Int. J. Electrochem. Sci., 8 **(2013)** 5136 - 5152

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Corrosion Protective Coating Based on Alkyd Resins Derived from Recycled Poly (ethylene terephthalate) Waste for Carbon steel

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Received: 6 February 2013 / *Accepted:* 11 March 2013 / *Published:* 1 April 2013

The goal of this investigation is to obtain alkyd resins using recycled poly (ethylene terephthalate), PET, and different vegetable oils. Glycolysis of PET waste using pentaerytheritol (PEr) was used to produce suitable hydroxyl oligomers, GPEr, for alkyd resin. The glycolysis was carried out in the presence of manganese acetate as a catalyst and m-cresol as a solvent at 220 ^{o}C. Alkyd resins were prepared using phthalic anhydride, PET waste, glycerin, sunflower oil or linseed oil and ethylene glycol to produce PET-based alkyd resin. GPEr was used instead of PRT waste to produce the second type of alkyd resin based on GPEr. The reactions were carried out in the presence of butylhydroxytin oxide as a catalyst to prepare alkyd resins. The curing characteristics of the resins produced were investigated. Corrosion resistivity based on salt spray and cathodic disbondment were evaluated for the cured alkyd as organic coating for carbon steel.

Keywords: Alkyd resins, PET, vegetable oil, organic coatings, corrosion, cathodic disbondment.

1. INTRODUCTION

The post consumer poly (ethylene terephthalate) (PET) recycling represents one of the most successful and widespread examples of polymer recycling [1-3]. The main driving force responsible for this extremely increased recycling of post-consumer PET is its widespread use, particularly in the beverage industry. 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]. 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 [4-9].

Due to the wide use of coatings in different fields such as the automotive, shipbuilding and textile industries, it is important for companies to develop new coatings using in their composition alternative sources which decrease the final product costs. The coatings properties such as hardness, flexibility, abrasion resistance, alkali and adhesion resistance, are basically dependent on the resin which is used in its formulation, therefore, the alkyd resin plays a very important role in the coating formulation [10]. Post-consumer PET was used in alkyd resin synthesis for coatings, replacing a fraction of phthalic anhydride and ethylene glycol [11-14]. Alkyd resins were produced derived from reaction of depolymerizd PET oligomers with maleic anhydride, phthalic anhydride and propylene glycol to form unsaturated polyester resins. Simultaneous glycolysis and neutral hydrolysis of waste PET flakes were used for preparation of the alkyd resins [11]. Long oil alkyd resins were prepared from depolymerization product of the waste PET, glycerin, sunflower oil fatty acids and glycol [12]. These alkyd resins were blended with different ratios of a commercial urea–formaldehyde and melamine–formaldehyde mixture and heated at 140 oC and used as organic coating resins [2]. In the present work, the goal is aiming to obtain alkyd resins based on two types of post-consumer PET waste. In this respect, PET waste can be used directly in the alkyd resin formulation or after chemical modifications. Per was used to depolymerize PET waste. The aim of this work was to use PET and establish lower molecular weight oligomers, having high ratio of OH group that could be used as polyols in the preparation of alkyd resins to reduce the cost and to modify their adhesion properties as modified organic coats to protect carbon steel from different corrosive environments. The protective coating power of the cured alkyd resins was evaluated on specimens of carbon steel. The corrosion study includes two different aspects of corrosion tests, the comparison of the field tests in urban and marine environments with the laboratory accelerated tests carried out in sodium chloride solutions. Simultaneously, corrosion protection mechanism was suggested in this investigation.

2. EXPERIMENTAL

2.1. Materials

The PET utilized was collected from beverage bottles, which were cut into pieces of approximately 5mm2. It was then washed with acetone and dried at 100 ◦C for 8 h. The chemicals phthalic anhydride (PA), pentaerytheritol (PEr), lithium hydroxide (LiOH), m-cresol, ethylene glycol (EG) and butylhydroxytin oxide (Bu(OH)SnO) were obtained from Aldrich chemical Co. Linseed oil and sunflower oil were obtained from commercial sources and used without any further purification. Lead octoate, manganese octoate and cobalt octoate were purchased from Aldrich Chemical Co.

2.2. Techniques:

2.2.1. Production of Alkyd Resins from Glycolyzed PET

a. Preparation of GPEr

The reaction of PET with PEr was discussed in previous article [6]. Depolymerization of PET (1 mol) was performed with PEr (1.1 mol) using a conventional four-neck glass reactor, equipped with stirrer, thermometer, nitrogen inlet and reflux system using m-cresol as a solvent (total weight % of the reactants in m-cresol was 85 %). The reaction mixtures were heated at 170- 190°C for 4h and at 200-220°C for 3h. The reaction temperature was lowered at 100°C for 1h and then allowed to cool at room temperature. Purification was performed through extraction of depolymerized oligomers by hot water extraction. After completion of the glycolysis, the product was cooled to room temperature, dissolved in a suitable quantity of methylene chloride and shaken vigorously with an equal volume of 5% aqueous sodium chloride solution to remove any unreacted PEr and residual catalyst. The organic layer was collected and washed several times with water. The GPEr oligomer was characterized by acid value (AV) and hydroxyl value (HV) determinations.

b. Preparation of alkyd resins

Alkyds were prepared from 1 mol of PA, 1 mol of GPEr, 0.5 mol EG and 0.5 mol of sunflower or linseed oils. The K constant was 1.15 and the ratio of basic equivalents to acid equivalents was 1.2. The reaction was carried out in a round bottom flask equipping with a Dean–Stark piece, gas bubbler, contact thermometer and mechanical stirrer system. The temperature of the reaction was kept constant at 220–240 ◦C. The reactions were followed with acid value (AV). Condensation reaction was allowed to continue until the acid value of the resin was approximately 6– 7 mgKOH/g. The acid values were determined by titration of samples dissolved in ethanol–toluene with 0.1N KOH solution. After the reaction the resins were dissolved in xylene (60% solution).

