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New Imidazolium Ionic Liquids from Recycled Polyethylene Terephthalate Waste for Curing Epoxy Resins as Organic Coatings of Steel

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Abstract: Imidazolium ionic liquid (IIL) was prepared from aminolysis of polyethylene terephthalate (PET) waste with pentaethylenehexamine (PEHA) to apply as hardener of epoxy resin. Its purified chemical structures, thermal stability, and thermal characteristics were identified as well as amino phthalamide aminolyzed products. The thermal, thermomechanical, and mechanical properties of the cured epoxy resins with different weight percentages of IIL were investigated to optimize the best weight ratio to obtain homogeneous networks. The adhesion, durability, and corrosion resistance of the cured epoxy resins on the steel surfaces were tested to confirm that the best weight ratio of epoxy: IL was 2:1. This ratio achieved higher adhesion strength and salt spray resistance to seawater extended to 1500 h.

Keywords: imidazolium ionic liquid; epoxy; curing; PET waste; dynamic mechanical; thermal

1. Introduction

Curing of epoxy resins with different hardeners plays an important factor in their industrial coating and adhesive applications in the aggressive environments [1,2]. There are two types of hardeners based on polyamides and polyamines are widely used in the epoxy coatings [1]. The adhesion strengths and mechanical properties of the cured epoxy are affected by the curing exothermic rate, temperature, and heat released during the curing process [3]. The higher curing rate and heat evolved during the curing of epoxy with polyamine hardeners produce cracks and holes, which reduce the mechanical and anticorrosive performances of epoxy resins [4–7]. Recently, the stability of hardener or curing agents for different storage conditions was developed to pack with epoxy resins as latent curing agent [8,9]. There are many types of advanced materials widely used as epoxy curing activators and promoters to control the curing of epoxy [10–12]. Ionic liquids (IL) based on imidazolium cation as thermos-latent initiator are used to control and promote the curing of epoxy resins [13–17]. In previous works [18–20], the curing of epoxy resins with polyamine hardeners were improved by using epoxy or amine modified additives that were chemically linked with epoxy matrix. The objective of the present work is directed to prepare polyamine-amide hardener having imidazolium IL from polyethylene terephthalate (PET) waste to use as effective curing agent for epoxy resin.

PET is widely used thermoplastic that generates tones of wastes that may otherwise disrupt the balance of ecosystem due to its non-biodegradation in the environment. The chemical recycling of PET to useful materials is an accepted technique among recycling methods (mechanical, thermal, and chemical) that follows the rules of sustainable developments [21]. There are different chemical depolymerization methods used for PET chain scission, such as methanolysis, glycolysis, hydrolysis, ammonolysis, aminolysis, and hydrogenation, which are based on the types of chemical reagents [22].

Two-pack epoxy coatings are prepared from glycolysis and aminolysis of PET and produce a dense coating with an excellent corrosion resistance [23–26]. Aminolysis of PET yields diamides or amido amine of terephthalic acid that are produced by several techniques and can be used as curing agents for epoxy resins [22]. PET aminolysis products as epoxy curing agents is still an expanding area that reported few works have been focused to apply as epoxy organic coatings [27,28]. It was previously reported that the aminolysis of PET with cycloaliphatic amines is advantageous in modifying slower curing for epoxy systems [27]. In this respect, the present work aims to produce for the first time polyamine amide imidazolium acetate ionic liquid (PAIIL) from aminolysis of PET waste with pentaethylenehexamine (PEHA) to alleviate the environmental pollution from PET waste. Moreover, the using different molar ratios of PAIIL as curing agent to prepare crosslinked epoxy coatings at low temperature is another objective of the present work. In this respect, the thermal, mechanical, adhesion, and anticorrosion performances of the cured epoxy with PAIIL were investigated to optimize their using as organic coating for steel.

2. Experimental

2.1. Materials

All chemicals used in this work were purchased from Sigma Aldrich chemicals Co. except polyethylene terephthalate (PET) waste that was collected from beverage drinking water bottles. The bottle label and other polymers contaminate were removed and PET wastes were cut into small pieces 1 mm^2, washed with water and soap, and dried. Pentaethylenehexamine (PEHA), sodium acetate, glyoxal (GO), and acetic acid were used to depolymerize PET waste. Epikote epoxy resin 828 (based on bisphenol A diglycidyl ether; DGEB) with epoxy equivalent weight 190–200 g/eq. (Hexion, Olana, Italy) was used as epoxy resin to apply as coatings for steel. Carbon steel alloy panels were cleaned by washing with xylene, ethanol, water, and soap, and dried. The surface of cleaned steel was blasted with blasting machine to obtain clean and rough surface (35–50 μm).

2.2. Preparation of Imidazolium Ionic Liquid from PET Waste

The de-polymerization of PET waste was occurred by mixing PET, PEHA using weight ratio (1:5 wt.%), and sodium acetate (1.5 wt.% related to PET weight). The reaction mixture was heated up to 120 °C for 1 h under nitrogen atmosphere to remove the humidity and water. The temperature was increased to 180–190 °C for 3 h and to 200–210 °C for 5 h. The ethylene glycol produced from reaction was separated from the reaction mixture using Dean-Stark trap during the depolymerization. The reaction mixture cooled and mixed with excess water under vigorous stirring. The powder was removed by filtration and washed with water to remove excess of PEHA. N, N-bis (14-amino-3,6,9,12-tetraazatetradecyl) terephthalamide (APA) was collected with yield 72 wt.% and subjected for nitrogen analysis.

APA (0.5 mol) was dissolved into acetic acid aqueous solution (100 mL; 50 vol.%) and GO (0.025 mol; 1.45 g) was added to the mixture at temperature −4 °C. The reaction temperature was increased up to 70 °C for 5 h and cooled for purification by washing with diethyl ether several times. The unreacted GO, acetic acid, and water were removed by using rotary evaporator under vacuum to obtain colorless liquid 1,3-bis(1-(4-(14-amino-3,6,9,12-tetraazatetradecyl) carbamoyl) phenyl)-1-oxo-2,5,8,11,14-pentaazahexadecan-16-yl)1,3-imidazolium acetate (PAIIL). The yield of PAIIL product was 95% yield percentage.

2.3. Characterization of APA and PAIIL

The chemical structures of APA and PAIIL were investigated by using Fourier transform infrared analysis (Nicolet Magna 750 FTIR spectrometer using KBr, Newport, NJ, USA) and hydrogen nuclear magnetic resonance (^{1}HNMR and ^{13}CNMR spectroscopy; 400 MHz Bruker Avance DRX-400 spectrometer; Toronto, ON, Canada). The thermal degradation stability of APA, PAIIL, and cured

DGEB/PAIIL films was determined by using thermogravimetric analysis (TGA; NETZSCH STA 449 C instrument, New Castle, DE, USA) under an N_2 atmosphere with heating rate 10 °C min^{-1}.

Gel permeation chromatography (GPC, Agillent 1100, which included a refractometer index detector and a set of three high resolution PL gel 10 µm), was used to determine the average molecular weights of APA and PAIIL using Agillent columns (500, 103, 104 Å). THF was used as the solvent with a flow rate of 1 ml/min, while monodisperse polystyrene was used as the reference.

2.4. Curing of DGEB/PAIIL System

The curing process of the DGEB epoxy using different weight percentages of PAIIL (DGEB/PAIIL; 4:1, 3:1, 2:1 and 1:1) was determined by using differential scanning calorimetry (DSC; Q10 DSC calorimeter from TA Instrument, Milano, Italy) in dynamic non-isothermal mode at a heating rate 5 °C min^{-1} from –30 to 300 °C. The DGEB/PAIIL blends were manually mixed and the samples (5–7 mg) were sealed in hermetic aluminum pans heated, cooled and heated under N_2 atmosphere. The glass transition temperatures T_g and the heat evolved during the reaction of the mixture (ΔH; curing exothermic peaks of DGEB/PAIIL) were recorded.

