55–5.61; elemental sulfur (S) with specific gravity = 2.04–2.06; N-cyclohexyl-2-benzothiazole sulphenamide (CBS) with specific gravity = 1.27–1.31, melting range = 95–100°C; all these chemicals are Aldrich company products and used as received without further purification. High abrasion furnace carbon black (HAF) N-330 and paraffin oil were purchased from Transportation & Engineering Company (TRENCO) – Alexandria, Egypt.

### B. Experimental techniques

**Glycolysis of PET waste:** predetermined weight of waste flakes were added in the reactor to cis-2-buten-1,4-diol in a molar ratio 1: 2.185 (PET: 2-BD). Zinc acetate was added as transesterification catalyst. The reactor was immersed in an oil bath and heated for 5 h at 230°C. The reaction was carried out under reflux in nitrogen atmosphere. After the 5 h period, the reactor was allowed to cool to room temperature and the reaction product was filtered. The glycolysated PET products (GP) were previously examined in our laboratory [18]. It consists mainly of unsaturated hydroxyl-terminated oligomers with average molecular weight of 628 g/mol and polydispersity of 1.22 and could be represented by the following structures:

\[
\text{HO-CH}_2\text{-CH=CH-CH}_2\text{-OOC-COO-CH}_2\text{-CH=CH-CH}_2\text{-OH}
\]

4, 4’-di (2, 3-butenhydroxy) terephthalate monomer (GP)

**Preparation of the rubber compounds:** The compounding of rubber blends were carried out according to ASTM –D3182-07 on a two-roll mill. The GP was incorporated in SBR/EPDM, at different loadings, in absence and
presence of paraffinic oil and carbon black (HAF). The compounds formulations are shown in Table 1. The other additives of the recipe were added in parts per hundred (phr) as follows: 5 phr zinc oxide, 1.5 phr stearic acid, 0.8 phr CBS, and 2 phr sulphur. An oscillating disc rheometer (MDR 2000), supplied by Alpha Technologies, UK, was used for measuring the optimum cure time of the different mixes at 150°C. An electrical press was used for vulcanization of the mixes, at 4 MPa and 150°C, each according to the corresponding cure time obtained from the rheometer.

<table>
<thead>
<tr>
<th>Ingredients, phr*</th>
<th>K0</th>
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<td>7.5</td>
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<td>15</td>
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* phr: part per hundred.

**Determination of the heat of mixing:** Schneier [19] stated that the heat of mixing may be an approximate measure of the polymer-polymer compatibility. He proposed the following equation for calculating the heat of mixing for a two component blend system.

$$\Delta H_m = \left\{ \frac{X_1 M_1 \rho_1 (\delta_1 - \delta_2)^2}{(1-X_1)M_2 \rho_2 + (1-X_1)M_1 \rho_1} \right\}^{1/2} \quad (1)$$

Where $X, \rho, M$ and $\delta$ are the weight fraction of polymer, polymer density, the molecular weight of monomer unit and solubility parameter of the polymer respectively.

**The mechanical properties** Tensile testing machine Zwick Z010, Germany was used to determine the tensile strength (T.S), modulus at 100 % strain (M@100%) and elongation at break (E%) according to ASTM D 412-06a.

**Determination of the strain – energy.** It had been stated before that the energy absorbed per unit volume ($W$) is expected to increase in deforming rubber blends; thus the energy absorbed can be written as [20],[21]:

$$W = \int \sigma (\varepsilon) d\varepsilon \quad (2)$$

where $\sigma$ is stress as a function of the strain $\varepsilon$. Strain-energy values (energy absorbed per unit volume) were obtained for all samples by integrating the area under the stress-strain curve obtained from the tensile testing machine.

**Swelling measurements.** The interaction between rubber and GP has been investigated using a swelling technique. The equilibrium swelling of the blend vulcanizates was carried out according to ASTM D 471-10. Assuming that swelling is completely restricted at the rubber- compatibilizer interface, the equation of Lorenz and Parks [22] has been applied to study the rubber- compatibilizer interaction.