2.2.2. Preparation of alkyd resin from PET waste:

a) Preparation of monoglycerides:

All reactions were carried out in a 500mL four-necked glass reactor, equipped with mechanical stirring, a reflux condenser and a nitrogen inlet. The reaction temperature was maintained using a Pt 100 thermocouple connected to a temperature controller. Considering the nature of reagents two synthetic routes were used, one for vegetable oil as described previous [13]. In a typical reaction using vegetable oil: the oil (97.34 g, 51.26%) and lithium hydroxide (0.89 g, 0.5%) were initially put in the reactor. The temperature was then increased to 235 ◦C, and finally the PEr (15.91 g, 8.38%), was added. The mixture was heated to 240 ◦C and maintained for 1 h. The extent of alcoholysis was followed by checking the solubility of the reaction mixture in methanol (ME test) and concluded when ME was bigger than 300%.

b) Preparation of alkyd resins:

When the alcoholysis step was concluded the Bu(OH)Sn (0.93 g, 0.49%), flakes of post-consumer PET (26.85 g, 14.14%), PA (42.50 g, 22.38%) and EG (5.41 g, 2.85%) were put in the reactor, then the mixture was maintained at 240 ◦C, and samples were taken at 20 min intervals to evaluate the acid value and to follow the polyesterification reaction until it achieved the desired acid value (AV< 18mg KOH/g of resin).

2.3. Resin Characterization:

AV and HV (mg KOH/g) were determined from the conventional titration procedure [4]. HV was determined by acetylation of samples dissolved in pyridine by acetic anhydride, followed by back titration of excess reagent with 1N NaOH solution. AV was determined by titration of samples dissolved in pyridine with 0.1N KOH solution. The number average molecular weight, Mn (g/mol) value of depolymerization product was calculated from HV and AV by the known formula of end group analysis method. The Mn value is calculated from Eq. (1):

$$Mn= [(2x56.1x1000)/(HV+AV)] \quad (1)$$

The molecular weight was measured by GPC (Waters model 510) using THF (HPLC grade) as eluent and Ultrastyragel 500; 1000; 10,000; 100,000 °A as column.

The structure of the oligomers was investigated by an infrared Bruker IFS 66 FT-IR Spectrometer.

^{1}HNMR Spectra were recorded on a Varian EM 360 spectrometer in deutrated chloroform (CDCl3) with 1% tetramethylsilane (TMS) as internal solvent.

Viscosity measurement was carried out using a standard method ASTM D 1545-89.

To evaluate the drying time, alkyd resins were applied to a glass substrate, with a film thickness of 100 Nm. For this test, the sample was prepared adding 60% in weight of xylene and the drying catalysts in the following quantities lead octoate (0.43%); manganese octoate (0.35%) and cobalt octoate (0.28%). Films were dried at 25±1 ◦C for 72 h. Drying time was determined by an Ericsen 415/E apparatus, which gave results according to DIN 53150.

2.4. Testing of the coatings:

For alkyd tests, 60% solutions of the resins in xylene the drying catalysts (lead octoate (0.43%); manganese octoate (0.35%) and cobalt octoate (0.28%) based on non-volatile) and 20 Wt% of TiO2 powder were mixed and applied with total dry film thickness (DFT) of 100 Nms. It is common to use mild steel panels (15 cm×l0 cm) to evaluate the different properties of coatings. The other side of panels is coated and protected against corrosion environments by using coal tar epoxy primer. The tested side was blasted and cleaned to apply the coated materials. Then the panels were subjected to different testing procedure to evaluate their mechanical properties and their durability. Adhesion strength (pull-off), pencil hardness, impact, T-bend, hot water, acid and alkali resistance and solvent resistance tests were measured according to ASTM methods as reported in the previous studies [4-9]. The coated panels were evaluated for salt-spray resistance in accordance with ASTM B117. The test conditions were 35 (±1.5) ◦C, 95±5% relative humidity, and 5 wt.% of aqueous sodium chloride solution. The acid and alkali resistances of coated panels were determined after immersion in 10% of HCl and 5% of NaOH aqueous solutions using distilled water. The duration of the test was 90 days at 38 ◦C. The degree of adhesion and visual inspection of blister and cracks were evaluated for the coated panels.

The degree of coating to resistance cathodic disbondment (CD) was tested in accordance with ASTM G 8. The coating panel was subjected to a potential of – 1.5 V in a 3% NaCl electrolyte solution at 65 o C for 48 hrs.

3. RESULTS AND DISCUSSION

PET has acquired an increasing use as valuable grade products and as recycled materials. Scraps from PET bottles and films can be used directly or after recycled at temperature above 200°C. The appropriate conditions for the preparation of oligoester polyols by glycolysis of PET using PEr were previously investigated [6]. All the depolymerization product of PET was carried out in the nitrogen atmosphere and in the presence of 0.5% Mn-acetate as trans-esterification catalyst at reaction time 8 hrs. The glycolysis of PET with PEr was carried out at a reaction temperature not more than 220oC. This can be attributed to the formation of alicyclic derivatives between hydroxyl groups of produced polyhydroxy glycolyzed PET [6]. Xylene and m-cresol were used to provide good miscibility to the reactants especially at high PEr and PET contents. Accordingly, the glycolysis reaction in the present work was conducted using 1 mol % of PET to 1 mol % of PEr droplets dispersed in xylene to produce GPEr. The oligoester obtained as WIF was used to determine the hydroxyl number of the produced GPEr oligomers. Based on the obtained value of the hydroxyl number after removing the free glycol (114 mg KOH/g), the amount of glycol consumed in producing oligomer is 30% of PEr. The hydroxyl number after removing the free glycol indicates that the extent of depolymerization was considerable and that the resulting oligomers were mostly terminated with hydroxyl groups. The number of reacted molecules of PEr (n) was calculated from the number of moles of the reacted PEr divided by the number of moles of PET. Thus, for the oligomer samples reacted for 8 h, 100 g of PET (=1.58 mmol) would have reacted with 20 g of PEr (=104 mmol) and the molecular weight should have been lowered to $(63{,}200/(1 + 104/1.58) = 960$ g mol^{-1}. The GPC data of number and weight average molecular weights and polydispersity for the different oligomers were determined as 985 g/mol, 1150 g mol^{-1} and 1.16, respectively.

