Tertiary recycling of poly (ethylene terephthalate) wastes for production of polyurethane-polyisocyanurate foams

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RAKSHIT MATHUR

(*Roll No: 2K11/PTE/11*)

Under the esteemed guidance

Of

DR. PRASUN K ROY

SCIENTIST 'E'

CENTRE FOR FIRE EXPLOSIVE AND FIRE SAFETY (CFEES)

DEFENSE RESEARCH DEVELOPMENT ORGANISATION (DRDO)

TIMARPUR DELHI 110054

&

DR. D. KUMAR

HEAD OF DEPARTMENT

DEPARTMENT OF APPLIED CHEMISTRY AND POLYMER TECHNOLOGY

DELHI TECHNOLOGICAL UNIVERSITY

(*FORMERLY DELHI COLLEGE OF ENGINEERING*)

Delhi-110042

CERTIFICATE

This is to certify that the M.Tech major project entitled **"Tertiary recycling of poly (ethylene terephthalate) wastes for production of polyurethane-polyisocyanurate foams"**, submitted by **Rakshit Mathur**, for the award of the degree of **"Master of Technology in Polymer Technology"** is a record of bonafide work carried out by him. Rakshit Mathur has worked under our guidance and supervision and has fulfilled the requirements for the submission of the dissertation. The project work has been carried out during the session 2012-2013.

To the best of our knowledge and belief the content therein is his own original work and has been submitted to any other university or institute for the award of any degree or diploma.

Dr. PRASUN K ROY   **Dr. D. KUMAR**
Scientist 'E'   Head of Department
Centre For Fire Explosive &   Department of Applied Chemistry
Environment Safety (CFEES) ,   & Polymer Technology,
Defence Research & Development   Delhi Technological University
Organisation (DRDO)   Bawana Road, Delhi-110042
Timarpur Delhi-110054

ACKNOWLEDGEMENT

DATE: (RAKSHIT MATHUR)

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ABSTRACT

The present work aims at tertiary recycling of poly (ethylene terephthalate) (PET) wastes to derive raw materials for production of polyurethane-polyisocyanurate foams. The first step involves glycolytic depolymerisation of PET in the presence of diethylene glycol (DEG), under the influence of microwave irradiation with an aim to reduce the energy intensiveness of the process. Experimental conditions like PET: DEG ratio, reaction time and concentration of glycerol were optimized to maximize the product yield. Multiple extrusion of PET led to reduction in its molecular weight, which increased its reactivity towards glycolysis. The time required for glycolytic depolymerisation of PET could be significantly reduced by employing microwave irradiation instead of conventional thermal process. The glycolysate was subsequently reacted with two different diacids: adipic acid (AA) and sebacic acid (SA) to obtain aromatic polyester polyols. For the purpose of comparison, analogous aliphatic polyester polyols were also prepared by reacting AA and SA with DEG under similar reaction conditions. The polyols were subsequently employed as a raw material for the preparation of polyurethane foams by reacting with diphenylmethane diisocyanate. The hydroxyl: NCO ratio in the formulation was decreased to introduce isocyanurate linkages, which resulted in the formation of polyisocyanurate foams with high compressive strength. Various characterization techniques were employed to determine the effect of the aromatic phenyl group and chain length of the diacid on the mechanical and structural properties of the resultant foams.

CHAPTER 1

INTRODUCTION

1.1 RECYCLING OF PET

In terms of the scrap values for recycled materials, PET is considered one of the easiest materials to recycle**,** and is second only to aluminum [1]. Because of this, recycling of PET has been one of the most successful and widespread among polymer recycling[2, 3]. Methods for recycling of PET can be categorized into four groups namely primary, secondary, tertiary, and quaternary recycling.

1.1.1   PRIMARY RECYCLING

Primary recycling or the re-extrusion is the oldest known technique for recycling of PET, and is commonly practised. It refers to the ''in-plant'' recycling of the scrap material generated in the production line. Though the process is simple and can be offered at low cost, but is not widely followed among the recyclers as it requires uncontaminated scrap, and single-type waste [4, 5].

1.1.2   SECONDARY RECYCLING

Secondary recycling or mechanical recycling, involves use of mechanical means for reprocessing of granules and separation of the polymer from its contaminants. The steps include size reduction and melt filtration for sorting and separation of wastes, removal of contaminants, crushing and grinding for reduction of size, extrusion by heat, and reforming[6]. Heterogeneity of the solid

waste, and the degradation of the product properties each time it is recycled are the two main issues related to secondary recycling. Degradation results as the chain scission reactions caused by the presence of water and trace acidic impurities which lowers the molecular weight of the recycled resin. Intensive drying, reprocessing with degassing vacuum, the use of chain extender compounds are some of the general strategies used for maintaining the polymer average molecular weight during reprocessing include. Waste with the same type of resin, but of different colour leads to an undesirable gray colour which is again remains an unresolved issue.

1.1.3 TERTIARY RECYCLING

Tertiary recycling or chemical recycling, which involves the chemical transformation of the PET polymer chain. The process can either be a total depolymerisation of the polymer back to its monomers or a partial depolymerization to its oligomers and other industrial chemicals by means of solvolytic chain cleavage. Since PET is a polyester with functional ester groups, reagents such as water, alcohols, acids, glycols, and amines can be cleaved for the purpose of cleavage. Also, PET can be transformed back to its monomer or oligomer units by pushing the reaction to the opposite direction through the addition of a condensation product as it is formed through a reversible polycondensation reaction. The low molecular products thus produced can then be purified and reused as raw materials for preparation of high quality chemical products[7].

Among the recycling methods, chemical recycling follows the principles of 'sustainable development', defined as development that meets the needs of present generation without compromising the ability of future generations to meet their needs[8], as it generates an alternative to existing raw materials (monomers) from which the same or some other polymer is made. Thus need for extra resources for the production of PET is reduced[9].

The reaction mechanism for PET depolymerization consists of three reversible reactions. First, rapid protonation of the carbonyl carbon in the polymer chain, where the carbonyl oxygen is converted to a second hydroxyl group. Second, the hydroxyl oxygen of the added hydroxyl-bearing molecule slowly attacks the protonated carboxyl carbon atom. Third, the carbonyl oxygen (which was converted to hydroxyl group in the first step) and a proton are rapidly removed to form water or a simple alcohol and the catalytic proton [10].