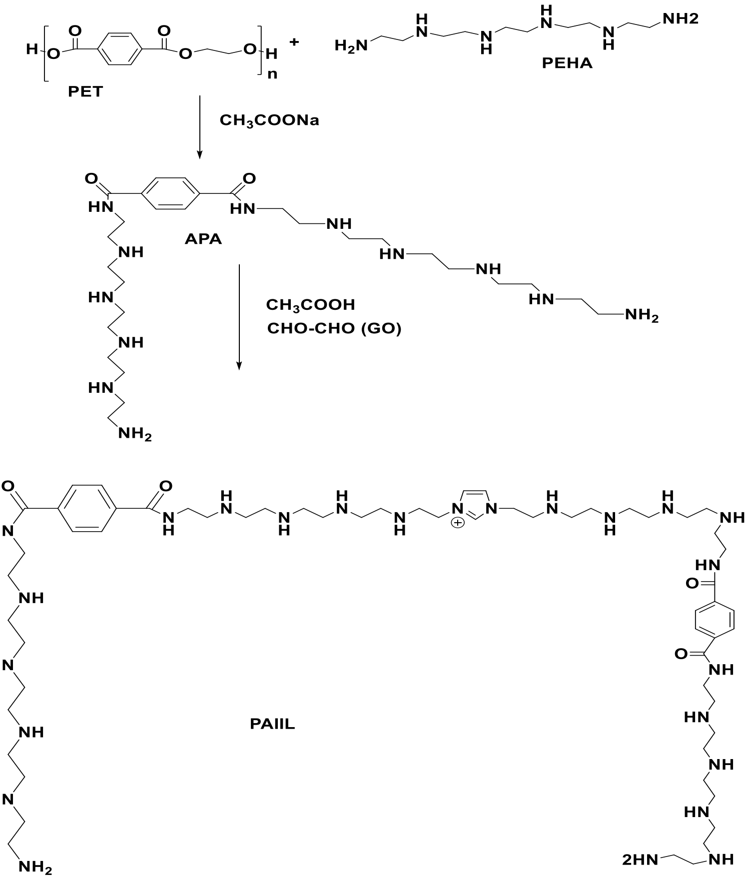
The T_g, storage, loss modulus and tan δ values of DGEB/PAIIL were determined using dynamic mechanical thermal analyzer (DMA; Q200, TA Instruments) in double cantilever mode at heating rate of 2 °C min^{-1} from 0 to 200 °C, frequency of 1 Hz. The DGEB/PAIIL was cured and casted into Teflon molds and hardened at 150 °C/2 h as rectangle-shaped samples with the dimensions of the $20.0 \times 10.0 \times 5.0\ \text{mm}^3$. The samples were cooled and heated from 0 to 300 °C at a rate of 2°C min^{-1} under N_2 atmosphere with a frequency of 1 Hz and amplitude of 40 µm.

2.5. Application of DGEB/PAIIL as Coatings for Steel

DGEB epoxy was blended using different weight percentages of PAIIL (DGEB/PAIIL; 4:1, 3:1, 2:1 and 1:1) and diluted with butyl acetate (10 wt.%) xylene solvent. The DGEB/PAIIL solution was sprayed on the blasted and cleaned steel panels to form a uniform dry film thickness (DT) of 100 µm for epoxy coatings keeping the 30 cm distance between the spray needle and steel panel surface. The DGEB/PAIIL films were cured for 7 days at room temperature. Posi Test AT-A automatic adhesion tester was used to determine the adhesion pull-off strength of cured films with steel surface according to American Society for Testing and Materials (ASTM D 4541-19. The corrosion resistance of the cured DGEB/PAIIL films was investigated according to ASTM B 117-03 after exposure to seawater spray (fog) at temperature and humidity 37 °C and 98% using cabinet manufactured by CW specialist equipment Ltd., 20 Model SF/450, (London, England). The durability and failure rates of the cured DGEB/PAIIL films were evaluated according to ASTM D-1654 of the 6 steel panels.

3. Results and Discussion

The aminolysis of PET by using PEHA was carried out using sodium acetate as a catalyst produced diamino-phthalamide (APA) as represented in Scheme 1. It is well known that the hydroxyl groups of the unreacted ethylene glycol (EG) could serve as a catalyst via hydrogen bond formation for the cross-linking reactions in the presence of amide and amine groups of APA [29]. The purification was carried out to remove the ethylene glycol side product and unreacted PEHA. The nitrogen content of the produced APA was found to be 28.9 wt.%, which agrees with the theoretical content of 28.19 wt.%. The number average molecular weights (Mn) of APA and PAIIL were determined from GPC as represented in Figure 1a,b, respectively. The Mn values of APA and PAIIL are 598 and 1295 g mol^{-1}, respectively agree with the nitrogen content values and confirm the depolymerization of PET to APA monomer. Moreover, the Mn value of PAIIL (Figure 1b) confirm that the prepared IIL is monomer unit as represented in the Scheme 1. The PAIIL was produced from the reaction of diamino-phthalamide of APA with GO in the presence of acetic acid (Scheme 1). The nitrogen contents of PAIIL was determined as 29.98 wt.%. The investigation of physicochemical characteristics, chemical structures, and thermal characteristics of APA and PAIIL were discussed in the forthcoming section.



Scheme 1. Aminolysis of PET waste to APA and PAIIL.

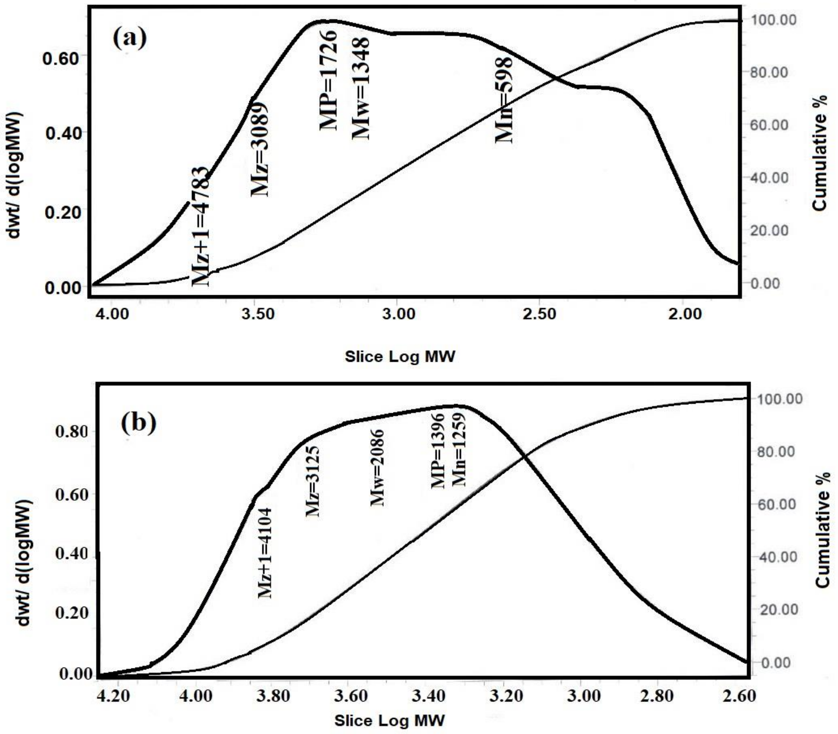


Figure 1. GPC data of (**a**) APA and (**b**) PAIIL.