$$\frac{Q_c}{Q_g} = ae^{-Z} + b \quad (3)$$

Where $Q$ is defined as grams of solvent per gram of rubber hydrocarbon, $a$ and $g$ refer to compatibilizer and gum mixes. $Z$ is the weight fraction of compatibilizer in the vulcanizates, $a$ and $b$ are characteristic constants of the system. $Q$ was calculated by:
The swelling data were also utilized to determine the molecular weight between two crosslink’s (M_c), by using Flory-Rehner relation equation [23]:

\[
\frac{1}{2(M_c)} = \frac{1}{2\rho V_0} \left[ \frac{1}{V_R} - \frac{1}{2V_0} \right] + \frac{\mu V_R}{\rho V_0}
\]

where M_c is the average molecular weight between two successive crosslink’s, \(\rho\) is the density of rubber, \(V_0\) is the molar volume of swelling solvent absorbed (toluene \(V_0=106.3\text{cc/mol}\)), and \(V_R\) is the volume fraction of the swollen rubber that can be obtained from the mass and densities of rubber samples and the solvent, \(\mu\) is the interaction parameter between the rubber and toluene which is 0.446 for SBR and 0.49 for EPDM [24]. The cross linking density \(\nu\) can be calculated from the equation:

\[
\nu = \frac{1}{2M_c} - \frac{1}{V_R}
\]

Differential scanning Calorimetric measurements (DSC). A Netzsch STA 409C/CD (Boston, USA) was used. The experiments were carried out under nitrogen atmosphere and operated at a heating rate 10°C /min within the temperature range from -100 to 200°C.

Scanning electron microscopy (SEM). SEM was done using (JXA-840 A) electron probe micro-analyzer Japan Jeol. Rubber specimen was broken in liquid nitrogen; cross section surface was covered with a very thin layer of gold to avoid electrostatic charging during examination.

III. RESULTS AND DISCUSSION

A. Heat of mixing

Heat of mixing can be taken as approximate measure of the free energy of mixing and may be used as an indicator of possible compatibility [25]. Singh et al [26] calculated the heat of mixing of some polymer blends using the Schneier equation, eq.1, and reported that the heat of mixing with values below a limiting value of \(41.85 \times 10^{-3}\) J/mol indicates compatible blends while the incompatible blends have mostly higher values.

![Image of heat of mixing graphs](image_url)
In order to study the effect of GP as a compatibilizer between SBR/EPDM, the heat of mixing for the SBR/EPDM blends over the entire range of weight percent composition were calculated using eq.2. Heat of mixing of SBR/EPDM blend in absence of GP is shown in Fig.1a. The heat of mixing of SBR and EPDM, over the entire range of compositions, is higher than the limiting value of compatibility indicating the incompatibility of SBR/EPDM blend. On the other hand, the heat of mixing of SBR and EPDM in presence of 5 phr GP, Fig. 1b, is below the limiting value of compatibility indicating a compatible blend. That means that GB increases the miscibility between the two rubbers.

B. Mechanical properties and strain energy

When a compatibilizer is added to a binary blend, it concentrates at the interface and induces chemical or physical interactions. These interactions reduce the interfacial tension between the rubber blend phases leading to formation of smaller dispersed phases. The size of dispersed phases decrease as the concentration of compatibilizer increases until the interface between the two phases is saturated. At this point an equilibrium particle size is observed. However, as the concentration of compatibilizer reaches its saturation point it can no longer act as an interfacial agent [27] - [29]. The mechanical properties, shown in Fig. 2, can be used to assess the compatibilizing action of GP for 50/50 SBR/EPDM blends. Comparing the mechanical properties of the K2 to that of K3-K6, containing 5, 7.5, 10 and 15phr GP, it is clear that the increase in the GP loadings in the rubber blends leads to an increase in the tensile strength (T.S) and modulus at 100% elongation (M@100%) properties. The increase in the T.S values may be attributed to the improvement of the interfacial bonding between SBR and EPDM rubbers in presence of GP. This in turns leads to an increase in the crosslink density in the SBR/EPDM rubber matrix which is ensured by the high M@100% values for SBR/GP/SBR compounds. Moreover, it is noticed from Fig. 2 the decrease in the elongation at break (E %) values of K3-K6. This again can be referred to the increase in the interfacial bonding between SBR and EPDM rubbers and consequently increase in the crosslink density which restricts the macromolecules stretching in the rubber matrix.

Another evidence for the acting role of GP as a compatibilizer for SBR/EPDM blend can be obtained by studying the strain energy of the rubber blends. According to eq. 2, the energy absorbed per unit volume (W) is expected to increase in deforming rubber blends. Therefore the higher the area under stress-strain curve, the higher the energy absorption capacity. It is clear from Fig. 3 that the strain energy of the SBR/EPDM blends containing different concentrations of GP, K3-K6, is higher than that of without GP, K0 and K2. This indicates that the compatibility of SBR/EPDM blends has been improved in presence of GP especially at 7.5 and 10 phr loadings.