As shown in Scheme1.[11], there are five main routes in PET chemical recycling depending on the cleaving reagent: glycol for glycolysis, methanol for methanolysis, water for hydrolysis, amines for aminolysis and acids for acidolysis. The research on PET chemical recycling has been since last five decades since then many patents were filed which led to numerous researches in order to fully understand the chemical pathways of the depolymerization methods, and improve desired products yield from these methods
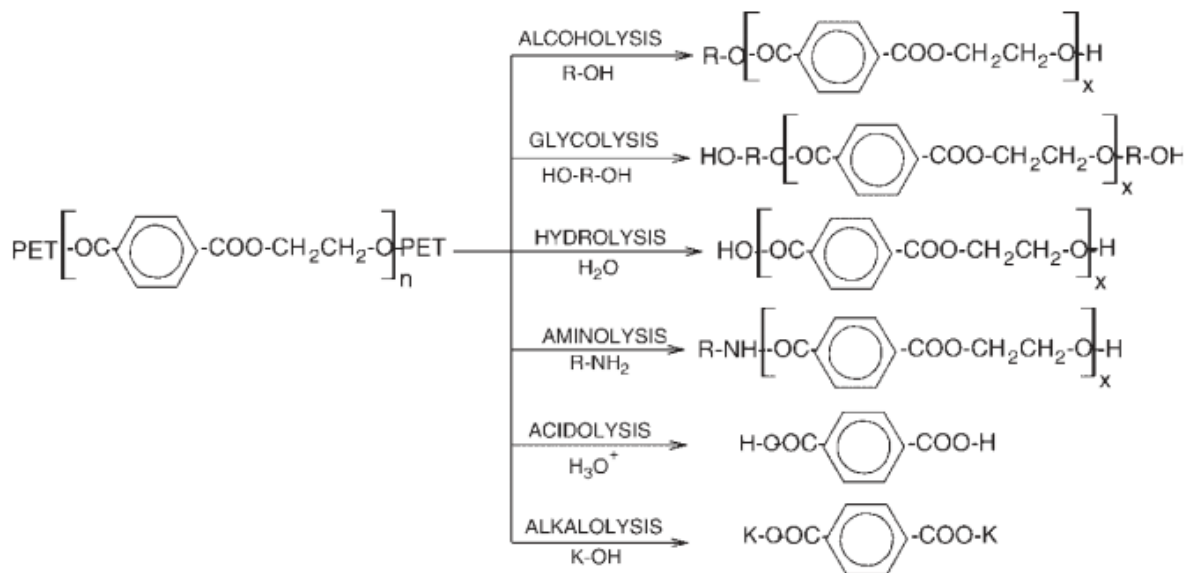
Scheme1: Different solvolysis methods for PET depolymerization.

1.1.4   QUATERNARY RECYCLING

Quaternary recycling is the recovery of energy content from the plastic waste by incineration. It involves recovery of the chemical energy stored in plastics waste in the form of thermal energy via incineration. When the collection, sorting and separation of plastics waste are difficult or economically not viable, or the waste is toxic and hazardous to handle, quaternary recycling is the best waste management option. However, it is thought to be ecologically unacceptable due to potential health risks from the air born toxic substances.

Apart from the above mentioned methods, direct reuse of a plastic material (i.e. PET) could be considered as a "zero order" recycling technique[12]. As refilling and reuse of PET bottles is a common practice in many countries.

1.2 GLYCOLYTIC DEPOLYMERISATION OF PET

The glycolysis of PET is molecular degradation of PET polymer chain by glycols, in the presence of a trans-esterification catalyst, mainly different class of metal acetates. In glycolysis ester linkages are broken and replaced with hydroxyl terminals. PET waste can be depolymerized by glycolysis to obtain oligomeric diols and polyols, or glycolyzed into its monomeric units, bis(2-hydroxyethyl) terephthalate or dimethyl terephthalate.

The glycolysis of PET has been found to depend on the reaction conditions represented in the glycolysis time, glycolysis temperature, catalyst concentration and glycol concentration. C. Chen et al. [13]found that the sequence of the main effects on the glycolysis conversion of recycled PET is in the following descending order: catalyst concentration > glycolysis temperature > glycolysis time. Baliga and co-workers [22] studied extensively the efficiency of different metal acetate catalysts on the rate of the glycolysis of PET waste bottles. Among the four metal

acetates studied were Pb, Zn, Co and Mn-acetates and the Zn-acetate was found to be the most suitable in terms of the amount depolymerization products.[13]

PET waste can be depolymerised by glycolysis obtaining oligomeric diols and polyols, or glycolysed into the constitutional repeating units of PET bis(hydroxyethylene)terephthalate (BHET) and a mixture of its oligomers as shown in (Scheme2).[14]
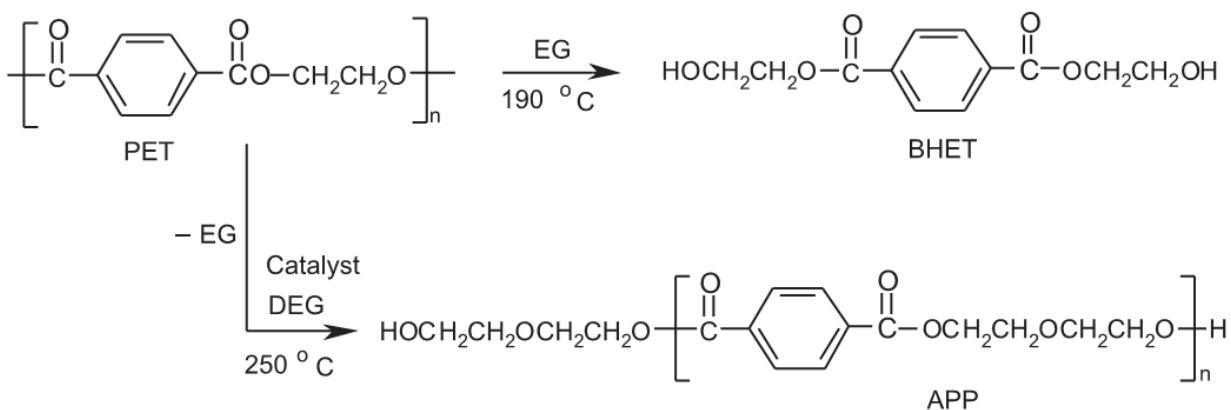
Scheme 2: Glycolysis of PET with EG and DEG to give BHET and APP (Aromatic Polyester Polyols) respectively