The structure of WIF of GPEr oligomer was also investigated through ^{1}HNMR spectroscopy that represented in Figure 1 for glycolyzed PET with PEr. In this respect, two peaks having the same protons number were used to compare their integration values. In the present work, integrations of CH_2 protons attached to OH group of PEr were compared to integration of CH_2 protons attached PET. It is found that peak integration at σ =4.4ppm (assigned to one methylene protons of ethylene glycol of PET) is 15.96 where that at σ = 4.18 ppm (assigned to methylene group of ethyl moiety of PEr) is 7.76. The data indicated that, PEr is found mainly at chain ends and approximately 30 mol %. The produced oligomers having high OHV and branching are good polyols for alkyd systems that cure quickly to form strong rigid alkyd resins.

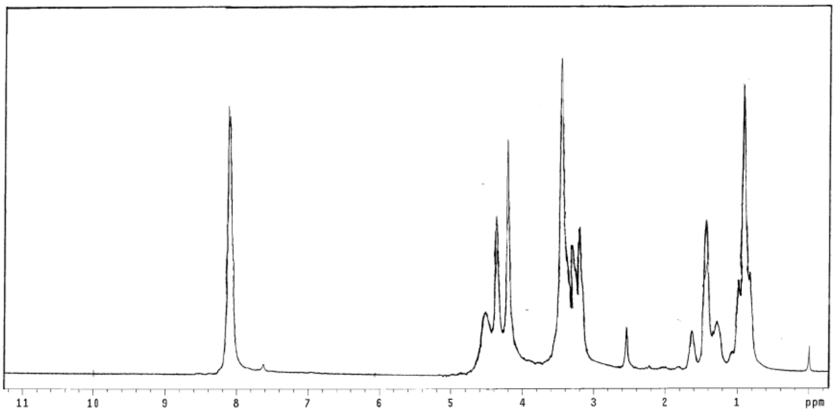


Figure 1. ^{1}HNMR Spectrum of Glycolized PET with PEr at Mol Ratios 1.

3.1. Preparation of Alkyd Resin from Vegetable Oil and PET Waste:

Alkyd resins were synthesized using different vegetable oils and catalysts with the incorporation of post-consumer PET. The properties of the products obtained are directly related with the nature of the vegetable oils, the choice of the reagents and their proportions. The oils can be drying, semidrying and non-drying. The differences among them are in the concentration and distribution of the fatty acids in the oil. In the drying oils, the fatty acids with three double bonds predominate. In nondrying or semi-drying oils the fatty acids with one or two double bonds predominate [15 -16]. The drying oil (linseed) and semi-drying oil (sunflower, tall oil) were used. The alkyd resins can be classified in three groups depending on the oil content: short in oil (<45%), medium in oil (45–55%) and long in oil (>55%). The lower the oil content the greater the possible incorporation of post-consumer PET enabling the removal and recycling of PET in larger quantities [15-16]. In this work we have synthesized resins with medium length in oil.

Table 1. Composition of the Alkyd Resins.

Type of Oils	Oil %	PET %	PEr %	EG %	PA%	butylhydroxytin oxide % (Bu(OH)SnO),
Sunflower	51.07	14.16	8.43	3.00	22.40	0.48
Linseed	51.08	14.17	8.43	2.96	22.42	0.47

The composition of alkyd resin was listed in Table 1. As polybasic acids were used phthalic anhydride and post consumer PET depolymerized in situ. The polymerization reactions were followed by the acid value values, which was measured until a value smaller than 18 was reached. The catalyst butylhydroxytin oxide probably promotes both the depolymerization of post-consumer PET. The preparation of alkyd resins from monoglyceride drying oil in the presence of PET and GPEr was represented in Schemes 1 and 2, respectively. The polyesterification reaction and the insertion of terephthalic acid originated from post-consumer PET were evidenced by infrared analysis. The obtained spectra for all the vegetable oils and alkyd resins were quite similar, so, the spectra of soybean oil and the alkyd resin obtained with this oil were chosen to demonstrate the band attributions and are shown in Figure 2 spectra (a and b), respectively. The disappearance of the broad band between 3500 and 2500 cm^{-1}, O-H stretching of the carboxylic acids, and appearance of new strong band at 1754 cm^{-1}, which refers to C =O stretching of ester, indicated the polyesterification reaction. The appearing of a strong band in 1091 cm^{-1} indicates the incorporation of the post-consumer PET in the product [17].