3.1. Characterization of APA and PAIIL

The chemical structures of APA and PAIIL were confirmed from FTIR, ^{1}HNMR, and ^{13}CNMR analyses as represented in Figures 2–4. The FTIR spectra of PET, APA and PAIIL were summarized in Figure 2a–c. The appearance of new bands at 1650 and 1560 cm^{-1} referred to amide type (I) and (II) vibrations in FTIR spectra of APA (Figure 2b) and PAIIL (Figure 2c) confirms the formation of terephthalamide unit instead of terephthalate. Moreover, the presence of two bands at 3550 and 3450 cm^{-1} attributed to NH_2 stretching vibration of APA spectrum (Figure 2b) elucidates the presence of NH_2 groups in its chemical structure. The appearance of less intense band at 3635 cm^{-1} in PAIIL spectrum (Figure 2c) confirms the lowering of NH_2 contents due to formation of imidazolium ion. However, the presence of absorption bands from 2800 to 3200 cm^{-1} in the PAIIL spectrum (Figure 2c) assigned of methylene and CH stretching from 2800 to 3000 cm^{-1} and attributed to $^{+}$N=C–H stretching vibrations mode of imidazolium ring cations [30]. The new intense band at 1150 cm^{-1} in spectrum of PAIIL (Figure 2c) was attributed to C-N bending of imidazolium cation. The acetate anion band C=O stretching was observed at 1600 cm^{-1} in FTIR spectrum of PAIIL (Figure 2c).

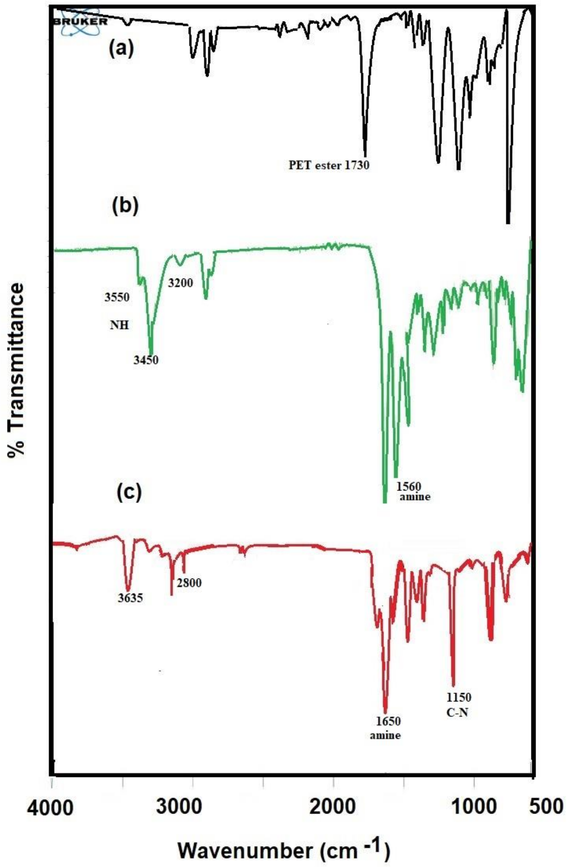


Figure 2. FTIR spectra of (**a**) PET, (**b**) APA and (**c**) PAIIL.

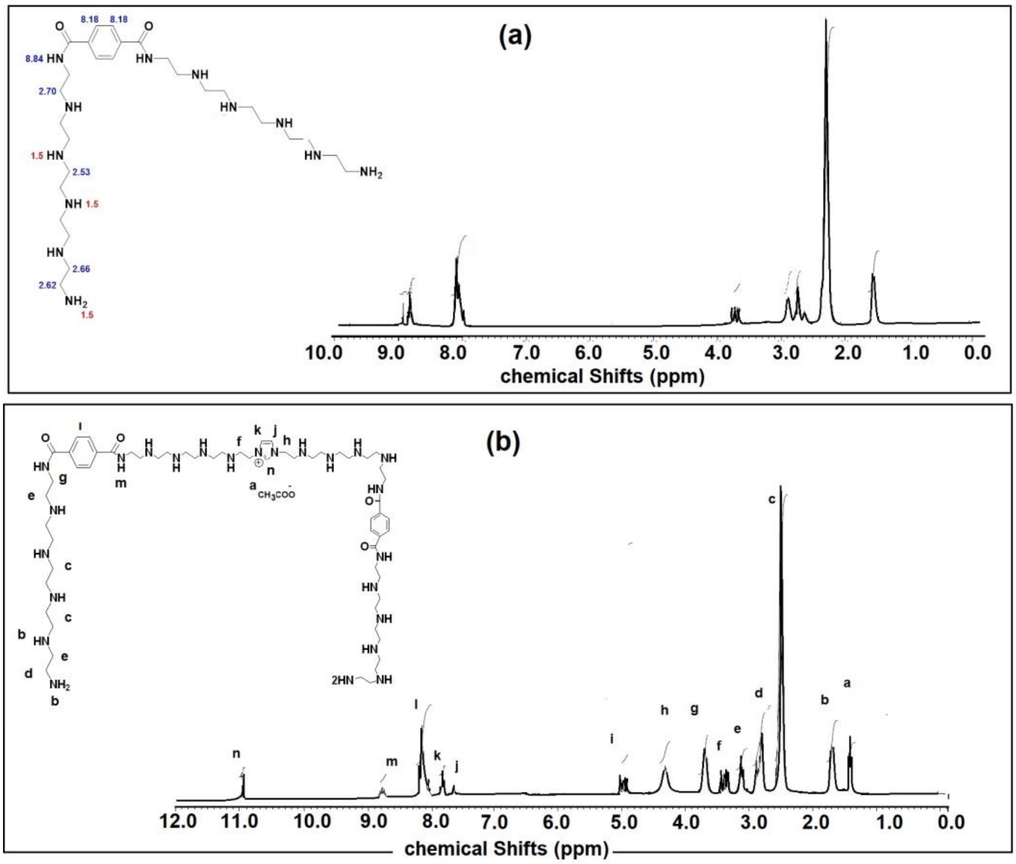


Figure 3. ^{1}HNMR spectra of (**a**) APA and (**b**) PAIIL.

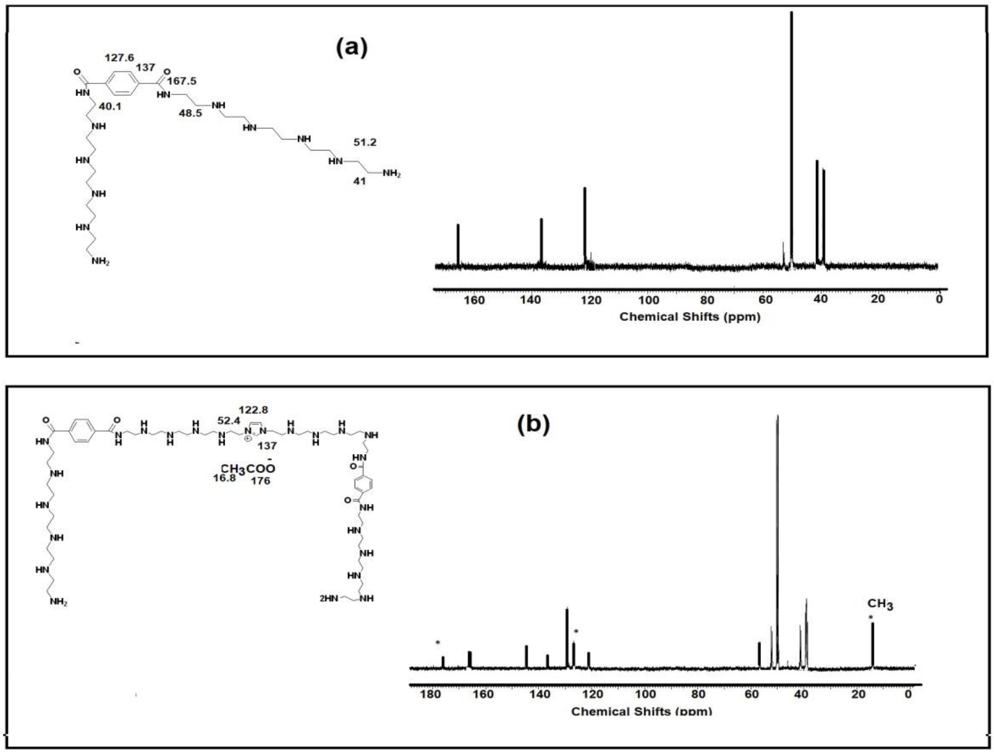


Figure 4. ^{13}CNMR spectra of (**a**) APA and (**b**) PAIIL.