Irena Vitakuskiene et al studied the recycling of industrial PET waste by glycolysis with EG directed to BHET, and glycolysis with DEG in the presence of glycerol and adipic acid directed to polyester polyols for an increased stability against crystallization, and investigated properties of aromatic polyester polyols (APP) obtained using various amounts and types of catalysts.[14]

1.3 MICROWAVE ASSISTED GLYCOLYSIS

Recently, recycling of PET using hydrolysis, glycolysis and aminolysis under microwave irradiation has been proposed [15-17]. PET recycling in a microwave reactor has been proved a very beneficial method resulting not only in material recovery but also in substantial energy saving.

Microwave have been used to speed up chemical reactions in the laboratories which led scientists to investigate the mechanism of microwave dielectric heating and to identify the advantages of the technique for chemical synthesis. During recent years, microwaves have been extensively used for carrying out chemical reactions and have become a useful non-conventional energy source for performing organic synthesis. This is supported by a great number of publications in recent years, related to the application of microwaves as a consequence of a great availability of dedicated and reliable microwave instrumentation.[18, 19]

1.3.1 MICROWAVE HEATING

Microwaves couple directly with the molecules of the entire reaction mixture, leading to a rapid rise in the temperature. Since the process is not limited by the thermal conductivity of the vessel, the result is an instantaneous localized superheating of any substance that will respond to either dipole rotation or ionic conductivity. Only the reaction vessel contents are heated and not the vessel itself; better homogeneity and selective heating of polar molecules might be achieved

The acceleration of chemical reactions by microwave exposure results from the interactions between the material and electromagnetic field leading to the thermal and specific (non-thermal) effects. For microwave heating, the substance must possess a dipole moment. A dipole is sensitive to external electric field and tries to align itself with the field by rotation. If submitted to an alternating current, the electric field is inversed at each alterance and therefore dipoles tend to move together to follow the inversed electric field. Such a characteristic induces rotation and friction of the molecules, which dissipates as internal homogeneous heating. The electric field of commonly used irradiation frequency (2450 MHz) oscillates 4.9×10^9 times per second. Thus, microwave heating is directly dependent on dielectric properties of a substance, dielectric

constant (ε') and dielectric loss (ε"). The ability of a material to convert electromagnetic energy into heat energy at a given frequency and temperature, is calculated using

$$\varepsilon'' \,/\, \varepsilon' = \tan \delta$$

where δ is the dissipation factor of the sample, ε" is the dielectric loss, which measures the efficiency with which heat is generated from the electromagnetic radiation and ε' is the dielectric constant which gives the ability of a molecule to be polarized by an electric field. The high value of dissipation factor d indicates large susceptibility to microwave energy.[20]

The conduction mechanism leads, due to the much stronger interaction of ions with electric field, to the generation of heat. The ions will move under the influence of an electric field, resulting in expenditure of energy due to an increased collision rate, converting kinetic energy into heat. The heat generated by both mechanisms adds up resulting in a higher final temperature.

Since the ability of a molecule to couple with the microwave radiation is a function of its molecular polarisability (i.e. a function of its dipole moment), only polar molecules interact with microwave energy. As a guide, compounds with high dielectric constants such as water, ethanol, acetonitrile, N,N-dimethylformamide (DMF), acetic acid, chloroform. dichloromethane, acetone, ethylene glycol etc., tend to heat rapidly under microwave irradiation, while less polar substances, such as aromatic and aliphatic hydrocarbons or compounds with no net dipole moment, such as carbon dioxide, carbon tetrachloride, diethyl ether etc. as well as highly ordered crystalline substances, are poorly absorbing. Thus, polar molecules in a non-polar solvent would absorb energy, but not the solvent or the reaction vessel, if it is made of teflon or ceramic or even pyrex. Sometimes it is possible to use mixtures comprising microwave active reactants and microwave inactive solvents. It has also been suggested that if microwave energy is absorbed by the solvent and not by the substrate, only modest rate increase will result relative to those

observed with conventional energy. If, on the other hand, the microwave energy is absorbed selectively by a reactant, by a complex or by an intermediate during the rate determining step, then large rate increase will result.

1.3.2 WORKING OF THE MICROWAVE REACTOR

In a microwave oven, microwaves are generated by a magnetron. A magnetron is a thermo-ionic diode having an anode and a directly heated cathode. As the cathode is heated, electrons are released and are attracted towards the anode. The anode is made up of an even number of small cavities, each of which acts as a tuned circuit. The anode is, therefore, a series of circuits, which are tuned to oscillate at a specific frequency or at its overtones. A very strong magnetic field is induced axially through the anode assembly and has the effect of bending the path of electrons as they travel from the cathode to the anode. As the deflected electrons pass through the cavity gaps, they induce a small charge into the tuned circuit, resulting in the oscillation of the cavity. Alternate cavities are linked by two small wire straps, which ensure the correct phase relationship. This process of oscillation continues until the oscillation has achieved a sufficiently high amplitude. It is then taken off by the anode via an antenna. The variable power available in domestic ovens is produced by switching the magnetron on and off according to the duty cycle. Microwave dielectric heating is effective when the matrix has a sufficiently large dielectric loss tangent (i.e. contains molecules possessing a dipole moment). The use of a solvent is not always mandatory for the transport of heat. Therefore, reactions performed under solvent-free conditions present an alternative in the microwave chemistry and constitute an environmentally benign technique, which avoids the generation of toxic residues, like organic solvents and mineral acids, and thus allows the attainment of high yields of products at reduced environmental costs. This emerging environmentally benign technique belongs to the upcoming area of green chemistry.