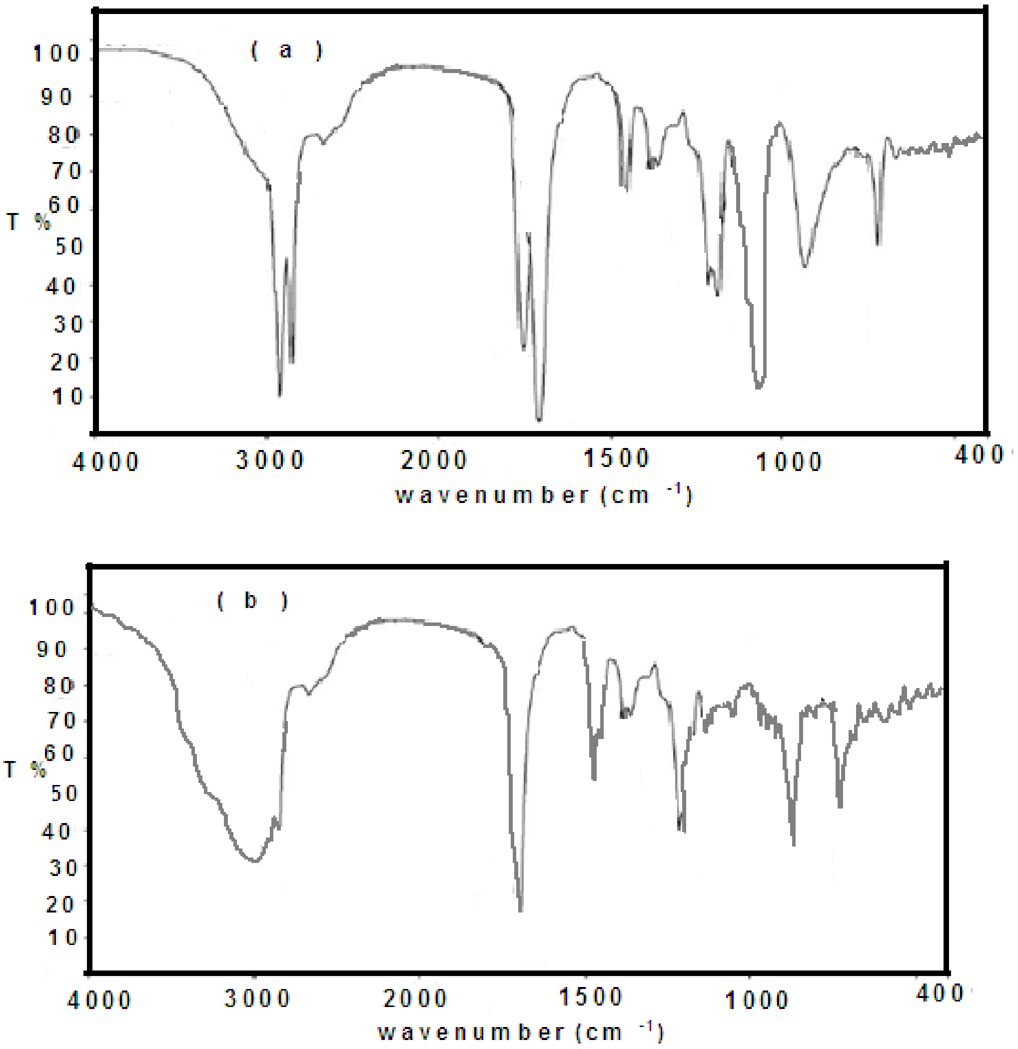
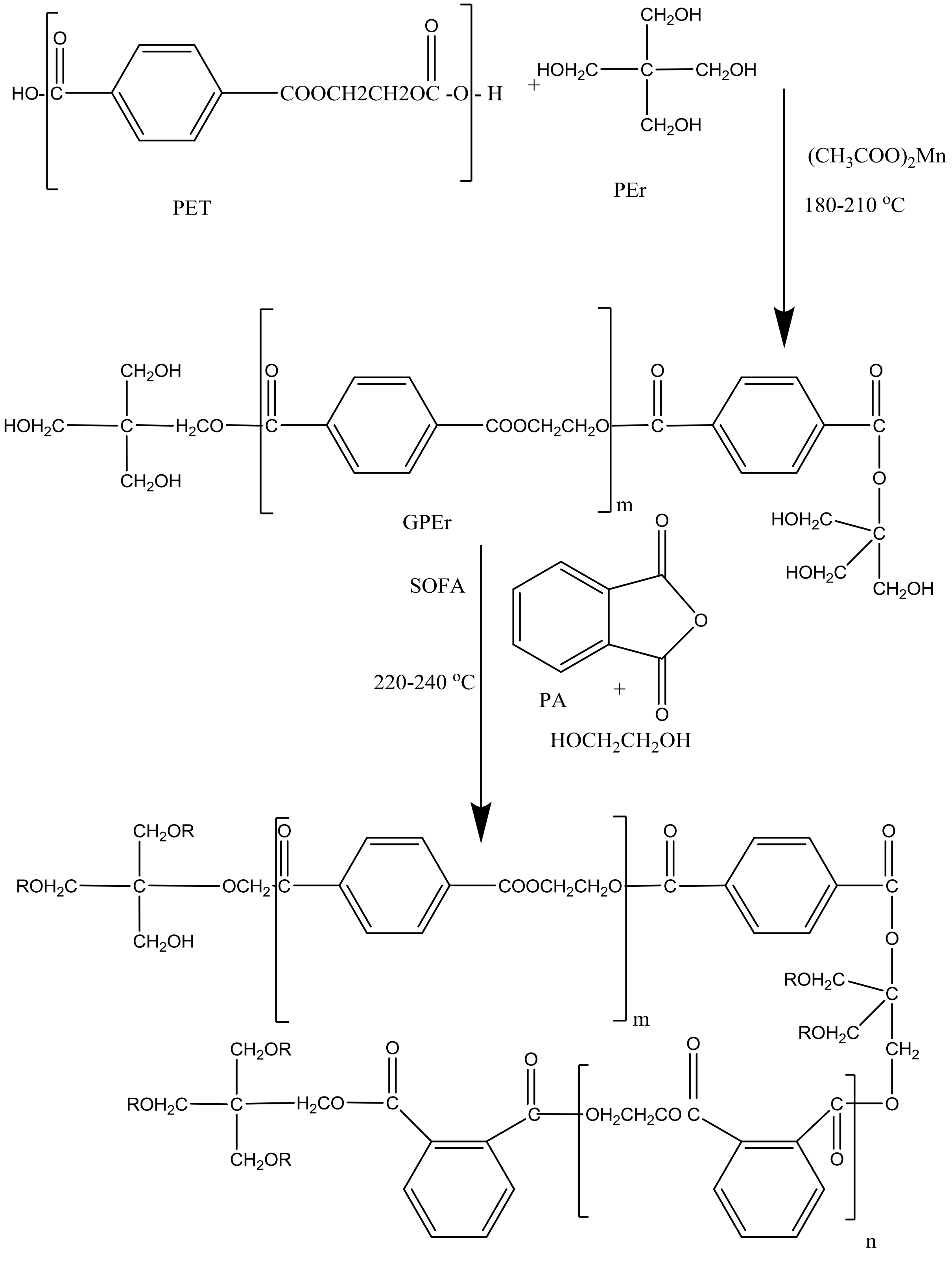
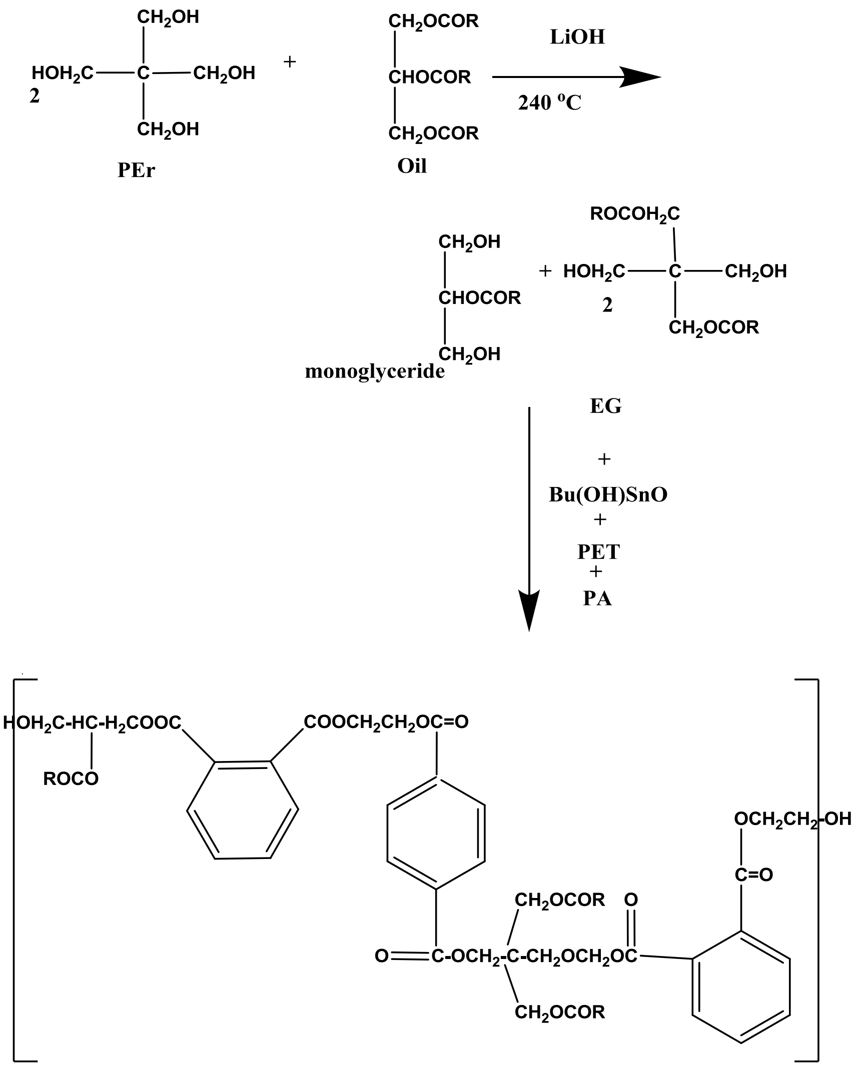


