The influence of Different Acid Chloride on The General Characterizations, Electrical and Ultrasonic mechanical of Terpolymers:

Abstract:

Unsaturated terpolyesters have been prepared and investigated by chemical and physical instruments. The effect of acid chloride in the general physical characterizations of terpolyesters was the aim of study. The solubility of terpolyesters has been tested in different solvents. The viscosity average molecular weight was determined according to Mark-Houwink equation using some standards polymers. The thermal stability and glass transition temperature was recorded by Thermogravimetric analysis and Differential thermal analysis respectively. The crystallinity has also been investigated by X-ray diffractogram. Moreover, the morphology and shape of terpolyesters was scanned by scanning electron microscopy. The electrical properties especially dielectrical constant of polymer material have been discussed with some detailed. Our target of study focused on the improvement of physical properties of new unsaturated terpolyesters with special interest to the electrical and mechanical properties to be applicable as insulator material.

Keywords: Unsaturated terpolyester, Characterization, Acid Chloride, Electrical, Ultrasonic mechanical.

1. Introduction

The copolymerization process in which three monomers used is call terpolymerization and polymers known as terpolymers. Terpolyester is the most popular kind due to its highly intensive application especially in the medical applications [1-3].

Recently, unsaturated polyesters have been discovered to be an important class of high performance and polymer engineering [4–7]. They have several applications and have been used as thermoset in polymer composites such as fiber-reinforced plastics and polymer concretes [8-10]. The production of unsaturated polyesters has been widely used due to their advantages involving low cost and thermal stability [11, 15]. However, unsaturated polyesters are generally difficult to process because of their high melting temperature or high glass-transition temperature by virtue of their rigid structure [16-18]. Hence, flexible aliphatic methylene units such as ethylene and hexamethylene were introduced in the backbone of the polymers. These methylene spacers enhance the processing and fabrication of polyesters.
addition, fumaric acid as the trans-diacid was used because it is relatively cheap, less corrosive and gives lighter-colored products, whereas the simplest diols increase the tendency of the polyester to crystallize [19,20].

Many studies were concerning with preparation of unsaturated polyester composites with especial interest to their mechanical properties [21-22]. Moreover, other studied the formation of nanocomposites silicate layered from unsaturated polyesters [23].

One of the most important properties is the dielectric constant which symbol by \( \varepsilon \) and defined as the ratio of the capacitance of a condenser containing the material to the capacitance under vacuum. The extent of charge inside condenser measured its capacitance. The electrical properties of polymer thin film especially the dielectric constant and their application as insulators have been recently discussed [24, 25]. Many articles have their attention in improvement the magnitude of electrical conductivity of insulating polymers materials [26, 27]. Many studies have also been measured the dielectric constant of natural polymers like cellulosic, [28] protein, and synthetic fibers [29]. The mechanical properties of solid polymers are related to Hooke’s law which describes the relation between stress to strain [30]. New technology used the ultrasonic spectroscopy to measure the elastic properties of polymers [31].this technique depending on Poisson’s ratio (\( \nu \)) that described the relation between transverse strain and longitudinal strain in the elastic loading direction [32]. Poisson’s ratio is closed to 0.5 for most polymeric material [33]. The mechanical properties of unsaturated polyester composites have a great interest of many scientists [34-35].

This study reports the preparation and characterization of new unsaturated terpolyesters. The influences of different acid chloride on the physical and chemical characterization of polymers have been discussed. We have focused on the thermal, morphological, electrical and mechanical properties of different unsaturated terpolyesters.