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1.3.3 MICROWAVE EFFECT VS THERMAL EFFECT

Although the first publications concerned with the possibilities of use of microwave irradiation in organic synthesis appeared in 1980's and in polymer chemistry even earlier at the end of 1960's, the sudden growth of interest in the application of microwave irradiation in almost all fields of chemistry took place at the end of 1980's. The application of microwaves in chemistry is therefore so attractive that form the very beginning it was realized that a number of chemical process can be carried out with a substantial reduction in the reaction time in comparison to conventional process. Reactions that usually take many hours or days, under influence of microwave irradiation can be run in considerably shorter time of several minutes or even seconds .These phenomena are not fully understood yet; however, there are two groups of theories that are proposed to explain the reduction of the reaction time under microwave conditions in comparison with process under conventional conditions.

According to the first group of theories, the kinetics and mechanism of the reactions are considered to be the same, in spite of the fact that the course of chemical process under microwave conditions is considerably shorter than under conventional conditions. The reduction of the reaction time is the result of sudden and, sometimes, uncontrollable temperature growth of the reaction mixture under microwave irradiation, which in turn leads to the increase of reaction rates following common kinetic laws.

The second group of theories supposes that during microwave irradiation of the reaction mixture there is a specific effect of microwave activation that cause an increase of the reaction rates for which bulk temperature of the reaction mixture is an inadequate to explain. Such an effect has been accepted to be called the non thermal microwave effect or the specific microwave, effect.

It is worth stressing that microwaves, in contrast to conventional heating methods, are means of volumetric heating of materials (Figure 1.1) [21], which causes more extensive heating inside the material in comparison with outer layers of the material, which in turn makes it difficult to measure the reaction temperature properly. Temperature measurement under microwaves conditions, particularly for the reactions in dense and solvent less media, is difficult. Therefore, it is a source of inappropriate interpretation of experimental results and divergence in descriptions of the same experiments.
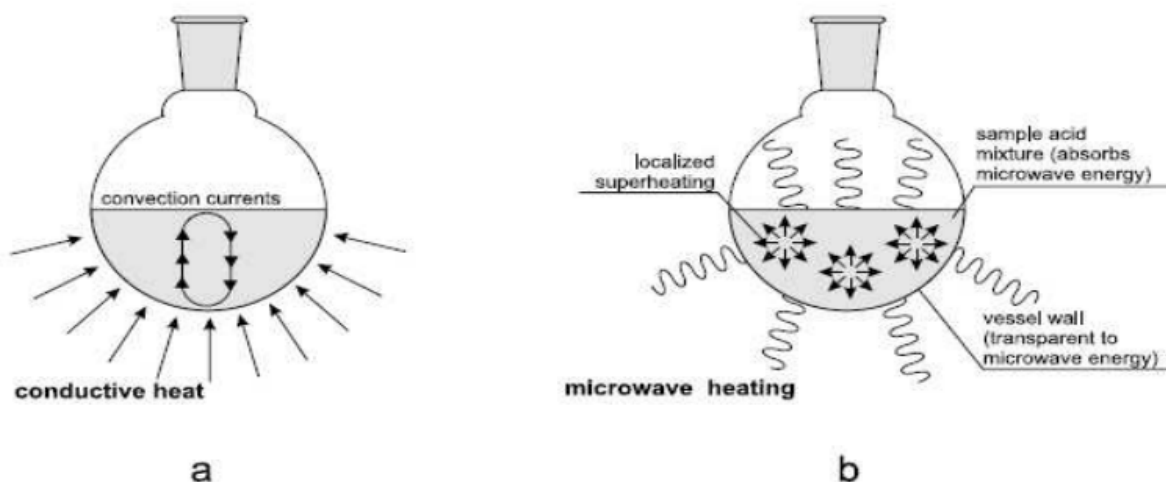
Figure 1.1: Different heating mechanisms for conventional and microwave heating.[21]

As a part of this project work we have attempted to perform glycolytic depolymerisation of PET to derive polyols, which have potential to be used as a raw material for cellular solids, i.e. polyurethane and polyisocyanurate foams. A brief description of the different kinds of foams is presented in the following sections.

1.4 POLYURETHANES AND POLYISOCYANURATES FOAM

The polyurethanes are a special group of heterochain polymers, characterised by the following structural unit.

21

$$\left[-OCONH\!\!-\!\!R\!\!-\!\!NHCOO\!\!-\!\!R' \right]_n$$
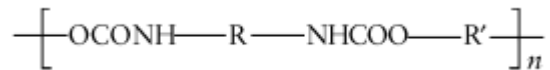
The urethane groups -NH-COO- are esters of carbamic acid, an hypothetically unstable (and impossible to obtain under normal conditions) acid [R-NH-COOH]. It is possible to synthesise the urethane groups by various methods , but the most important one is the reaction between an isocyanate and an alcohol.

$$R\!\!-\!\!N\!\!=\!\!C\!\!=\!\!O \;\; + \;\; HO\!\!-\!\!R' \longrightarrow \;\; R\!\!-\!\!NHCOO\!\!-\!\!R'$$

isocyanate   alcohol   urethane
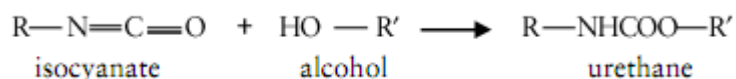
The first urethane was synthesised, by this route, as early as 1849 by Wurtz. In 1937, following very systematic and intensive research works at IG Farbenindustrie, in Germany, Dr. Otto Bayer synthesised the first polyurethane, by the reaction of a diisocyanate with a polyester having two terminal hydroxyl groups.

$$n\,O\!\!=\!\!C\!\!=\!\!N\!\!-\!\!R\!\!-\!\!N\!\!=\!\!C\!\!=\!\!O \;\; + \;\; n\,HO\text{\textasciitilde\textasciitilde\textasciitilde}OH \longrightarrow$$