Figure 2. FTIR spectra of (a) alkyd resins based on GPEr and b) Sunflower fatty acid.



R= SOFA ester

Scheme 1. Preparation of Alkyd Resins from GPEr Oligomer and SOFA



R= unsaturated fatty acid group

Scheme 2. Alkyd resins based on PET and monoglycride of vegitable oils.

The physicochemical properties such as viscosity, AV and Grender colors of the prepared alkyd resins were evaluated and listed in Table 2.

Table 2. Physico-chemical Characteristics of Alkyd Resins Based on PET Waste.

Designation	Viscosity		Acid value mg KOH/g	Color Gardner
	Gardner @25 °C	C Poise @25 °C		
Sunflower oil /PET	Y-Z/55%	2000	6.8	5
Sunflower / GPEr	M/55%	1200	6.3	6
linseed oil /PET	Approx.Z	2200	6.2	8
Linseed / GPEr	Z1	2400	7.3	8

As it can be seen from Table 2 the obtained alkyd resins have the same viscosity value of the resin obtained in the literature [18]. It is evidenced from the results presented in Table 2 that the presence of post-consumer PET increased the resin viscosity. When we utilized sunflower oil the obtained viscosity presented a small value than that obtained with linseed oil.

3.2. Curing of Alkyd Resins:

The alkyd resins are long chain polyester polymers containing a number of reactive double bonds. Lead octoate (0.43%), manganese octoate (0.35%) and cobalt octoate (0.28%) were used to form crosslinked alkyd networks. The curing exotherms were determined at temperature of 45 ^{o}C. The maximum heat evolved, T_{max}, upon curing and time required for complete curing, t_{max}, were determined as described in the previous works [19-20] and listed in Table 3.

Table 3. Physico-chemical Characteristics of Alkyd Resins Based on PET Waste.

Designation	Hardener (Wt%)	t_{max} (minute)	T_{max} (^{o}C)	Drying time (hrs)
Sunflower oil /PET	lead octoate (0.43%) manganese octoate (0.35%) cobalt octoate (0.28%).	260	55	8
Sunflower / GPEr		240	60	7
linseed oil /PET		210	68	6
Linseed / GPEr		200	70	5

It is well known that the alkyd resins of lower molecular weight are cured more easily than alkyd of higher molecular weight. Further reaction of the remained double bond of higher molecular weight alkyd may be buried in the microgel particles of alkyd and may lead to increases values of t_{max} and decreases T_{max} values. The oil content or length of oil is one important variable to be investigated in the study of alkyd resin formulation. The progressive decrease of the oil or fatty acid content corresponds proportionally to an increase of the three dimensional polymer. The reduced level of oil in the resin produces a polymer with an increased hardness and viscosity, lower elasticity, solubility and adherence. Determination of drying time of the resins is estimated by adherence or non-adherence of paper or glass beads. There are seven drying stages of this method, and the maximum drying degree is 7. Stage 1 is determined with glass beads and the remaining stages are determined with disks of typewriter paper (loads range from 5 to 5000 g/cm^2). The glass beads are allowed to remain on the film for 10 s, and the loads on the disks remain for 60 s. The drying time of the resins were evaluated and as depicted in Table 3 the resin with linseed oil presented the smallest time to be tack free (5 hrs) while the resin with sunflower was tack free in an intermediate time (7 hrs). These results confirm the influence of the oil in the drying properties of the resin. The influence of the reaction parameters is being studied aiming the augment of the post consumer PET content in the alkyd resin.

3.3. Testing of Alkyd Resins as Organic Coatings:

The produced alkyd resins were applied on carbon steel as described in the experimental section. The applied films were completely cured for 7 days at room temperature. The mechanical properties such as impact resistance, adhesion resistance, abrasion resistance, bending test and pencil hardness test were evaluated. The data of mechanical properties of the cured alkyd films were measured and listed in Table 4.