2. Experimental

2.1. Materials

4-Hydroxy-3-methoxybenzaldehyde (vanillin) (99%, Aldrich, Germany), 4-Hydroxybenzaldehyde (99%, Aldrich, Germany) and 3-Hydroxybenzaldehyde (99%, Aldrich, Germany). 4-Nitrobenzoic acid from (98%, Merck, Germany). Adipoyl, sebacoyl, isophthaloyl and terphthaloyl dichlorides (99%, Merck Germany), Cyclohexanone (98%, Fluka Germany). Other chemicals were purchased from Aldrich, Merck, Fluka or Acrôs companies and purified by standard methods.
2.2. Instrumentations

The infrared spectra for all solid samples were recorded on IR–470 infrared spectrophotometer, Shimadzu; and Pye Unicam SP3-100 spectrophotometer (Japan) using KBr pellet technique. Nuclear Magnetic Resonance spectra for monomers and models were recorded on a Varian EM-390 (90MHz) spectrometer and GNM-LA (400MHz) (USA) spectrophotometer at room temperature in DMSO or CDCl₃ using TMS as the internal reference. Nuclear Magnetic Resonance spectra for polymers were recorded on a Bruker AVANCE 500 (USA) spectrometer (500 MHz) at room temperature in CF₃COOD. The ultraviolet visible spectra were scanned on U. V.-Visible spectrophotometer, Labomed, (USA), Spectro Double Beam 8 Auto cell, U. V D 3200, 190-1100nm in conc. H₂SO₄ as solvent The solubility of the polymer were examined using 0.02 g of polymer In (3-5 ml) of solvent at room temperature. The inherent viscosities of the polymer solution (0.5 %w/v) In conc. H₂SO₄ were determined at 30°C using an Ubbelohde suspended level viscometer VWR (Germany). X-ray diffract graphs of the polymer were obtained with Philips X-ray Pw 1710 (Japan) diffractometer, using Ni-filtered CuKα radiation. Thermo-gravimetric analysis (TGA), differential thermal analysis they are carried out in air with Shimadzu TGA-50. Perkin Elmer Differential Scanning Calorimeter Pyris 1 was used for the determination of Tg of solid polymers. The thermogram was recorded at heating and cooling rate of 5 °C/min. X-ray diffraction of polymers was recorded on Bruker AXS D8 Advance diffractometer with Cu Kα characteristic radiation at a voltage of 40 KV and a current of 40 mA. The scanning rate was 0.4°/min; the range of 2θ was from 20° to 80° at room temperature.

The morphology of the polymer were examined by Scanning Electron Microscopy (SEM) using a JSM-5400 LV instrument; images were recorded with a Pentax Z-50P Camera with IL ford film at an accelerating voltage of 15KV (USA).

2.3. Electrical properties

The dielectric constant (ε), parallel resistance (Rp) and parallel capacitance (Cp) were determined for specimens in the form of discs. They were prepared as discussed lately, the diameter 10mm and thickness about 7mm. The measurements have been carried out at room temperature and frequency rang 100Hz-1MHz using HIOKI 3532-50 LCR Hi TESTER.

2.4. Ultrasonic Velocity measurements

Ultrasonic waves travel through any solid material at a specific velocity related to the material characterization and its density. Here we used the pulse technique which is widely used to generate ultrasonic measurements for solid and fluids. A pulse of sinusoidal voltage is
applied to a piezoelectric transducer that is directly contacted with the samples under investigation. Then, the electrical pulse converted to acoustical pulse that transmitted into the medium. The pulse propagates down the medium, and reflected to the opposite face. The time intervals between successive echoes can be measured and velocity of the wave is determined. Once time intervals duration is obtained and the thickness of the samples determined the velocity of the ultrasonic wave of the sample can be calculated by equation (1);

$$v = \frac{2d}{\Delta t}$$  \hspace{1cm} (1)

Where d is the thickness of the sample and $\Delta t$ is the time intervals (32).