Diisocyanate   Polyester diol

$$\left[-OCONH\!\!-\!\!R\!\!-\!\!NHCOO\text{\textasciitilde\textasciitilde\textasciitilde} \right]_n O\!\!-\!\!$$
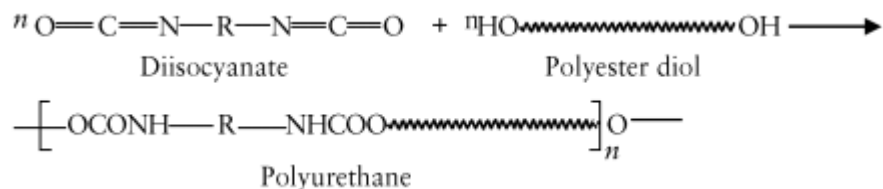
Polyurethane

The main field of polyurethane application is the furniture industry, where it is widely used for the production of mattresses from flexible slabstock foams. Automotive manufacture is the second important application for flexible and semiflexible polyurethanes (seat cushioning, bumpers, sound insulation, and so forth). Rigid polyurethane foams are used in thermal insulation of buildings and refrigerators, cold stores, pipe insulation, refrigerated transport, thermal insulation in chemical and food industries. The polyurethane elastomers are used for shoe soles, footwear, athletic shoes, pump and pipe linings, industrial tyres, microcellular elastomers, etc. Polyurethane adhesives, sealants, coatings and fibres represent another group of polyurethanes with specific applications.[22]
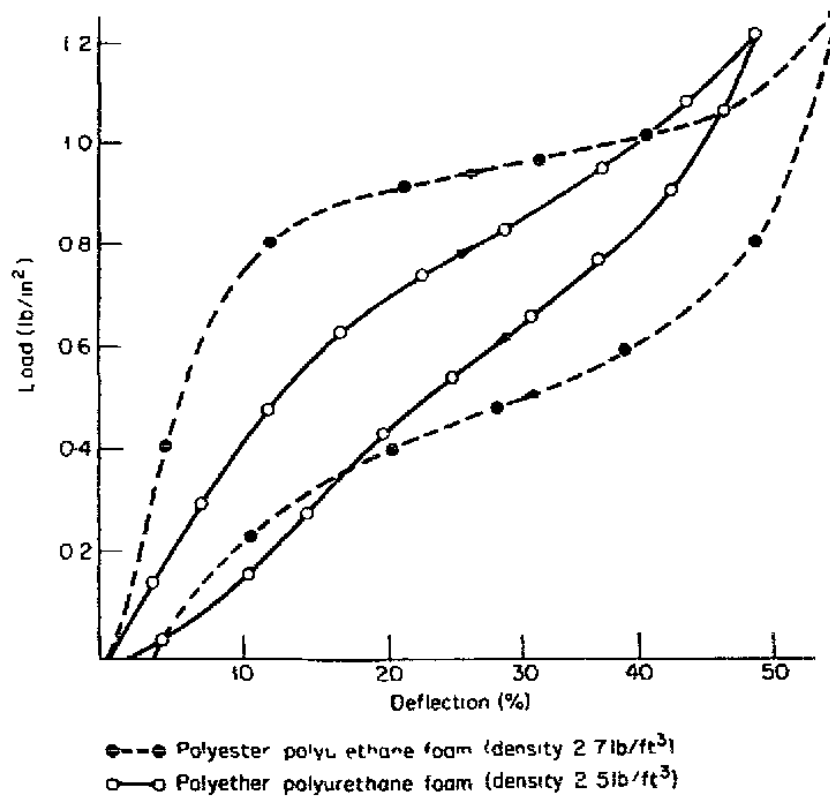
Figure 1.2: Typical load deflection curves for flexible polyurethane foams[22]

Reaction Profile is the term given to the time for the foam to go through its different stages of reaction. The reaction is usually measured in seconds, with the time beginning as soon as the isocyanate and polyol components are first mixed together.

Cream Time – this is the first event measured, and occurs usually a short time after mixing when the mixed liquids turn "cloudy" in appearance and the liquid begins to rise from its initial stable state.

Gel Time – this is the time when the expanded foam begins to polymerise or gel. It is recognized by touching the expanded foam (with gloves or tools) and noticing a thin polymer strand or string, like a cobweb, being formed. At this time the foam should have filled the part or cavity. If the foam is still rising after the gel time this will cause stretch marks in the final foam.

Rise Time – this is when the reacted foam has reached its largest volume, or maximum height.

Tack Free Time – As the name suggests, this is when the final foam has lost its tackiness and can then be handled if required.

1.4.1 FLEXIBLE FOAMS

Flexible polyurethane foams are open-cell structures which are usually produced with densities in the range 1.5-3 lb/ft^3. Typical load deflection curves for polyether and polyester foams are shown below. Compared to polyether foams, polyester foams have higher tensile strength, elongation at break and hardness; consequently polyester foams are preferred in such applications as textile laminates and coat shoulder pads

Polyurethane foams are resistant to a wide range of solvents. In this respect polyester foams are generally superior to polyether foams, particularly in resistance to dry cleaning solvents; in this further reason for preferring polyester foams in textile applications.

Polyurethane foams are subject to degradation by aqueous acids and alkalis and steam. Ester, amine and urethane groups represent sites for hydrolytic attack. Since the ether groups not ready attacked polyether foams are generally more resistant to hydrolysis than polyester foams.

The gas used in the production of flexible foams is usually carbondioxide formed by the interaction of isocyanate and water. In the system containing a diisocyanate, a polyol and water, two principal reaction proceed simultaneously, namely :

Diisocyanate + polyol $\longrightarrow$ polyurethane

Diisocyanate + water $\longrightarrow$ carbondioxide
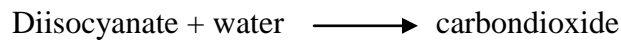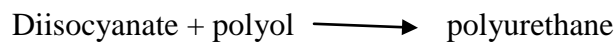
As indicated above, satisfactory foam is obtained only if these two reaction are controlled.

Polyether foams

Flexible polyether foams are most commonly produced by a "one-shot" process In this procedure, diisocyanate, polyol, water, catalysts and surfactant are all mixed simultaneously. After 1-2 minutes the foam reaches its maximum height.