Table 4. Mechanical Properties of Alkyd Resins Based on PET Waste.

Designation	Hardener (Wt%)	Impact resistance J/mm	Pull- off resistance MPa	Abrasion resistance g/1000 cycle	Pencil hardness	Bending test
Sunflower oil /PET	lead octoate (0.43%) manganese octoate (0.35%) cobalt octoate (0.28%).	10	18	0.030	H	pass
Sunflower / GPEr		15	25	0.010	H	pass
linseed oil /PET		6	7	0.100	HB	pass
Linseed / GPEr		7	10	0.110	H	pass

The percentages of the adhesion strength of the alkyd resin films are 100%. The data reported on adhesions (pull-off) indicate that all cured alkyd resins based on sunflower oil have superior adhesion properties with steel than other cured resins. This can be attributed to the formation of uniform homogeneous network of resins and presence of terminal hydroxyl groups which increased the adhesion with steel. The data indicated that the alkyd resins based on sunflower oil and PET possess good mechanical properties. These behaviors indicate that the ratios of crosslink density affect the mechanical properties of coatings. This behavior leads to speculate that the high cross-linking density networks decreases the mechanical properties of the formed network. The variation of hardness results (by pencil test) from soft (minimum cross-links) to hard coatings (maximum cross-link density) indicates that the best results are determined at sunflower-PET systems. This can be attributed to lower molecular weight of alkyd influences the ultimate cross-link density and increases molecular mobility resulting in higher cross-link density. This can be attributed to increasing numbers of double bonds and hence this facilitates the curing of double bonds embedded in the three dimensional network. This observation can be attributed to the increased content of curable double bonds, thus greatly increasing the cross-link density [21].

Abrasion resistance of the cured alkyd coatings was tested by the Taber braser (ASTM- D 4060 – 95). The data of abrasion resistance of the cured alky resins were measured and listed in Table 4. The data indicated that there is no significant difference between the abrasion resistance values of the films. It was also noted that the chemical structures of the cured alkyd resins affected the impact of coatings films. It was observed the deformation of coating films of alkyd which based on PA more than that based on PET. Moreover, the films were deformed when linseed oil was used instead of sunflower oil in preparation of alkyd resins. These behaviors indicate that the ratios of cross-linking agent affect the mechanical properties of coatings. This behavior leads to speculate that the high cross-linking density networks decreases the mechanical properties of the formed network. The variation of hardness results (by pencil test) from soft (minimum cross-links) to hard coatings (maximum cross-link density) indicates that the best results are determined for cured alkyd based on PET. The presence of more terephthalate repeating units between the cross-links results in the existence of harder domains and better separation between the cross-links in the packed cross-linked structure and as a result the mechanical properties are improved [22].

The chemical resistances of the cured resins were evaluated through hot water, solvents (MEK rub test), acid and alkali resistance measurements. The data of chemical resistance of the cured alkyd films were measured and listed in Table 5.

Table 5. Coating characteristics of cured alkyd resins based on PET.

Designation	Hardener (Wt%)	MEK (rub test)	Alkali Resistance (days)	Acid resistance (days)	Hot water immersion
Sunflower oil /PET	lead octoate (0.43%) manganese octoate (0.35%) cobalt octoate (0.28%).	Pass	75	80	Pass
Sunflower / GPEr		Pass	90	90	Pass
linseed oil /PET		Pass	70	80	Pass
Linseed / GPEr		Pass	90	90	Pass

The use of polar solvents such as ketone is often used to assess the degree of cure of a cross-linked composition for solvent resistance, methyl ethyl ketone (MEK) or acetone is recommended. In addition to immersion testing, solvent resistance may be assessed by a solvent rub test. In this respect, MEK has used to determine the degree of curing of the present coating systems by both immersion and rub methods. The failure of tests was determined either by disruption or dissolution of the coating films from panels. The higher the degree of crosslinking indicates the less free volume and segmental mobility remain available in the polymer. So that solvent molecules can hardly penetrate the cross-linked network at all. In this respect, it was found that the all prepared alkyd resins have good solvent resistance. The high solvent resistance of the cured alkyd systems based on PET indicates the xylene solvent is not trapped in the cured system. The effect of hot water immersion (24 hrs) was determined; the films were not affected by the water after 24 hrs. Both of the PET-based resins and PA resins have the same water resistance values. The acid and alkali resistances of coated panels were determined after immersion in 10% of HCl and 5% of NaOH aqueous solutions using distilled water. The duration of the test was 90 days at 38 ◦C. The degree of adhesion and visual inspection of blister and cracks were evaluated for the coated steel panels. The data indicate that the cured alkyd resins based on GPEr of PET have excellent chemical resistances as organic coatings among other cured resins. The data of acid and alkali chemical resistance for cured alkyd resins indicates that these networks possess high resistance to alkaline and acidic aqueous solutions, although they have ester groups. The high alkaline and acidic resistance can be referred to high cross-link density of networks. This can be attributed to high cross-link density of network decreases their exposure to environment [23]. This can be referred to decrease of crosslink density of network and increase the attack of ester groups of network to acidic and alkaline solutions.

3.4. Testing corrosion resistance of coating

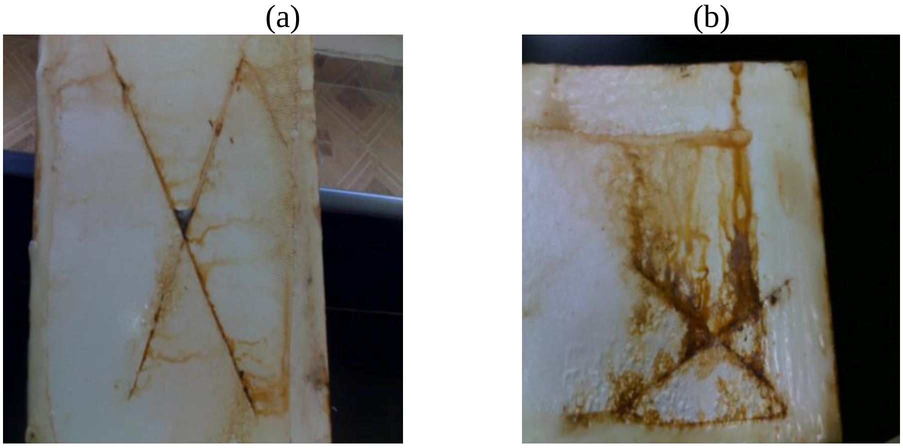


Figure 3. Salt spray resistance of a) a) Sunflower/PET and b) linseed/PET coatings after 750 Hrs.