Fig 2: The tensile strength, modulus at 100% elongation and elongation at break, %, of the different SBR/EPDM compounds.
Moreover, from Fig.s 1 and 2 it is worthy to note that the addition of HAF carbon black and paraffinic oil enhances the role of GP as a compatibilizer for SBR/EPDM blends. This can be observed on comparing the mechanical properties and strain energy of the sample control sample K0 to that of K1, K2 and K3 containing 5phr GP, HAF/paraffinic oil and GP/HAF/oil respectively.

Fig 3: Strain energy values (MJ/m³) of the different SBR/EPDM compounds.

C. Swelling measurements

The swelling measurements were used to determine the values of (1/Q), (Q_c/Q_g), molecular weight between cross-links (M_c) and crosslink density (\(\theta\)) for each composite. The effect of interaction between SBR/EPDM and the compatibilizer can be determined by the value (1/Q) as previously shown by Kranbuehl et al. [30]. Higher values of (Q_c/Q_g) lead to lower interaction between the compatibilizer and the rubber matrix. Comparing the 1/Q and Q_c/Q_g values of K1 and K3, Fig. 4, it is obvious that the presence of HAF and paraffinic oil in K3 (SBR/EPDM/5phr GP) tremendously increase the rubber-compatibilizer interaction and leads to an increase of the
crosslink density to nearly four times that of K1 (SBR/EPDM/GP) as shown in Fig. 5. This may be due to that the presence of the paraffinic oil and HAF facilitates the role of the compatibilizer in the formation of smaller dispersed rubber phases due the decrease of the interfacial tension between them. Meanwhile, as the GP content increases the \((1/Q)\) values increase and the \((Q_c/Q_g)\) decreases indicating stronger rubber compatibilizer interaction; in other words lead to formation of more crosslink’s.

Also, Fig. 5 illustrates the decrease of \(M_c\) values and the increase of cross-linking density \(\nu\) as the GP content increases in the compound. This is new evidence to the formation of additional physical and chemical crosslink’s as the compatibilizer acts as a bridge to bond the SBR/EPDM rubber chains within the matrix [31]. Thus, we can say that the GP can act as a compatibilizer for SBR/EPDM blends.

![Fig 5: The Molecular weight between cross-links \(M_c\) and crosslink density \(\nu\) of the different SBR/EPDM compounds.](image)

**D. Differential scanning calorimetry studies (DSC)**

![Fig 6: DSC graphs of SBR/EPDM blends: K0 (control sample); K1 (EPDM/SBR/5phr GP); K3 (EPDM/SBR/5phr GP/HAF/Oil); K7 (EPDM/SBR/15phr GP/HAF/Oil).](image)
DSC was used as an additional evidence to support proving the former assumptions. The thermal behavior of SBR/EPDM rubber blends with and without the compatibilizer was analyzed by DSC. Figure 6 shows the DSC traces of the samples. The glass transition temperature (Tg) was recorded as the half height of the corresponding heat capacity jump. It can clearly be seen that, for SBR/EPDM rubber blends without the compatibilizer K0 there are two distinct glass transitions, the lower glass transition is due to the SBR rubber phase (-53.48°C) while the higher is due to EPDM rubber phase (-37°C). On adding 5phr GP to SBR/EPDM blend (K1) and SBR/EPDM/HAF/oil (K3) only one Tg appears at -30.6 & -40°C respectively. These data illustrate that Tg of SBR/EPDM rubber blends become one glass transition upon incorporation of the GP. This indicates that GP improved and increased the miscibility between SBR and EPDM rubber due to the reduction of interfacial energy and the increase of interaction between rubber phases; which takes place by segmented interaction rather than polymeric interaction as previously stated [32] - [35]. At higher compatibilizer content, 15 phr, the Tg of the sample K7 is shifted to the large temperature (-9.5°C). These findings are in good agreement with Al Malaika et al. who reported that compatibility of polymers causes shift of their glass transition temperatures [36].

E. Scanning electron microscopy

![SEM graphs of different SBR/EPDM blends: K0 (control sample); K1 (EPDM/SBR/5phr GP); K3 (EPDM/SBR/5phr GP/ HAF/ Oil); K7 (EPDM/SBR/15phr GP/ HAF/ Oil).](image-url)
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