Synthesis and Characterization of Unsaturated Polyester Resin and Studying Their Thermo Properties

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Abstract

In the first step of this work, two samples of Unsaturated Polyester based on itaconic acid and 1,2-propylene glycol were prepared by polycondensation. The prepared unsaturated polyesters were identified using IR spectroscopy. In the second step of the work, the prepared unsaturated polyester resins in the previous step has been crosslinked, by chain growth polymerization, using UV radiation and presence of photoinitiator, the crosslinking reaction was tracking using the IR spectroscopy after that thermal properties were studied.

Keywords: Unsaturated Polyester, itaconic acid, polycondensation, crosslinking.

Introduction

In the last years, unsaturated polyesters (UPs) and unsaturated polyester resins (UPRs) have attracted a significant attention from both the academia and industry, since they are produced from inexpensive monomers, are easy to synthesize and process and have a wide range of applications. One way to prepare UPs is by polycondensation of diols and aromatic or aliphatic dicarboxylic acids, at high temperatures, in the absence of solvents using, frequently, maleic anhydride as the unsaturated component.

The UPs are afterwards crosslinked in the presence of a monomer that functions also as solvent, usually styrene, to yield the UPRs. The resulting viscous solution can be transformed into a hardened product by means of catalysts which generate a free radical copolymerisation reaction between the monomer and the unsaturation sites present in the polyester backbone [1].

Polyesters are one of the most versatile synthetic copolymers. Polyesters are produced in high volume that exceeds 30 billion pounds a year worldwide. They are widely used commercially as fibres, plastics, composites and for coatings applications too. They are heterochain macromolecules that possess carboxylate ester groups as an integral component of their polymer backbones. Polyesters have received a great deal of attention since the early work of Carothers, who initiated study on many step-growth polymerizations. His work involved A-B w-hydroxy acids, the polymerization of certain lactones and the esterification of A-A linear diols with B-B terminal aliphatic dicarboxylic acids. The resulting copolymers were of low molecular weight (8,000-10,000 g/mol), hard, crystalline solids and susceptible to conversion from the molten state to filaments which could be stretched below their melting point with an ultimate increase in strength.

Carothers worked with aliphatic straight-chain polyesters, which were soluble in organic liquids, low melting and had poor resistance to hydrolysis. These polyesters were not used as textile fibres. The extension of these concepts later led to the discovery of nylon-6,6 in 1935 and Whinfield and Dickson developed poly(ethylene terephthalate) (PET) in 1941. A partially aromatic organic structure was necessary to increase melting temperature (Tm) above 250°C. A large number of polyester structures have found use in industry today which displays a wide variety of properties and applications. The physico-chemical and thermomechanical properties of the UPs and UPRs are determined by the combinationthe type of reactive solvent used, and the conditions of crosslinking [2].

Apparatus Section

Mechanical stirrer, optical absorption spectrum infrared device model FT-IR-4100 from the Japanese company Jasco, UV type metal halide lamp TL, MHTD-150watt, Differential Scanning Calorimetry (DSC20), Thermogravimetry Analyser (TG 50).

Chemicals Materials

Itaconic acid (IA, 99%), propylene glycol (PG, 99%), Phthalic anhydride(PA,99%), p- Toluene sulfonic acid (PTSA), Xylene(95%), Hydroquinone(99%), Potassium hydroxide(85%), Pyridine(98%), Acetone(98%), Styrene(99%), Acrylic acid.

Experimental study

1. Synthesis of Unsaturated Polyester Resin (UPR-1):

A mixture of 1.1 mol Propylene glycol (PG),0.3 mol Itaconic acid(IA), 0.7 mol Phthalic anhydride (PA), 0.5% p- Toluene sulfonic acid (PTSA) and Xylene as solvent was charged in a three-neck reaction kettle equipped with mechanical stirrer, thermometer, nitrogen-gas introducing tube, separator and water condenser. The mixture was mechanically stirred and heated at 120 °C under nitrogen gas stream for about one hour then continues heating at 150-180 °C until an acid number of 40 was reached. During esterification reaction, water formed as by product and was continuously removed from the reaction mass as it inhibits the rate of reaction. The Xylene was completely distilled out and reaction product was allowed to cool. When the temperature reached to 160 °C, (300ppm) of hydroquinone was added as inhibitor and when resin temperature dropped below the boiling point of reactive diluent (Styrene/ Acrylic acid) in our study, the polyester resin were mixed with (styrene / Acrylic acid) by 45 weight percent of resin. The polymer obtained was characterized IR spectroscopy[3].