In the present work, the continuous salt spray and cathodic disbondment tests were used, as described in method section, to study the effect of salts on the properties of coating films. The data of salt spray were measured and listed in Table 6. The salt spray test was stopped when the films show poor adhesion. The photos of cured alkyd based on sunflower oil were selected to show salt spray tests results and represented in Figure 3. The results salt spray indicated the strong adhesion of alkyd coatings and steel substrate show good results.

Table 6. Salt spray and cathodic disbondment resistances of cured alkyd resins.

Designation	Hardner (Wt%)	Cathodic Disbanding radius (mm)	Salt spray resistance		
			Exposure time (h)	Disbanded area (%)	ASTM rating
Sunflower oil /PET	lead octoate (0.43%) manganese octoate (0.35%) cobalt octoate (0.28%).	10	646	2.9	7.7
Sunflower / GPEr		5	750	2	8
linseed oil /PET		10	500	2	8
Linseed / GPEr		10	500	4.4	7

This was observed from the improvement in coating performance of alkyd based sunflower and PET after 750 h of exposure to the salt spray environment. Coating performance was consistently improved for each exposure time for coatings. This can be attributed to relationships between coating properties and performance. In this respect, the adhesion of substrate with coat is the main problem for coating failure. Strong adhesion also prevents moisture vapor from passing through the coating and condensing in a poor area of adhesion, leading to a blistering of coating. This is of particular significance when it comes to the choice of suitable coating systems. In our systems, it was observed that increasing of hydroxyl contents of cured alkyd resins increases the adhesion of coat with steel. It has been shown that the concentration of resultant hydroxyl group has a deleterious effect on the adhesion of the alkyd coating to the steel metal.

The high salt spray resistance of cured alkyd resins can be attributed to the PA of PET that has high resistance to osmosis and electroendosmosis by comparing to aliphatic [24]. Buried steel are often protected from corrosion by applying cathodic protection (CP) using an impressed current. Cathodic disbondment (CD) is one of the main failure processes for organic coatings on steel structures under CP, and may lead to loss of corrosion protection for the metal substrate. CD may be defined as the loss of adhesion between a protective coating and the metal substrate. This was refereed to generation of hydroxyl ions formed from oxygen reduction due to a cathodic potential on the metal substrate [25]. Cathodic delamination is one of the major modes of failure for anticorrosive coatings subjected to a physical damage and immersed in seawater. The corrosion process involves an anodic reaction in which solid iron is transformed into ferrous irons and a cathodic reaction, which involves electrochemical reduction of oxygen. The cathodic activity underneath the coating results in a so called cathodic delamination, i.e., weakening of the adhesion between the coating and the steel surface. The cause of cathodic delamination has been reported to be the result of a chemical attack at the coating–steel interface by free radicals and peroxides formed as intermediates in the cathodic reaction during the corrosion process [26]. Substrates with inadequately applied or physically damaged coatings may experience corrosion around the defect regions because the presence of water, oxygen, and ions will promote the electrochemical reactions at the electrolyte-coating–steel interface. The mechanism of cathodic delamination is not completely understood at the microscopic level, but it is recognized that there are three possible modes of failure. These are (i) dissolution of the oxide film in the local alkaline environment which is formed, (ii) degradation of the polymer in the local alkaline environment, and (iii) loss of adhesion at the organic coating/oxide-coated metal interface [27, 28]. That is, the failure can occur within the oxide, within the polymer, or at the oxide/polymer interface, respectively. The data of CD were determined and listed in Table 6. The CD test was measured at 65^{o}C for 48 hrs. The photos of cured alkyd based on sunflower oil were selected to show CD tests results and represented in Figure 4.

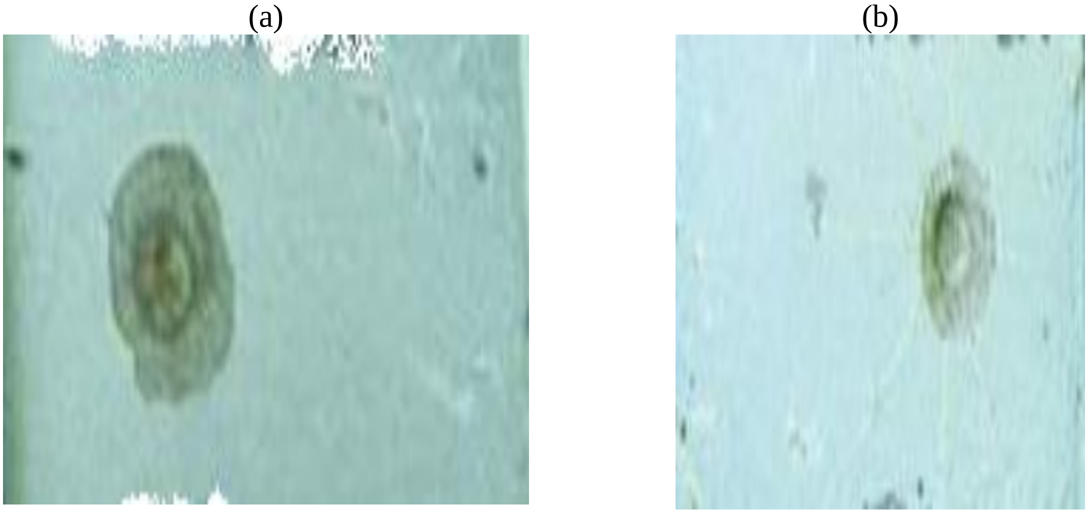


Figure 4. Cathodic disbondment of a) linseed/PET and b) Sunflower/PET coatings at 65 ^{o}C after 48 Hrs.