The ^{1}HNMR spectra of APA and PAIIL (Figure 3a,b) show the appearance of new peaks in PAIIL spectrum (Figure 3b) at 10.92, and 1.49 ppm referred to $^+$N=CH–N and CH$_3$COO$^-$ protons and elucidated the formation of imidazolium acetate IL. The higher de-shielded proton of imidazolium and lower shielded methyl protons of PAIIL might be due to a rotation of the ionic pair (quasi-molecule) around the axis of symmetry of ionic pair of imidazolium cation and CH$_3$COO$^-$ anion [30]. The other peaks of phenyl and ethylene imine amides were marked in spectra of APA and PAIIL (Figure 3a,b). The ^{13}CNMR spectra of APA and PAIIL (Figure 4a,b) also confirm the appearance of new peaks at 176, 137, and 17 ppm in PAIIL spectrum (Figure 4b) referred to COO, N=C–N, and CH$_3$ of imidazolium acetate IL [31].

The thermal characteristics of APA and PAIIL were investigated from their DSC thermograms represented in Figure 5a,b, respectively. It is reported that PET thermoplastic polymer has three temperature transitions as glass transition (T_g), crystallization (T_c), and melting (T_m) temperatures that determined as 79.8, 148, and 230.6, respectively [32]. The APA thermogram (Figure 5a) shows the same characteristics of T_g, T_c, and T_m at 47.5, 74.5, and 155 °C, respectively. The PAIIL thermogram (Figure 5b) shows only T_g and T_m at –54.5 and –17.5 °C to elucidate the formation of IIL with low T_g and T_m values. The disappearance of T_c from the PAIIL (Figure 5b) and appearance in APA (Figure 5a) thermograms proves the disordering and ordering of the surface layer of crystals, respectively. The surface layer of PAIIL melts gradually prior to the bulk melting point due to formation of quasi-liquid to dissolve its crystallinity [33].

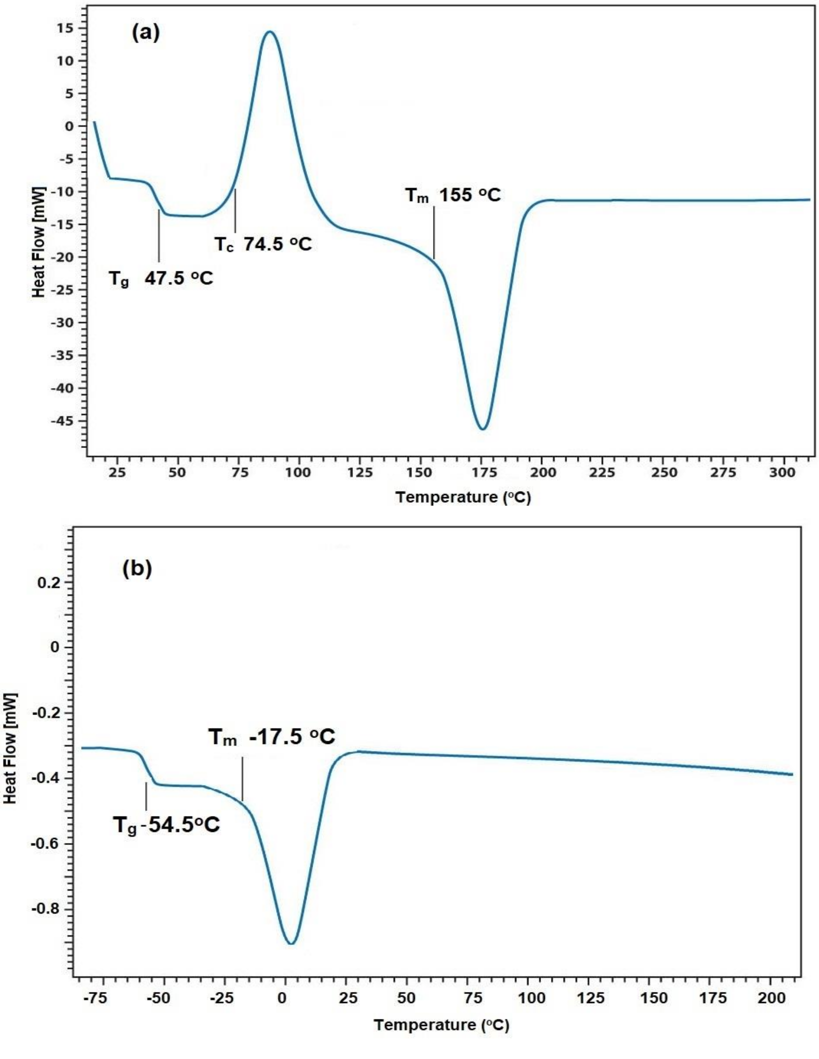


Figure 5. DSC thermograms of (**a**) APA and (**b**) PAIIL.

The thermal stability of APA and PAIIL against thermal degradation was investigated from their TGA-DTG thermograms summarized in Figure 6a and b. It can be noticed that the thermal stability of either APA (Figure 6a) or PAIIL (Figure 6b) was lower than PET bottle waste that started degradation at 385 °C [34]. APA (Figure 6a) or PAIIL (Figure 6b) start the degradation at 275 and 210 °C, respectively, after loss water. APA (Figure 6a) or PAIIL (Figure 6b) have a weight loss 55 and 48 wt.% from their original weights above 275 and 210 °C, respectively. The lowering of thermal stability of PAIIL than APA can be referred to the presence of acetate anion that can accelerates the PAIIL degradation of imidazolium cations although the lowering of APA basicity with formation of imidazolium cation in the PAIIL. The second peak of APA (Figure 5a) or PAIIL (Figure 6b) starts from 390 and 345 °C to loss 22 and 12 wt.%, respectively. The remained residue % due to the degradation of APA (Figure 5a) or PAIIL (Figure 6b), due to carbonization above 500 °C are 12 and 34 wt.%, respectively. These data confirm that the PAIIL has higher thermal stability makes it promising for curing reaction of epoxy resin as liquid polyamino amide hardener rather than solid polyamine–amide (APA).