Table1.1: A typical formulation for flexible polyether foam[22]

Polyether triol	: 100 parts by weight
80:20 Tolylene diisocyanate	: 40
Water	: 3.0
Triethylenediamine	: 0.5
Stannous octoate	: 0.3
Silicone block copolymer	: 1.0

Polyester foams

Flexible polyester foams are nearly always prepared by a one-shot process; most commonly they are produced as slabstock by a continuous method exactly comparable to that described previously for polyether foam.

Table 1.2: A typical formulation for flexible polyester foam[22]

Polyester(slightly branched)	: 100 parts by weight
65:35 Tolylene diisocyanate	: 33
Water	: 4.0
N-methylmorpholine	: 2.0
N,N Dimethylcetylamine	: 2.0
Ammonium oleate	: 2.0(surfactant)

1.4.2 RIGID FOAMS

The principle underlying the production of rigid polyurethane foams is fundamentally the same as that used for flexible foams, namely a reacting isocyanate/polyol mixture is simultaneously expanded by gas generation. The essential difference between the two products lies in their degree of cross-linking; whereas flexible foams are lightly cross-linked, rigid foams are highly cross-linked. This high degree of cross-linking is achieved by using relatively low molecular weight polyols for coupling with the isocyanate.

Table 1.3: A typical basic formulation for rigid polyether foam[22]

Polyether polyol	: 100 parts by weight
Crude diphenylmethane	: Stoichiometric +5% diisocyanate
Trichlorofloromethane	: 50
Triethyleneamine	: 0.5
Silicone block copolymer	*: 1.0*
Glycerol	*:10(cross-linking)*

Rigid polyurethane foams are closed-cell structures which are usually produced with a density of about 2 lb /ft^3. Since the major interest in rigid foams has been for thermal insulation, the thermal conductivity of the foams is a physical property of some importance.

The chemical properties of rigid polyurethane foams are similar to those of flexible foams.

1.4.3 OPEN CELL FOAMS

Open-cell-structured foams contain pores that are connected to each other and form an interconnected network that is relatively soft. Open-cell foams will fill with whatever they are surrounded with. If filled with air, a relatively good insulator is the result, but, if the open cells fill with water, insulation properties would be reduced. Foam rubber is a type of open-cell foam. densities ranging from 0.4 to 1.2 lbs/ft^3. One of the advantages that these lower densities provide is a more economical yield, since foam density is directly related to yield (lower density = higher yield). R-value of open-cell foams is slightly more than half that of closed-cell foams, more permeable to moisture vapor. As per ASTM C168 R-value is the quantity determined by the temperature difference, at steady state, between two defined surfaces of a material or construction that induces a unit heat flow rate through a unit area. Open cell foams are

incredibly effective as a sound barrier, having about twice the sound resistance in normal frequency ranges as closed-cell foam. Other characteristics of open-cell polyurethane foam usually include a softer, "spongier" appearance, as well as lower strength and rigidity than closed-cell foams.

1.4.4 CLOSED CELL FOAMS

Closed-cell foams do not have interconnected pores. The closed-cell foams normally have higher compressive strength due to their structures. However, closed-cell foams are also in general denser, require more material, and as a consequence are more expensive to produce. The closed cells can be filled with a specialized gas to provide improved insulation. The closed-cell structure foams have higher dimensional stability, low moisture absorption coefficients, and higher strength compared to open-cell-structured foams. All types of foam are widely used as core material in sandwich-structured composite materials.

In addition, the closed-cell nature of this foam provides for a highly effective air barrier, low moisture vapor permeability and excellent resistance to water. The most common foam density for closed-cell polyurethane foam is approximately 2.0 pounds per cubic feet. Years of research and commercial experience has shown that the 1.75 – 2.25 lb/ft^3 density range provides the optimum insulating and strength characteristics for most building applications.

1.5 BASIC CHEMISTRY OF POLYURETHANE FOAMS

This section focuses on the basic chemical reactions involved in the formation of flexible polyurethane foams. Since flexible polyurethane foam production requires a variety of chemicals and additives, this section will review specific chemicals and their importance in the foaming process.

Flexible polyurethane foam chemistry particularly features two reactions – the 'blow' reaction and the 'gelation' reaction. A delicate balance between the two reactions is required in order to achieve a foam with a stable open-celled structure and good physical properties. The commercial success of polyurethane foams can be partially attributed to catalysts which help to precisely control these two reaction schemes. An imbalance between the two reactions can lead to foam collapse, serious imperfections, and cells that open prematurely or not at all.

1.5.1 BLOW REACTION

The first step of the model blow reaction (Scheme 3) involves the reaction of an isocyanate group with water to yield a thermally unstable carbamic acid which decomposes to give an amine functionality, carbon dioxide, and heat.
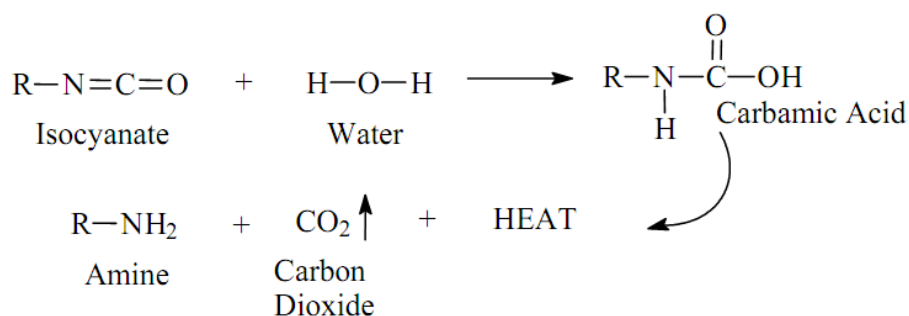
Scheme 3: Blow Reaction

In the second step, the newly formed amine group reacts with another isocyanate group to give a disubstituted urea and additional heat is generated. The total heat generated from the blow

reaction is approximately 47 kcal per mole of water reacted, along with the carbon dioxide released in the first step and serves as the principal source for 'blowing' the foam mixture, though some auxiliary blowing agents are also usually utilized. Also, since the typical isocyanates utilized in foam production are difunctional, the second part of the blow reaction serves as a means to chain extend the aromatic groups of the typically used isocyanate molecules to form linear hard segments. However, it should be noted that this reaction scheme can also produce covalent cross-linking points when molecules with functionality greater than two, such as diethanol amine, are added to the formulation.