Figure (1): unsaturated polyester preparation apparatus

2. Infrared Spectra:

An IR spectrum of prepolymer polyester resin(based on styrene) is shown in figure-2 and An IR spectrum of prepolymer polyester resin(based on Acrylic acid) is shown in figure-3. A Nicolet Impact 400DFT-IR Spectrophotometer was employed for the measurements. The spectrum was run by applying resin sample on KBr cell covering the range of frequencies from 4000-400 cm-1 with scanning period of 20 seconds. The crushed powder sample (2-3mg) in the form of a pellet was prepared by mixing with dry KBr (1g).

The spectrophotometer was set at 100% transmittance with pure KBr pellet [4].

3. Determination of The number average molecular weights by using end group analysis:

The endpoints in the linear polystyrene are the ends of carboxylic and hydroxyl endings, which determine the concentration of carboxylic endings by determining the acidity number (AV) according to the method (ASTM D 4662-03) [5]. The hydroxyl number (HV) determines the concentration of the hydroxyl endings, For the method (ASTM D 4274-99, TEST A) [6]. Where the acidity number of the final product is determined by taking a thoroughly balanced sample and resolving it with a specified amount of acetone and then calibrating it and calibrating the test with a solution of 0.5N potassium hydroxide with Phenol Phthalate as a detector while determination of the hydroxyl number is done on the basis of the sample of the sample with a solution without acetic acid in the pyridine (the detector of the acella) in a thick walled enclosure for two hours at a temperature of 98 ° C. Then we simmer the surplus of the water without vinegar acid by adding distilled water, Vinegar produced in the sample and tested with N0.5 solution of potassium hydroxide. (The witness is acetone in the case of acidity number, in the case of hydroxyl number, the witness is the shop and the detector used).

4. The Cross-Linking Polyester Resins:

Mix 5 ml of the prepared resin and add 2% weight of Triarylsulfonium hexafluoroantimonate salts, mixed 50 wt% in propylene carbonate as an insecticide as a Photoreceptor. Mix the mixture well, then put two points from the previous mixture on a clean glass plate and place a second glass plate on it and squeeze it manually until the sample is fully distributed. The inner surface of the two plates. The two plates under the ultraviolet light of the 150Watt metal halide bulb are located 10Cm away from the vertical sample.[7]

5. Summary and conclusions:

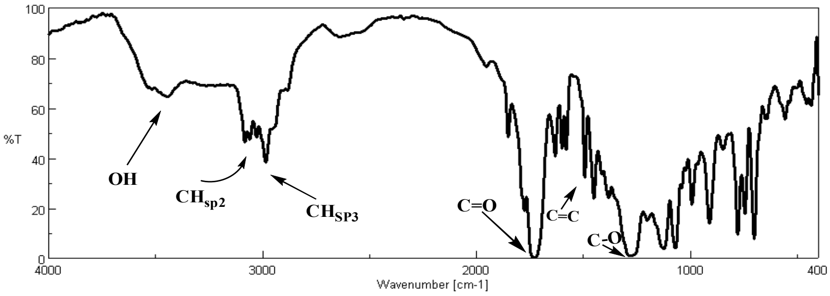
- two samples of Unsaturated Polyester based on itaconic acid and 1,2-propylene glycol and Phthalic anhydride were prepared by polycondensation in Molar ratios as shown in table 1

Table 1: Molar ratios taken for reactants

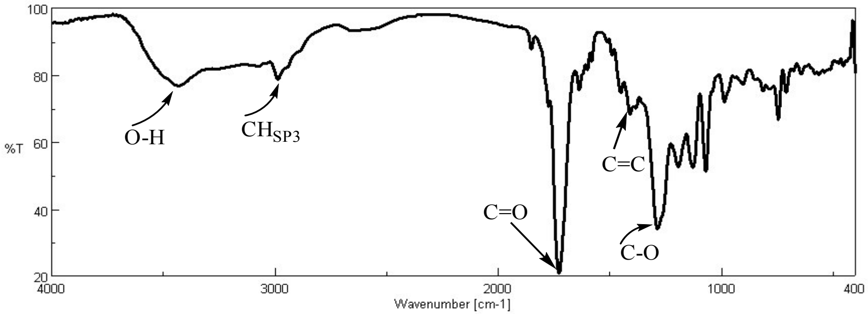
Sample	PG)(	PHA)(	IA)(	Cross-Linking factor
1	**1.1**	**0.5**	**0.5**	**Styrene**
2	**1.1**	**0.5**	**0.5**	**Acrylic acid**

- **Infrared Spectra**:

  A strong absorption band at 745cm^{-1} and a weak band at 1069 cm^{-1} can be attributed to -C-H bending arising from 1 and 3 position in benzene ring. A broad-spectrum absorption bend at 1285cm-1 confirms the presence of –C-O-C- of ester linkage. A strong absorption peak appearing at 1450 cm^{-1} was assigned to –C=C– group of polyester. A medium absorption band at 1461 cm^{-1} can beattributed to –C-H bending. The presence of –C=O and symmetric –CH stretching was confirmed by the presence of strong bend at 1727 cm^{-1} and 2984 cm^{-1} respectively. The band at 1727cm^{-1}confirms the presence of –C=O ester group. In addition to this, disappearance of anhydride peak at 1755 cm^{-1} in phthalic anhydride and hydroxyl peak at 1375 cm^{-1} proplyene glycol confirms the formation of polyester.