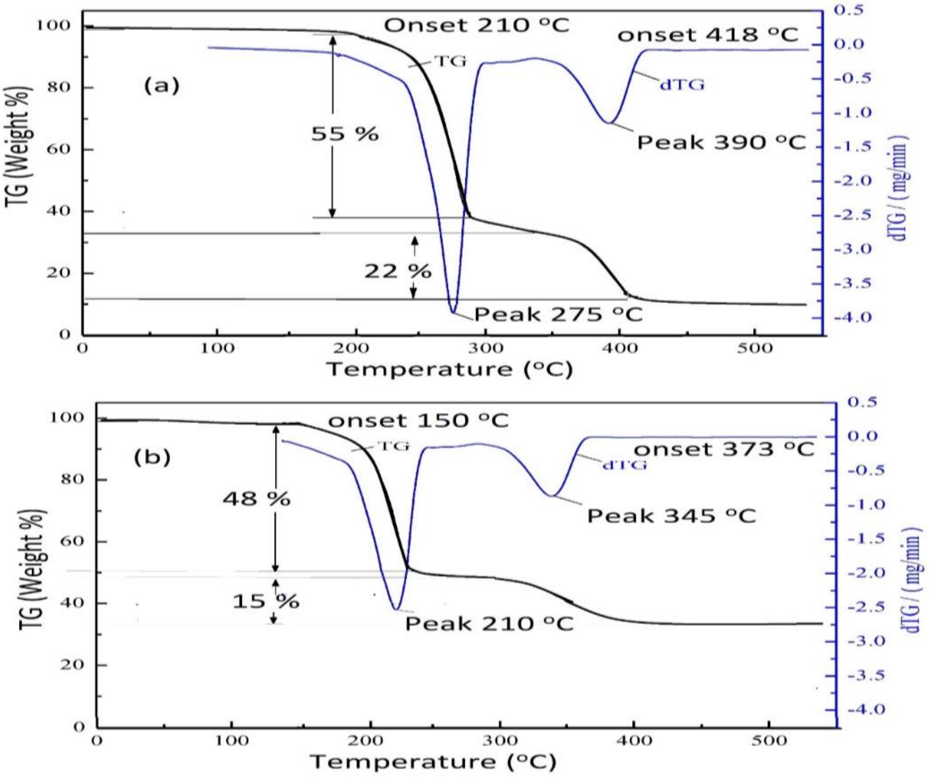
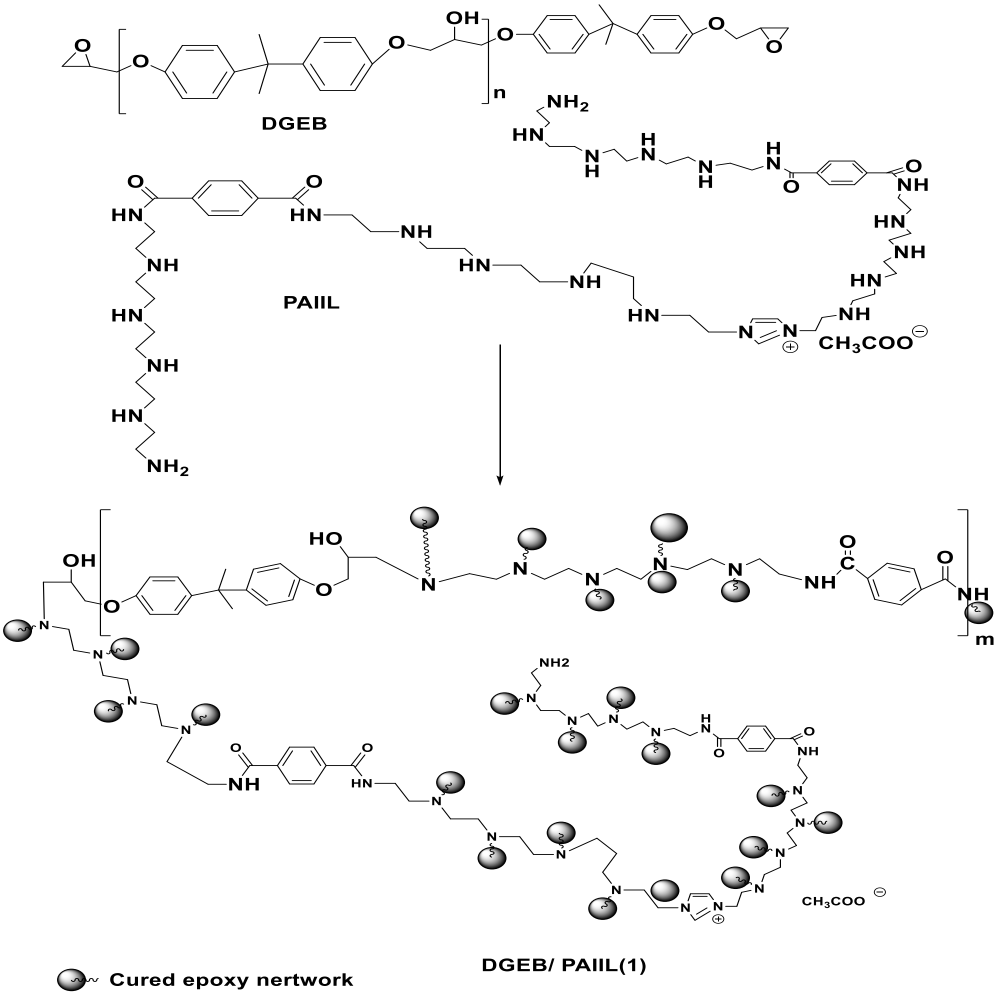


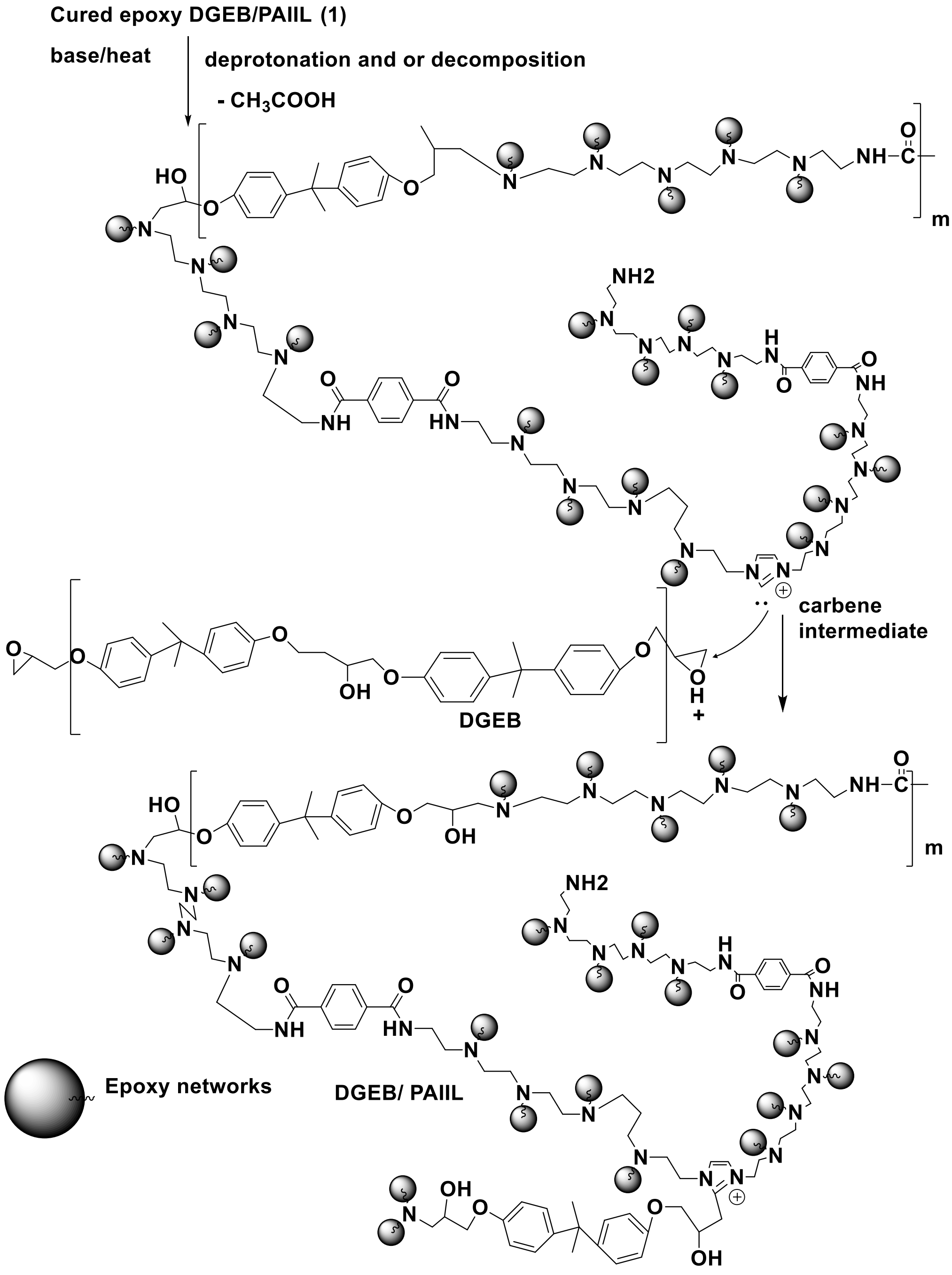
Figure 6. TGA-DTG thermograms of (**a**) APA and (**b**) PAIIL.