There are other secondary reactions, involving the formation of biuret and allophanate linkages which could lead to the formation of covalent cross-linking points. In the formation of biuret, a hydrogen atom from the disubstituted urea reacts with an isocyanate group to form a biuret linkage as shown in the scheme.[22]
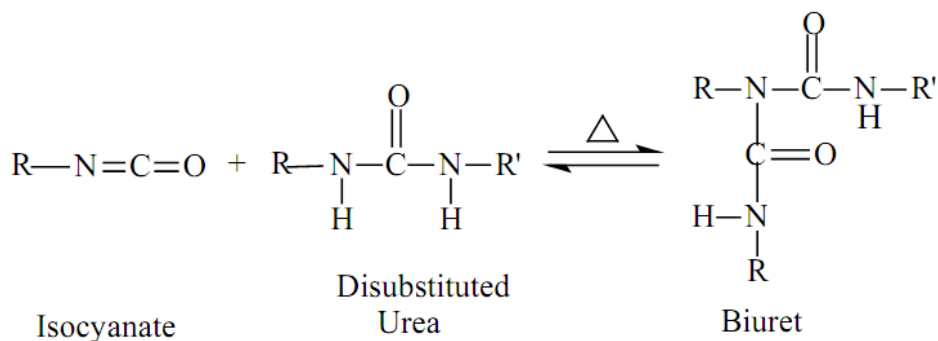
Scheme 4: Formation of Biuret

1.5.2 GELATION REACTION

The gelation reaction, also sometimes called the polymerization reaction, involves the reaction of an isocyanate group with an alcohol group to give a urethane linkage as shown in Scheme 5. The heat of this reaction is reported to be approximately 24 kcal per mole of urethane formed. Since polyurethane foams usually utilize polyfunctional reactants (typically difunctional isocyanates and trifunctional polyols), this reaction leads to the formation of a crosslinked polymer.

$$R-N=C=O \quad + \quad R'-CH_2-OH \quad \xrightarrow{-\triangle} \quad R-N-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-R'$$

Isocyanate   Alcohol   Urethane
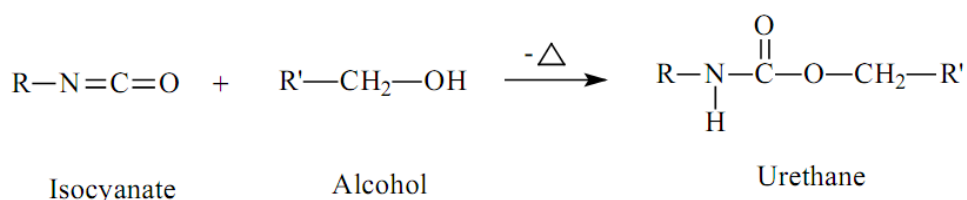
Scheme 5: Gelation reaction

The reaction of a urethane group with an isocyanate group to form an allophanate group is another possible way to further cross-link the polymer as shown in Scheme 6. In uncatalyzed systems this reaction is known to be insignificant Also, this reaction is generally not favorable under the catalytic conditions used for flexible foam production.

$$R-N=C=O \quad + \quad R-N-\overset{\overset{\displaystyle O}{\|}}{\underset{H}{C}}-O-CH_2-R' \quad \rightleftharpoons \triangle$$

Isocyanate   Urethane   Allophanate
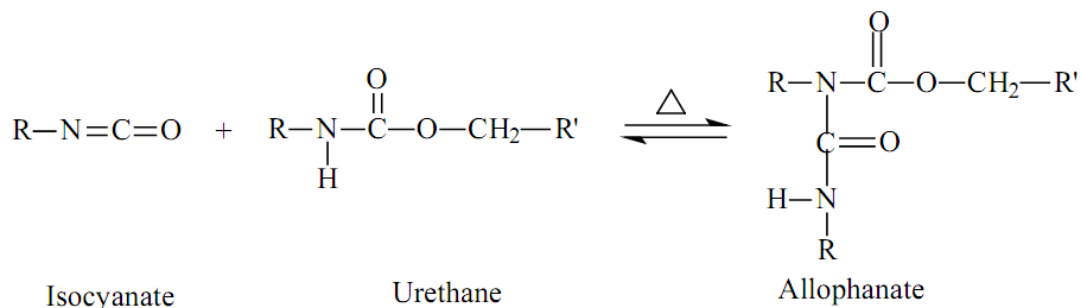
Scheme 6: Allophanate formation

It is important to note that both reaction schemes described above occur simultaneously, and therefore it is critical to control the relative rates of these reactions in order to obtain a foam with a stable cellular structure and good physical properties. If the blow reaction takes place too fast

in comparison to the gelation reaction, it would result in the cells opening before there is sufficient viscosity build-up to provide the foam struts with enough strength to uphold the foam, leading to the collapse of the foam. On the other hand, if the gelation reaction is faster than the blow reaction, it may result in a foam with closed cells, which is not desirable. The relative rates of reaction of the isocyanate component with other foam reactants at 25 °C under uncatalyzed conditions are provided in Table 1.4. These can serve as a guideline to make appropriate catalyst adjustments to achieve a suitable balance of the two reaction schemes. Familiarity with the above two reaction schemes is adequate to develop a fundamental understanding of the solid-state morphology which develops in flexible polyurethane foams.

Table 1.4: Relative rate of reaction of isocyanate with other components[22]

Active Hydrogen Compound	Typical Structure	Relative Reaction Rate (Uncatalyzed at 25 °C)
Primary Aliphatic Amine	RNH_2	100,000
Secondary Aliphatic Amine	R_2NH	20,000-50,000
Primary Aromatic Amine	$ArNH_2$	200-300
Primary Hydroxyl	RCH_2OH	100
Water	H_2O	100
Carboxylic Acid	RCOOH	40
Secondary Hydroxyl	R_2CHOH	30
Urea	RNHCONHR	15
Tertiary Hydroxyl	R_3COH	0.5
Urethane	RNHCOOR	0.3
Amide	$RCONH_2$	0.1

There are many different components needed to synthesize a flexible foam. The seven major ones are isocyanate, polyol, water, physical blowing agents, catalyst, surfactants, and cross-linking agents. The desired end properties of the foam dictate the choice of specific components along with their required quantities. For example, one way to adjust foam modulus would be by controlling the percentage of hard segments formed from the water-isocyanate reaction.