In general, the solids are subjected to three types of stressing condition: uniaxial stress, triaxial stress and pure shear. If a uniaxial stress is applied on a body, then elongation in the same direction will be produced. Young’s modulus (E): Is defined as the ratio of the linear stress to linear strain as. Shear of rigidity (G): Is defined as the ratio of the shear stress to the shear strain. Bulk modulus (K): Defined as the ratio of the hydrostatic stress to the volumetric strain. Micro-hardness (H): Is a measure of the resistant of material to being penetrated and eroded by another material’s shear projection. The four constants held as equations 2-6;

$$L = \rho V_l^2$$  \hspace{1cm} (2)

$$G = \rho V_s^2$$  \hspace{1cm} (3)

$$E = 2 (1+ \nu) G$$  \hspace{1cm} (4)

$$K = L - (4/3) G$$  \hspace{1cm} (5)

$$H = (1- 2 \nu) E / 6 (1+ \nu)$$  \hspace{1cm} (6)

Where $\rho$ is the density of the material, L is the longitudinal elastic modulus, $V_l$ and $V_s$ are the longitudinal and transverse ultrasonic velocities and $\nu$ is Poisson’s ratio [32,33].

2.5. Synthesis of Monomers 1, 2, 3 and Their Models 4a, 4b, 4c

The monomers 1 and 3 and their models were synthesized as described in our previous work [34, 35]. A new monomer 2 and its model were prepared by the same procedure by condensation of m-hydroxy benzaldehyde with cyclohexanone for 3 hrs. as brown needles from ethanol, yield 91%, m. p 215 °C.

Model IIa was obtained by the reaction of 2, 6- bis (3-hydroxybenzylidene) cyclohexanone and benzoyl chloride as yellow plates from benzene yield, 93%, m. p 216 °C.

$^1$H NMR (90 MHz, DMSO-d6, $\delta$): = 9.75 ppm (s, 2H, 2OH group), at 7.65 ppm (s, 2H of 2CH=C); at 6.8 - 7.35 ppm (m, 8H of Ar -H), at 2.85 ppm (m, 4H of 2CH2) and at 1.85 (pented, 2H of CH=2 of cyclohexanone).

IR (KBr) (2 monomer): $v = $ IR spectra recorded from KBr pellets showed characteristic
bands for C=O cyclohexanone at 1690-1700 cm\(^{-1}\); C=C stretching at 1590-1600 cm\(^{-1}\);
phenylene rings at 1590-1510 cm\(^{-1}\).

\(^1\)H NMR (90 MHz, CDCl\(_3\), \(\delta\)):
8.25-8.60 ppm (m, 4H 30, 34, 35, 39 Ar-H), 7.50 – 8.10 ppm (m, 12H 14-19, 31-33, 36-38 Ar-H), 7.15 –7.25 ppm (s, 2H, 8, 9- CH=C), 2.60-2.90 ppm (t, 4H, 2, 4- 2CH\(_2\)), 1.25 – 1.85 ppm (pent., 2H 3-CH\(_2\)) of cyclohexanone.

IR (KBr) (IIa model): \(\nu = 1735\) (s) (C=O of ester group), \(1670\) (s) (C=O of cyclohexanone), 1600 (s) (C=C).

**2.6. Synthesis of 4, 4-Azodibenzoyldichloride**

This has been done in two steps the first is the formation of azobenzene 4, 4-dicarboxylic acid followed by conversion to acid chloride azobenzene 4, 4-dicarboxylchloride as described previously [34, 35].

**2.7. Synthesis of Terpolymers**

In a three necked, round – bottomed flask (500 cm\(^3\) volume) equipped with a mechanical stirrer (2000 rpm/min), dry nitrogen inlet and out let, and dropper, a mixture of three different monomers (mol/mol) of diarylidene cyclohexanone, and a suitable quantity of sodium hydroxide; that is stoichiometric quantity (0.02mol) of 100% excess (0.04 mol) dissolved in 100 ml of water was introduced. After mixing (0.02 mol.) of acid chloride dissolved in 40 ml methylene chloride was added over a period 2-3 min. at 25°C and vigorously stirring. After complete addition of acid chloride, the stirring was continued for 60 min., during which yellow solid product separated out. The solid polymer was filtered off, washed by water, hot ethanol, hot acetone, and dried under reduced pressure (1 mmHg) at 100°C for two days. Three terpolyesters were separated and casted from methylene chloride.