3.2. *Curing of DGEB Epoxy with PAIIL*

The PAIIL liquid polyamino-amide was selected rather than APA solid polyamine as a hardener for epoxy resin based on DGEB. It is well known that the epoxy resin based on DGEB prepolymers were crosslinked with different types of the curing agent either with epoxy ring opening in case of using polyamides and polyamine or reaction of their hydroxyl groups with anhydrides curing agents. The PAIIL chemical structure (Scheme 1) contains three functional groups that can be used to crosslink DGEB via oxirane ring opening mechanism through amino-amide and lone pair of imidazolium cations [35]. In this respect, the proposed mechanism for curing of epoxy resin either with amino-amide or imidazolium cations was represented in Schemes 2 and 3, respectively. The presence of di-functional primary amine groups in PAIIL is responsible to open the oxirane ring with formation of the hydroxyl groups (Scheme 1) that responsible on the adhesion of cured epoxy films with steel substrate. The concentration of the hydroxyl groups is increased with the second proposed mechanism for oxirane ring opening with imidazolium ILs (Scheme 3) that influenced by anions of imidazolium [35]. The reaction of imidazolium (IILs) with epoxy group was completed either by decomposition of IILs (de-alkylation) in basic condition or deprotonation (proton exchange) that affected by the basicity of their ions [35,36]. The dealkylation mechanism usually was occurred with using dialkylimmidazolium acetate IILs to form cured epoxy without imidazolium cations via formation of highly crosslinked networks. The cured epoxy networks were characterized by the appearance of carbonyl groups that accelerated with increasing the curing temperatures up to 200 °C [35,37].



Scheme 2. Curing of DGEB resin with amino-amide groups of PAIIL.



Scheme 3. Curing of DGEB resin with imidazolium cations of PAIIL.

The chemical structure of DGEB epoxy resin cured with different weight percentages of PAIIL (DGEB/PAIIL; 4:1, 3:1, 2:1 and 1:1) was identified from FTIR spectra Figure 7a,b. The appearance of new bands in spectrum of DGEB/PAIIL weight ratio (2:1; Figure 7b) at 3501 and 1614 cm^{-1} referred to stretching vibration of the O–H group, and the CONH group elucidates that the curing of EGDB with PAIIL according to Scheme 2. Moreover, the disappearance of the DGEB epoxy ring (Figure 7a) at 910.64 cm^{-1} from the spectrum of DGEB/PAIIL (Figure 7a) indicating that all epoxy ring was consumed in the reaction, which is in support of Schemes 2 and 3. The disappearance of carbonyl bands from 1700 to 1750 cm^{-1} attributed to de-alkylation mechanism of IIL [35–37] confirms that the de-protonation mechanism (Scheme 3) was preferred to cure DGEB resin with PAIIL.

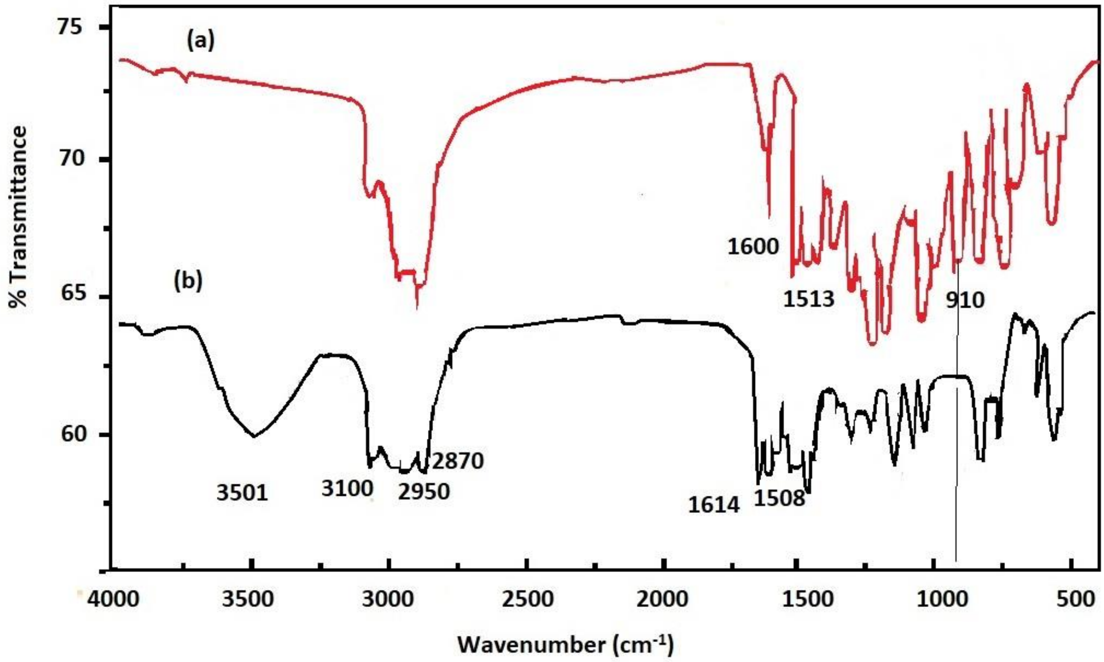


Figure 7. FTIR spectra of (**a**) DGEB and (**b**) DGEB/PAIIL weight ratio (1:1).

Thermal stability of the cured DGEB epoxy resin with different weight ratios of PAIIL (DGEB/PAIIL; 4:1, 3:1, 2:1, and 1:1) was investigated from TGA thermograms represented in Figure 8. It was found that the initial degradation temperature (IDT) was reduced with increasing PAIIL concentrations (DGEB/PAIIL; 1:1) that decomposed at 180 °C. Moreover, The IDTs of DGEB/PAIIL; 4:1, 3:1, and 2:1 are 380, 300, and 350 °C, respectively. These data elucidate that the increasing of PAIIL contents (1:1) produces high acetic acid contents (Scheme 3) that increases the degradation rate of polymer chains and IIL [38]. It was also observed that the residual content % (RS%) above 550 °C was reduced with increasing the PAIIL contents to confirm that the char formation is produced due to complex dehydration reaction that was decreased with increasing acetate contents. The higher thermal stability of DGEB/PAIIL 4:1 and 2:1 than 3:1 (Figure 7) indicates that both 4:1 and 2:1 form moderate and higher crosslinking densities more than 3:1, attributed to heterogeneity of epoxy networks [39]. The lowering thermal stability of DGEB/PAIIL 3:1 than 4:1 or 2:1 could be attributed to the homogeneity of the crosslinked networks besides degradation of chains and forming of chains at higher degradation temperature [40]. This observation agrees with the lowering RS% of DGEB/PAIL in the order 1:1 < 2:1 < 3:1 < 4:1 as 6, 14, 21, and 23 wt.%, respectively (Figure 8).