Figure(2): An IR spectrum of prepolymer polyester resin(based on styrene)



Figure(3): An IR spectrum of prepolymer polyester resin(based on Acrylic acid)

- **Determination of The number average molecular weights by using end group analysis**:

  In Table 2, the acidity number (AV), The hydroxyl number (HV) values of the prepared samples and The number average molecular weights were recorded by using end group analysis, depending on the following relationships:

$$\mathbf{Av} = \frac{(V2-V1)(0.0561)(1000)N}{W}$$

where:

A = KOH solution required for titration of the sample, mL,
B = KOH solution required for titration of the blank, mL,
N = normality of the KOH solution, and
W = sample used, g.

The previous relationship is used to calculate both AV and HV.

The value of The number average molecular weights for each sample is calculated based on the following relationship:

$$\overline{\mathrm{M}}_{\mathrm{n}} = \frac{2 \times 1000 \times 56.1}{AV + \mathrm{HV}}$$

Table 2: Experimental values of samples prepared

Sample	AV(mg KOH /g polymer)	HV(mg KOH /g polymer)	$\overline{M}_n$ (g/mol)
1	**40.44**	**2.61**	**2606.27**
2	**41.98**	**2.45**	**2525.32**

❖ Thin film preparation Cross-Linking Polyester Resins:

The samples were simulated for a period of 3.5 to 4 minutes and Figure 4 shows the interlocking polyester plate after removing it from the two glass plates. The obtained slide shows clear stransparency and gloss that can be used in the paints.

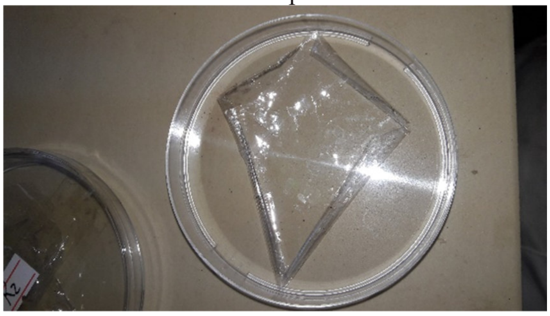


Figure (4): Polyster plate after Cross-Linking

❖ study the thermal analysis:

1. Thermogravimetric Analysis (TGA):

Thermogravimetric Analysis (TGA) is a thermal analysis technique that measures the amount and rate of change in weight of a material as a function of temperature or time in a controlled atmosphere.In this study Thermogravimetric analysis was carried out on a TG 50instrument 8 (Mettler-Toledo), at a heating rate of 10 ºC/ min in a nitrogen atmosphere. Mass loss was characterized in the range from 30 ºC to 700 ºC and typical samples weight was 8-9 mg.

The thermal stability was studied by using of TGA. These measurements are used primarily to determine the thermal stability or oxidative stability of these materials [8].

The study was conducted for two sheets of polystyrene, which were prepared for the same mullet but using two different Cross-Linking factors.

Figure (5) shows the TGA curve of sample T1 an Unsaturated Polyester sample using styrene as a Cross-Linking factor.

Figure (6) shows the TGA curve of sample T2 with the same unsaturated polyester sample but using acrylic acid as a Cross-Linking factor.

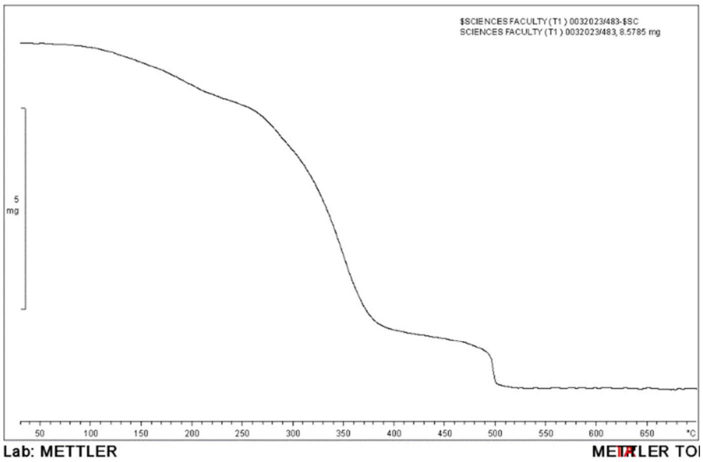
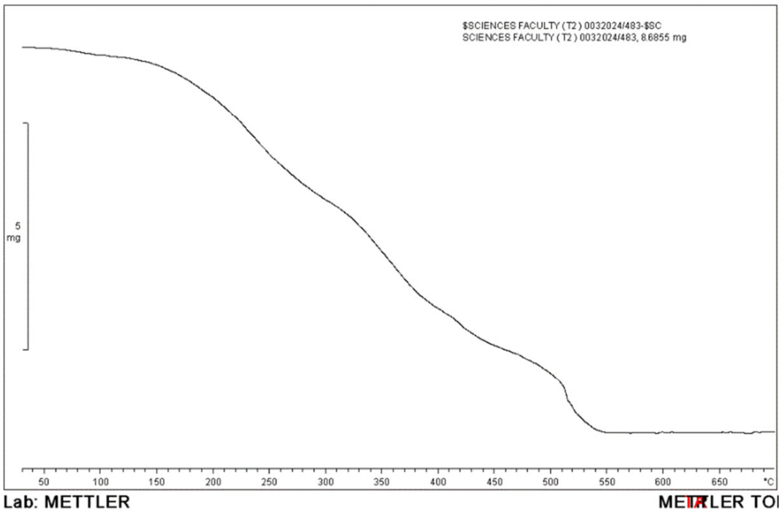