**Table 1.** Mole ratios of monomers, acid chlorides, physical states, yield%, viscosity average molecular weight and glass temperature of synthetic terpolyesters 4a, 4b and 4c.

<table>
<thead>
<tr>
<th>Code</th>
<th>Acid chloride (0.06mol) in 100ml dry CH(_2)Cl(_2)</th>
<th>Yield [%]</th>
<th>Mv (10^3) g/mol</th>
<th>(T_g) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 a</td>
<td>6.10 g</td>
<td>80</td>
<td>8500</td>
<td>345</td>
</tr>
<tr>
<td>4 b</td>
<td>7.00 g</td>
<td>86</td>
<td>10300</td>
<td>105</td>
</tr>
<tr>
<td>4 c</td>
<td>9.20 g</td>
<td>89</td>
<td>9600</td>
<td>325</td>
</tr>
</tbody>
</table>
3. Results and Discussion

Scheme 1 describe the preparation of unsaturated terpolyesters by interfacial condensation polymerization of three monomers 1, 2 and 3 with different acid chloride involving aliphatic, aromatic and azo compound.

![Synthesis of terpolyesters 4a, 4b and 4c](image)

3.1. Polymer Characterizations

3.1.1. IR spectra

KBr FT IR spectra showed characteristic bands $\nu = 1730-1745$ cm$^{-1}$ for C=O ester; $\nu = 1690-1700$ cm$^{-1}$ C=O cyclohexanone; $\nu = 1590-1600$ cm$^{-1}$ C=C stretching; $\nu = 1590-1510$ cm$^{-1}$ phenylene rings; and $\nu = 1250-1260$ cm$^{-1}$ C-O-C bonds (ether linkage). All data was in logic with the chemical structure.
3.1.2. $^1$H NMR Spectra

BRUKER DRX-500 spectrometer was used to record H-proton $^1$H-NMR of terpolyesters in CF$_3$COOD. The $^1$HNMR for unsaturated terpolyesters (4a, 4b, 4c) was shown in Figure 1. Each spectrum recorded the presence of; 0.93-1.10, 1.36-1.73, 3.20-3.62 ppm (m-CH$_2$-cyclohexanone), 4.12-4.38 ppm (m-OCH$_3$), and 7.07-8.98 (m-Ar-H). Moreover, polymer 5d with sebacate main chain showed at 2.52-2.96 ppm (m-CH$_2$).
3.1.3. Solubility

Unsaturated terpolyesters were tested for solubility in different solvents e.g. N-methyl-2-pyrrolidone (NMP), dimethyl formamide (DMF), m-cresol, dimethylsulphoxide (DMSO), CHCl₃–acetone mixture, dichloroacetic acid (DCA), and concentrated H₂SO₄. Table 2, cleared the majority of the terpolyesters were completely insoluble in NMP, m-cresol, CHCl₃–acetone mixture. While, in the protic solvents as (DCA) (Cl₂CHCOOH) or (TFA) (F₃CCOOH) terpolyesters are completely soluble at room temperature. As similar, in (conc.H₂SO₄) all are completely soluble at room temperature. It was observed the change in acid chloride from aliphatic and aromatic influenced sharply in the solubility of terpolyesters. We have also detected the slight solubility of unsaturated terpolyesters with aliphatic acid chlorides in the main chain in DMSO and DMF.

Table 2. Solubility characteristics of copolyesters series 4a, 4b and 4c.

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>4b</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>4c</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

1(DMF), 2 (DMSO), 3 (NMP), 4 (m-cresol), 5 (Chloroform: acetone 1: 1), 6 (DCA), 7 (TFA), 8 (Conc. H₂SO₄). (+) Soluble at room temperature (RT); (±) partially soluble at RT; (-) insoluble at RT.