The flexibility or rigidity of the cured DGEB epoxy resin with different weight percentages of PAIIL (DGEB/PAIIL; 4:1, 3:1, 2:1 and 1:1) were determined from DSC and DMA measurements represented in Figure 9a,b, respectively. It is very important to use lower heating rates for DMA (2 °C min^{-1}) than DSC (5 °C min^{-1}) due DMA analysis sensitivity that usually uses relatively much bigger sample than DSC. So, the DGEB/PAIIL sample has enough time to reach thermal equilibrium with the chamber environment with the heating rate 2 °C min^{-1}. Moreover, the heating rate 5 °C min^{-1} was selected as preferred slow heating rate for dynamic non-isothermal DSC analysis to reflect the intrinsic nature of the curing process, like the apparent activation energy and frequency that are very important for investigating the relationship between the properties and structures of thermosetting epoxy resin [41]. The glass transition temperatures (T_g) and the total heat of the curing reactions enthalpy (ΔH; J g^{-1}) of; 4:1, 3:1, 2:1, and 1:1 wt.% were determined from their area under peaks of DSC thermograms (Figure 9a) and summarized in Table 1. The presence of shoulder peak before the second exothermic peak in all curves (Figure 9a) confirms the presence of two curing reaction mechanisms as represented in Schemes 2 and 3 [35]. Moreover, the order of curing reactions of DGEB/PAIIL at lower temperatures was arranged in the order 4:1 > 3:1 > 2:1 > 1:1. The DMA analysis determined in terms of variation tanδ versus temperature of all cured DGEB/PAIIL epoxy resins (Figure 9b and Table 1) shows the same results of T_g that determined from the maximum of the tanδ peaks. These mean that the increasing of PAIIL (wt.%) produces rigid networks with increasing T_g which may be referred to decomposition of PAIIL due to large amounts of acetic acids produced the curing of DGEB/PAIIL weight ratio (1:1) to decrease the plasticizing effect of imidazolium cations [35–37]. The T_g data of the DGEB/PAIIL determined from DMA were increased than that determined from DSC experiment were attributed to the higher temperatures used to DSC under dynamic mode. This difference can be referred to the cooling to −30 °C, heating to 300 °C and cooling of DGEB/PAIIL under non-isothermal mode in DSC technique. DMA specimens are tested under dynamic conditions under heating up to 200 °C.

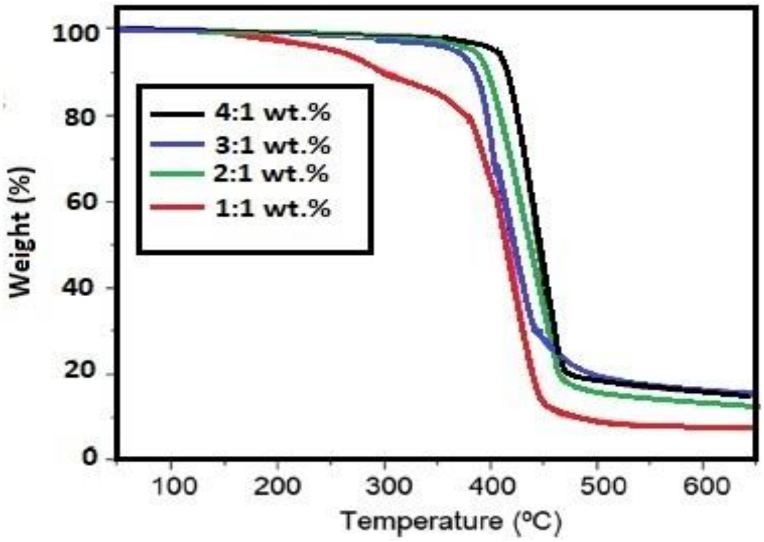


Figure 8. TGA thermograms of DGEB/PAIIL systems.

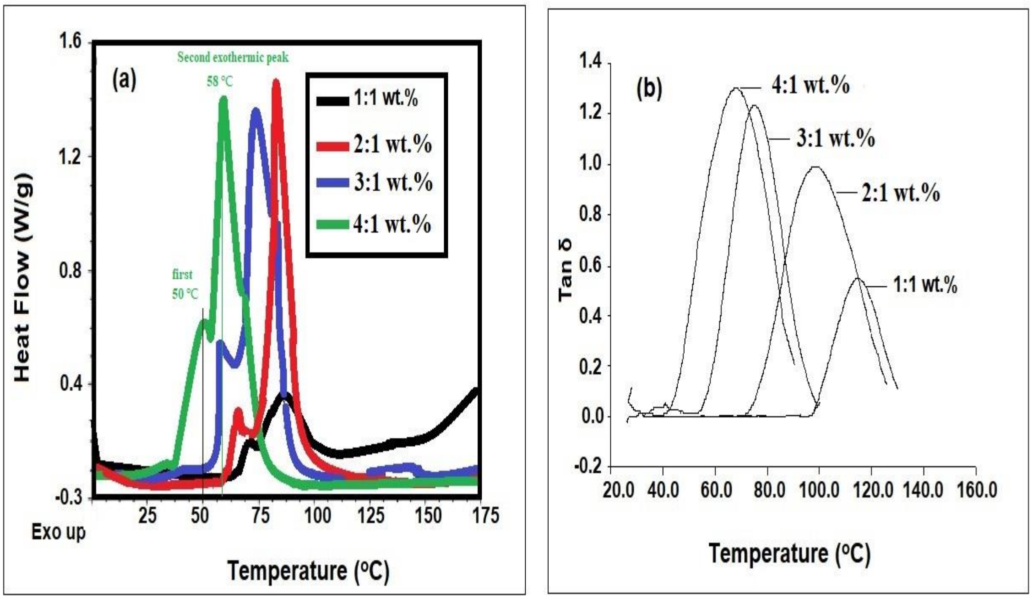


Figure 9. Thermal characteristics of DGEB/PAIIL using (**a**) DSC and (**b**) DMTA thermograms.

The DGEB/PAIIL systems were heated in DSC and DMA up to 280 and 140 °C, respectively. The lower temperature of DMA analysis was not enough to produce high CH_3COOH (Scheme 3) that decreases T_g data of DSC due to plasticizing effects of uncured PAIIL.

Table 1. DSC and DMA data of DGEB/PAIIL.

DGEB/PAIIL (wt.%)	T_g DSC (°C)		ΔH (J g^{-1})		T_g DMA (°C)
	First	Second	First	Second	
1:1	72	90	20	462	115
2:1	64	84	30	510	98
3:1	57	72	35	515	75
4:1	50	58	45	522	67

The relation between storage modulus, loss modulus, tanδ, and temperature for the cured DGEB/PAIIL weight ratio (4:1) system determined from DMA was selected and represented in Figure 10. The storage modulus (G_e) of DGEB/PAIIL to attain the maximum plateau of 4:1, 3:1, 2:1, and 1:1 are 2642, 2242, 3785, and 2500 MPa, respectively. The crosslinking densities (ρ, mol dm^{-3}) cannot easily determined from the selling measurements of the crosslinked epoxy resins due to their higher resistivity towards organic solvents and water. It can be calculated as: $\rho = G_e/RT_e$; where R = universal gas constant (8.314 J mol^{-1} K^{-1}), and T_e values determined from relation of the loss modulus data to be $T_e = T_g + 65$ °C (Figure 10). Although the semi-empirical relation of ρ and G_e was more correctly applied to lightly crosslinked elastomers but was previously applied in the curing of epoxy with ILs [35]. The data summarized in Table 2 confirm that the crosslinking densities of DGEB/PAIIL 4:1 and 2:1 are the most suitable weight ratios to obtain highly crosslinked epoxy networks. These data agree with that determined from DMA (Figure 10) to confirm that DGEB/PAIIL 4:1 and 2:1 have been cured for the shortest time at the lowest temperature and indicating a relatively uniform networks [35–37]. It is also noticed that DGEB/PAIIL weight ratios 3:1 and 1:1 undergo more pronounced lower temperature beta transitions before going through the glass transition temperature at similar temperatures to indicate that their networks containing different structural domains (heterogeneous).