Figure (5) Curved TGA for sample T1

From the previous curve it becomes clear that the aging begins at (250 ° C) and ends at (500 ° C) with a loss of weight within the limits of (50%).

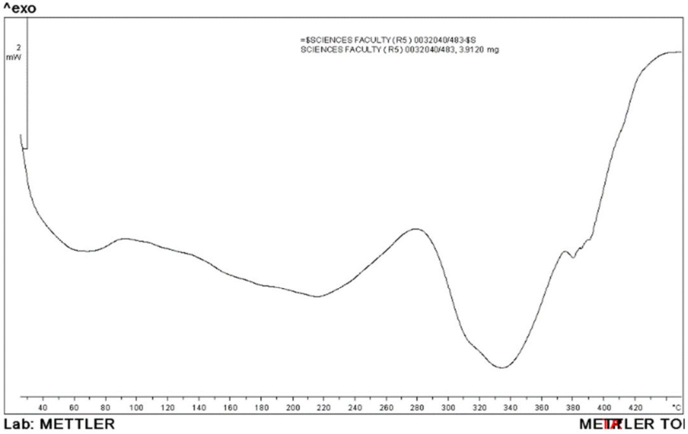


Figure(6) Curved TGA for sample T2

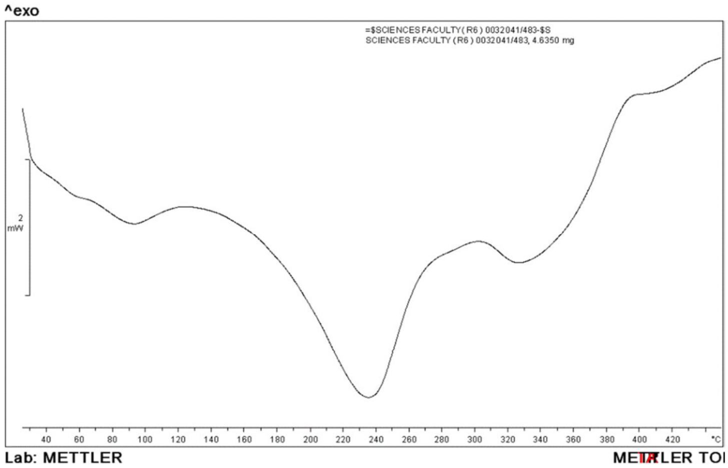
From the previous curve it becomes clear that the aging begins at (150 ° C) and ends at (500 ° C) with a loss of weight within the limits of (50%).

2. Differential Scanning Calorimetry(DSC):

Differential Scanning Calorimetry, or DSC, is a thermal analysis technique that looks at how a material's heat capacity (Cp) is changed by temperature. In this study Differential Scanning Calorimetry test was carried out on a DSC20 at a heating rate of 10 ºC/ min in a nitrogen atmosphere. Mass loss was characterized in the range from 40 ºC to 400 ºC and typical samples weight was 3.5-4.7 mg.



Figure(7): Curved DSC for sample R_5



Figure(8): Curved DSC for sample R_6

Figure (7) shows the DSC curve of sample R_5 an Unsaturated Polyester sample using styrene as a Cross-Linking factor.

Figure (8) shows the DSC curve of sample R_6 with the same unsaturated polyester sample but using acrylic acid as a Cross-Linking factor.

- **Determination of glass transition degree through differential thermal analysis curves:**

From Figure (5) we note that the glass transformation degree of the sample (R_5) is equal to 100 ºC while 75 ºC for the sample R_6. Hence, we can say that styrene as Cross-Linking factor is better than acrylic acid.

References

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