The CD data indicated that, the good adhered alkyd coatings with steel substrate provided resistance to cathodic disbondment. Generally, for good adhesion of organic coatings to steel, conditions are required which permit oxidation of the organic coatings [29]. It was suggested that, introducing polar functional groups improves the CD performance of organic coatings [30, 31]. This was attributed to the formation of dipole-dipole interaction between polar groups of organic coatings and metal oxide of steel substrate. Indeed, there is a slight decrease in CD resistance for higher loadings of polar groups due to the possibility of degradation of the polar moieties in the presence of alkali generated during CD reactions. This result, therefore, varies our hypothesis that the introduction of amount of functionalized ester groups does improve CD performance. Essentially these types of alkyd materials can be used in petroleum pipeline, tanker, salt barges and ships, general chemical tankers, as well as exterior coatings for the bottoms, boot-topping and decks.

4. CONCLUSIONS

Corrosion resistance of carbon steel was evaluated using as protective coatings with two different alkyd resins modified conveniently with GPEr and PET. All coatings were characterized by the usual techniques, as spectroscopy and viscosity measurements. The more important conclusions derived from the obtained results in this work are :

1. The data reported on adhesions (pull-off) indicate that all cured alkyd resins based on sunflower oil and GPEr have superior adhesion properties with steel than other cured resins. This can be attributed to the formation of uniform homogeneous network of resins and presence of terminal hydroxyl groups which increased the adhesion with steel.
2. .The data indicated that the alkyd resins based on sunflower oil and GPEr possess good mechanical properties. These behaviors indicate that the ratios of crosslink density affect the mechanical properties of coatings.
3. The data indicate that the cured alkyd resins based on GPEr have excellent chemical resistances as organic coatings among other cured resins. The high alkaline and acidic resistance can be referred to high cross-link density of networks. This can be attributed to high cross-link density of network decreases their exposure to environment.
4. The results salt spray and cathodic disbondment indicated the strong adhesion of alkyd coatings based on PET and steel substrate show good results.

ACKNOWLEDGMENT

The project was supported by the US-Egypt Joint Science & Technology Fund (Contract/Agreement No.: 355), Academy of Scientific Research and Technology, Egypt.

References

1. T.M. Coelho, R. Castro, J.A. Gobbo Jr. *Conserv. Recycl.* 55 (2011) 291–299.
2. A. Torlakoglu, G. Guclu, Waste Management 29 (2009) 350–354.
3. E.S. Barboza, D.R. Lopez, S.C. Amico, C.A. Ferreira, *Conserv. Recycl.* 53 (2009) 122–128.
4. A. A. Abdel-Azim, Ayman M. Atta, *Polym. J.* 29 (1998)21.
5. A. M. Atta, *Prog. in Rubber, plastics and Recycl. Technol.* 19 (2003) 17.
6. A.A. Abdel Azim, A.M. Atta, R.A El-Ghazawy, *Cellular polym.* 25 (2006) 35.
7. A.M. Atta, Manar E. Abdel-Raouf, S. M. Elsaeed, A. A. Abdel-Azim, *Prog. Org. Coat.* 55, (2006) 50.
8. A. M. Atta, Ahmed F. El-Kafrawy, M. H. Aly, A.A. Abdel-Azim, *Prog. Org. Coat.* 58(1) (2007) 13.
9. A. M. Atta, M. A. Elsockary, O. F. Kandil, N. O. Shaker, J. *Disp. Sci. Technol*. 29, (2008) 27.
10. T.C. Patton, *Alkyd Resin Technology*. John Wiley and Sons, New York, USA. Stuart, B.H., (2002) 43-98.
11. G. P. Karayannidis, D. S. Achilias, I.D. Sideridou, D. N. Bikiaris, European *Polym. J.* 41 (2005) 201.
12. G. Guclu, M. Orbay, *Prog. Org. Coat.* 65 (2009) 362.
13. J. Dullius, C. Ruecker, V. Oliveira, R. Ligabue, S. Einloft, *Prog. Org. Coat.* 57 (2006) 123.
14. C.O. Akintayo, K.O. Adebowale, *Prog. Org. Coat.* 50 (2004) 138–143.
15. G. Byrnes, *J. Prot. Coat Linings* 73 (1996) 54.
16. A.I. Aigbodion, F.E. Okieimen, *Ind. Crop. Prod.* 13 (2001) 29.
17. N. Dutta, N. Karak, S.K. Dolui, *Prog. Org. Coat*. 49 (2004) 146.
18. C. Kawamura, K. Ito, R. Nishida, I. Yoshihara, N. Numa, *Prog. Org. Coat.* 45 (2002) 185.
19. A.M. Atta, R. Mansour, M.I. Abdou, A.M. Sayed, *J.Polym. Adv. Technol.* 15 (9) (2004) 514.
20. A.M. Atta, R. Mansour, M.I. Abdou, A.M. Sayed, *J. Polym. Res.* 12 .127 (2005)

21. A.M. Atta, A.M. Elsaeed, R.K. Farag, S.M. El-Saeed, *React. Funct Polym*. 67 (2007) 549–563.
22. M.E. Kelly, in: P.E. Bruins (Ed.), Unsaturated Polyester Technology, Gordon and Breach, New York (1976) p. 343.
23. P.K.T. Oldring (Ed.), Chemistry and Application of Phenolic Resins or Phenoplasts, Wiley ISITA, London, 1998.
24. D.A. Meldrum, C.T. Lin, *J. Coat. Tec*hnol. 65 (818) (1993) 47.
25. J.F.Watts, in handbook of adhesion, Edn. by Packham DE, Longman Group, New York (1992) 67-68.
26. P. A. Sørensen, C. E. Weinell, K. Dam-Johansen, S. Kiil, *J. Coat. Technol. Res.* 7 (2010) 773–786.,
27. J. F. Watts. *J. Adhesion* 31 (1989) 73.
28. H. Leidheiser, Jr., *Corrosion* 38 (1982) 374.
29. K. Bright, B.W. Malpass, D.E. Packham, *Br Polym J.* 3 (1971)205.
30. D. Roy, G.P. Simon, M. Forsyth, *Polym Int.* 50 (2001)1115.
31. A. J. Kinloch, C. F. Korenberg, K. T. Tan, J. F. *Watts Mater Sci.* 42 (2007) 6353.