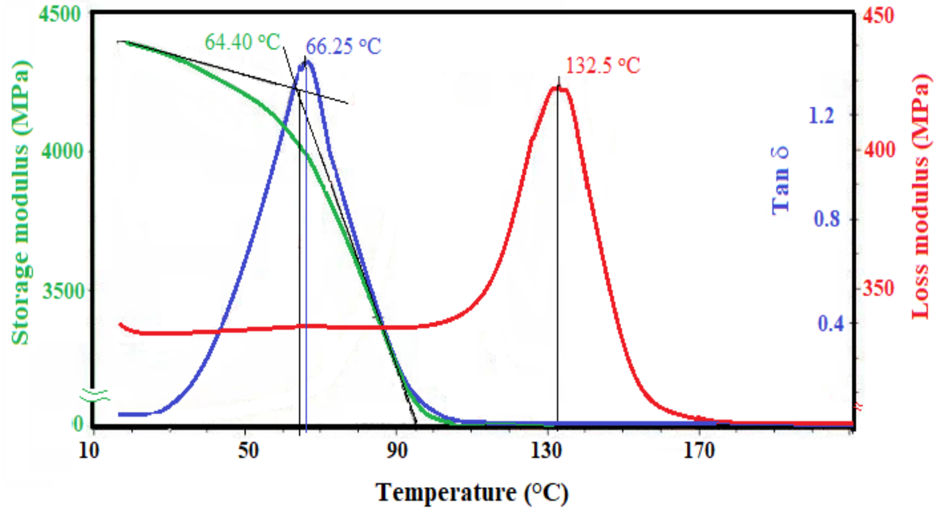


Figure 10. DMTA analysis of the cured DGEB/PAIIL (4:1) system.

Table 2. DMA and crosslinking densities data of DGEB/PAIIL.

DGEB/PAIIL (wt.%)	T_g (°C)	G_e (MPa)	T_e (K)	$\rho \times 10^3$ (mol dm^{-3})
1:1	115	2200	453	0.5841
2:1	98	2800	436	0.7724
3:1	75	2600	413	0.757
4:1	67	4200	405	1.247

3.3. Adhesion and Salt Spray Resistance of DGEB/PAIIL

The previous data about the thermomechanical characteristics (Tables 1 and 2) elucidate that the DGEB was cured in the presence different wt.% of PAIIL to produce homogeneous networks with DGEB/PAIIL 4:1 and 2:1 rather than 1:1 and 1:3 that obtained heterogeneous networks. The good miscibility of DGEB with PAIIL at all wt. produces transparent epoxy coatings. In the present section, the adhesion strength values (MPa) of the cured epoxy films with steel surface were determined from pull-off measurements and represented in Table 3. It is noticed that a significant improvement in the pull-off adhesion upon curing DGEB/PAIIL 4:1 and 2:1 that attributed to production of more hydroxyl groups as represented in Schemes 2 and 3. The improvement in adhesion property of epoxy coating is a positive result can be referred to the formation of homogeneous epoxy networks provided by DGEB/PAIIL weight ratios 4:1 and 2:1 can facilitate the curing of epoxide rings of DGEB with amino-amides and imidazolium groups of PAIIL [40,42].

Table 3. Salt spray resistance of DGEB/PAIIL coating films at different exposure times 720.

DGEB/PAIIL (wt.%)	Adhesion Strength (MPa)	Exposure Time	Disbanded Area %	Rating Number (ASTM D-1654)
1:1	4.5	500	5 ± 0.05	7
2:1	15	1500	2 ± 0.08	8
3:1	9.0	1000	10 ± 0.08	5
4:1	12.5	1500	2 ± 0.04	8

The corrosion resistance of DGEB/PAIIL coatings against seawater fogs and humidity was investigated from salt spray resistances measurements as summarized in Figure 11a–d and Table 3. The formation of rust under coatings is responsible for the adhesion failure between the epoxy coatings and steel (Figure 11a–d). The rusts occurred under coatings early for DGEB/PAIIL 1:1 and 3:1 after exposure to 500 and 1000 h, respectively (Figure 11a,c). The higher salt spray resistances of DGEB/PAIIL weight ratios 4:1 and 2:1 extended to 1500 h (Table 3 and Figure 11b,d). This improvement was attributed to the formation of superior homogeneous cured epoxy resins having high adhesion with steel to act as a barrier to salt, water, and oxygen from the aggressive environment [42,43].

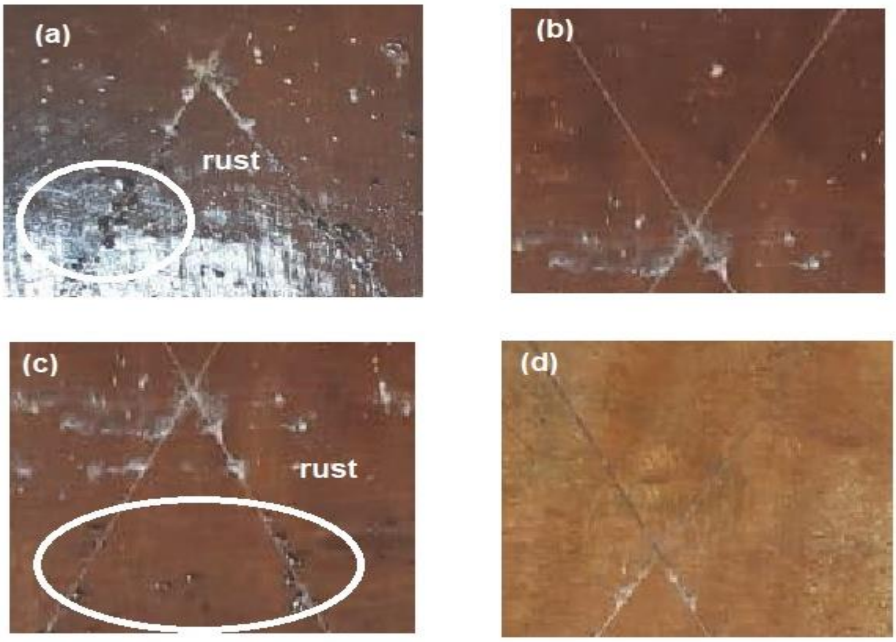


Figure 11. Salt spray resistance of DGEB/PAIIL coatings using different weight ratios (**a**) 1:1, (**b**) 2:1, (**c**) 3:1 and (**d**) 4:1.

4. Conclusions

Imidazolium ionic liquid was prepared from aminolysis of PET waste with PEHA to obtain liquid PAIIL with low glass transition and melting temperature at −54.5 and −17.5 °C to elucidate the formation of amorphous IL. The PAIIL was cured with DGEB epoxy with different weight ratios to act as curing agent to open oxirane ring either with its imidazolium cations or amino- amide groups. The curing mechanisms of PAIIL were elucidated from thermal, thermomechanical, and FTIR measurements to confirm that the deprotonation mechanism of imidazolium cations was preferred to open oxirane ring besides its curing with amino-amide groups. The curing data prove that the best ratio of DGEB/PAIIL weight ratio was 2:1 obtained flexible epoxy films resist the corrosion in seawater fog environments. DGEB/PAIIL (2:1 wt.%) coating achieves higher salt spray resistance up to 1500 h.

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