3.1.4. The molecular weight (Mv)

Mark-Hounwink equation was used for determination of intrinsic viscosity which further used for the determination of viscosity average molecular weight of terpolyesters as discussed in recent articles and lectures [36-37]. Table1 summarized all viscosity average molecular weights (4a-4c). We noticed an increase in the viscosity average molecular weight of terpolyester 4b that has sebacoyl in the main chain refereeing to the highly polydispersity of aliphatic polymers than the aromatic one.

3.1.5. Differential thermal analysis (DTA)

Differential thermal analysis (DTA) was used to record the glass transition temperature of unsaturated terpolyesters with different acid chlorides in air at a heating rate of 10 °C min⁻¹ as shown in Figure 3 and were summarized in Table 1. Polymer 4b has flexible chain is due to the presence of - (COO) - and - (CH₂) - units in the main. The chain rigidity is enhanced by
the presence of aromatic groups in the main chains as demonstrated in polymers 4a, 4c [38].

The higher $T_g$ value of polymer 4c with azo group attributed to the highly hindrances to internal rotation about primary valance bonds, and hence raises $T_g$ [39]

![Figure 3. DTA of unsaturated terpolyesters 4a, 4b and 4c](image)

3.1.6. X-Ray Analysis

The X-ray diffractograms (Figure 4) showed a broad peak at $2\theta = 20^\circ$. This peak is associated to the intra-chain segments distance of 0.45 nm (determined using the Bragg’s law). Figure 4 showed some results;

1. Unsaturated terpolyesters 4b with eight methylene groups (sebacoyl), increase the polymer chain flexibility.

3. Unsaturated terpolyesters (4a, 4c) with both azo –N=N- group and unsaturation bonds effect side by side in the polymer towards some extent of crystallinity [36-37].
Figure 4. X-ray diffraction patterns of terpolymers 4a, 4b, 4c

3.1.7. Morphological Features

scanning electron microscopy (SEM) was used to scan the surface and the morphology of the synthesised terpolymers. The surface of terpolymer 4a Figure 5, magnification of X=200 likes fibrous aggregates; terpolymers 4b in Figure 6, magnification of X=200 appeared as fibrous aggregates; terpolymers 4c with azo group in the main chain with magnification of X=750 in Figure 7 showed waxy-looking masses.

Figures 5. SEM images of terpolymers 4a surface at 200nm magnifications.
Figures 6. SEM images of terpolyester 4b, surface at 200nm magnifications.

Figures 7: SEM images of terpolyesters 4c, surface at 750 nm magnifications.

3.2. Electrical Properties of Terpolyesters

The electrical properties of unsaturated terpolyesters have been tested with special attention to dielectrical (ε) constant of solid polymers. Table 3 summarized the electrical parameters of unsaturated terpolyesters with different acid chloride in the main chain. From Table 3 and Figure 8, 9 for polymers 4a and 4c with aliphatic and aromatic acid chloride exhibited insulator properties, while others with aromatic azo acid chlorides have some electricity due to the polarization and the electron displacement of the azo group with aromatic conjugation as shown in Figure 10.
Table 3: The values of relative dielectric constant ($\varepsilon$), parallel resistance ($R_p$) and parallel capacitance ($C_p$) for selected copolyesters and terpolyesters.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>d(m) $10^{-3}$</th>
<th>$\varepsilon^a$</th>
<th>$R_p^b$ ($\Omega$) $10^7$</th>
<th>$C_p^c$ $10^{-11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>3.21</td>
<td>81-86</td>
<td>8-10</td>
<td>1.57</td>
</tr>
<tr>
<td>4b</td>
<td>5.19</td>
<td>101-111</td>
<td>7-9</td>
<td>1.24</td>
</tr>
<tr>
<td>4c</td>
<td>1.51</td>
<td>72-75</td>
<td>5-7</td>
<td>1.35</td>
</tr>
</tbody>
</table>

$^a$ dielectric constant
$^b$ parallel resistance
$^c$ parallel capacitance

Figure 8. Relation between dielectric constant and frequency for terpolyester 4a.

Figure 9. Relation between dielectric constant and frequency for terpolyester 4b.
Figure 10. Relation between dielectric constant and frequency for terpolyester 4c.

3.3. Mechanical Properties

Values of longitudinal, transverse ultrasonic velocities and elastic moduli constants for terpolyesters 4a, 4b and 4c are cleared in Table 4. The ultrasonic changes may be explained on the basis of physical properties of terpolyesters as shown in Table 4, 5. They are heterogeneous and have higher long chain. Terpolyester 4b is more elastic than terpolyester 4a due to the presence of methylene group which increase the movement of polymer chain [44]. Terpolyester with azo groups 4c in the main chain showed average elasticity between those with aromatic and aliphatic groups, this can be attributed to the mobility of azo group in presence of aromatic chain groups [44].

Table 4: Densities, ultrasonic velocities (longitudinal, transverse) and Poisson’s ratio for copolyesters and terpolyesters.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\rho^a$ (Kg/m$^3$) $10^3$</th>
<th>$V_L^b$ (m/s)</th>
<th>$V_s^c$ (m/s)</th>
<th>$\nu^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>1.42</td>
<td>6013</td>
<td>3235</td>
<td>0.30</td>
</tr>
<tr>
<td>4b</td>
<td>1.31</td>
<td>6528</td>
<td>3223</td>
<td>0.35</td>
</tr>
<tr>
<td>4c</td>
<td>1.44</td>
<td>6347</td>
<td>3246</td>
<td>0.33</td>
</tr>
</tbody>
</table>

$^a$ density
$^b$ longtodial velocity
$^c$ transverse velocity
$^d$ Poisson’s ratio
Table 5: Elastic moduli for selected copolyesters and terpolyesters

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(L)^{a} GPa</th>
<th>(G)^{b} GPa</th>
<th>(E)^{c} GPa</th>
<th>(K)^{d} GPa</th>
<th>(H)^{e} GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>51.02</td>
<td>14.76</td>
<td>38.06</td>
<td>31.44</td>
<td>2.11</td>
</tr>
<tr>
<td>4b</td>
<td>55.39</td>
<td>13.50</td>
<td>36.17</td>
<td>37.40</td>
<td>1.45</td>
</tr>
<tr>
<td>4c</td>
<td>48.24</td>
<td>13.28</td>
<td>34.78</td>
<td>30.55</td>
<td>1.69</td>
</tr>
</tbody>
</table>

^a Longitudinal Modulus
^b Shear Modulus
^c Young's Modulus
^d Bulk Modulus
^e Micro-Hardness

4. Conclusion

The study reported synthesis and characterization of new terpolyesters based on new bisphenol with different acid chlorides. The influences of acid chloride on the physical characterization were our aim of study. The solubility of terpolyesters was very poor in organic and inorganic solvent except in very strong acids such as sulphuric and triflouroacetic acids. XRD results showed amorphous cases with aliphatic acid chloride while it showed some semi-crystalline aromatic and azo terpolyesters. The $T_{gs}$ values showed higher value for terpolyesters with aliphatic chain. The heterogeneous surface with the formation of layers has shown by SEM images. The dielectric constant of terpolyesters with aliphatic or aromatic chains demonstrated the insulator characters while with azo groups in the main chain demonstrated some electrical properties due to highly polarizability. The mechanical properties of terpolyesters were investigated by ultrasonic impulses and was used to determine different kinds of elastic moduli. It has been observed that terpolyesters with aliphatic acid chloride in the main chain have more elasticity than others with aromatic acid chloride in the chains.

References


R. O. Ebewel, B. Raton Polymer Science and Technology (chain flexibility P.111) London