In other cases, it might be required to have a foam with more cell openness – this would be possible by controlling the type and quantity of surfactant used. Table 4 lists the components which are commonly involved in a formulation and gives a typical range of quantities for each component utilized.

Table 1.5: Typical formulations of Isocyanurate Foams

Component	Parts by Weight
Polyol	100
Inorganic Fillers	0-150
Water	1.5-7.5
Silicone Copolymer Surfactant	0.5-2.5
Amine Catalyst	0.1-1.0
Tin Catalyst	0.0-0.5
Chain-Extender	0-10
Cross-Linker	0-5
Additive	Variable
Auxiliary Blowing Agent	0-35
Isocyanate	25-85

1.5.3 POLYOLS

The soft phase of polyurethane foams is usually a polyfunctional alcohol or polyol phase which on reacting with isocyanate groups covalently bonds with urea hard segments through urethane linkages. Glycols such as ethylene glycol, 1,4-butanediol, and 1,6-hexanediol are relatively much lower in molecular weight as compared to the polyols used in flexible foam production. These are more commonly used for chain extension to form hard segments (in polyurethane elastomers) and therefore will be referred to as 'chain extenders'. Polyols used for flexible foam formulations

are higher molecular weight (ca. 3000 to 6000 g/mol) and have average functionalities in the range of 2.5 – 3.

Polymerization processes allow production of a wide range of polyols, differing in molecular weight, functionality, reactivity, and chain structure. Selecting the right polyol is an important issue, and the choice is governed by the desired foam properties and economics.

At present, there are two kinds of polyols commercially available for flexible foam production, hydroxyl terminated polyethers and hydroxyl terminated polyesters. Around ninety percent of the flexible polyurethane foam market utilizes polyether polyols based on propylene oxide in comparison to polyester polyols, because of their lower cost, better hydrolysis resistance, and greater ease in handling.

Also, polyurethane foams, due to their low density cellular structure, expose a large surface area to the atmosphere. This further makes polyether polyols advantageous over polyester polyols due to the known greater hydrolytic stability of the polyether backbone.

1.5.4 ISOCYANATES

The two most common sources of isocyanate functionalities in foam production come from toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI), of which the former is more commonly used in North America, where as the latter one has a greater markert demand in European countries.

Foam properties can be modified to a certain extent by modifying the isocyanate used. For example, after suitable catalyst adjustments are made to enhance the relatively low reactivity, the 65:35 isomer blend has been noted to form foams with higher load-bearing properties.

1.5.5 CATALYSTS

Since polyurethane foam production relies on two competing reactions, a balance between them is required to make foams with good open-celled structures and desired physical properties. While it is true that these reactions may proceed in the absence of catalysts, they generally proceed at rates too slow to be practical. Suitable catalysts are thus used to carry out these reactions in a faster, controlled, and balanced manner. This correct balance is required due to the possibility of foam collapse if the blow reaction proceeds relatively fast. On the other hand, if the gelation reaction overtakes the blow reaction, foams with closed cells might result and this might lead to foam shrinkage or 'pruning'. Catalyzing a polyurethane foam, therefore, involves choosing a catalyst package in such a way that the gas produced becomes sufficiently entrapped in the polymer. The reacting polymer, in turn, must have sufficient strength throughout the foaming process to maintain its structural integrity without collapse, shrinkage, or splitting.

Polyurethane foam formulators generally choose catalysts from two major classes of compounds – tertiary amines and metal salts, primarily of tin. Since catalysts differ both in activity and selectivity towards the polyurethane foaming reactions, the two kinds are combined not only to provide the desired balance of 'blowing' vs. 'gelation', but also to tune these reactions according to the needs of the production equipment.

1.5.6 SURFACTANTS

Flexible polyurethane foam production relies greatly on the performance of non-ionic, silicone based surfactants which are added to realize a variety of functions. Some of the main functions performed are reducing surface tension, emulsifying incompatible ingredients, promoting bubble nucleation during mixing, stabilization of the cell walls during foam expansion, and reducing the

defoaming effect of any solids added. Below a certain minimum concentration of surfactant, the foam can result in serious imperfections such as splitting, densification, or collapse. Addition of more than required quantities of surfactant has its own drawbacks. This usually results in an over-stabilization of the foam, resulting in closed cells, which result in a decreased airflow through the foam. Also, a high number of closed cells in the foam leads to foam shrinkage on cooling, which is undesirable.

1.5.7 BLOWING AGENTS

Water acts as a chemical blowing agent and reacts with an isocyanate group resulting in a primary amine and carbon dioxide. Increasing the water content influences both the cell structure and the solid-state morphology of the foam. Higher water contents typically result in foams with lower density due to the increased blow.

Although the carbon dioxide produced from the water-isocyanate reaction acts as the principal source to blow the foam, some formulations also employ physical or auxiliary blowing agents. These are low boiling solvents, inert towards chemical reactions, and they are generally used to produce softer foams by reducing the foam density.

Until the early 1990's the auxiliary blowing agent primarily used to produce soft lowdensity foams was chlorofluorocarbon. Also, amongst the currently used HCFCs, 141b has the highest ozone depleting potential.[22]

1.6 MOTIVATION FOR THE PRESENT STUDY

Successful demonstration of blow moulding technique for the production of Poly (ethylene terephthalate) (PET) bottles, way back in the 1970's, has led to a massive increase in the overall usage of this polymer for packaging purposes.[23] Because of its excellent barrier properties against oxygen and carbon dioxide,[24] PET has become the choicest of materials for bottling beverages, particularly mineral water and carbonated soft drinks. In addition, it finds extensive application in the textile industry, which consumes more than 60 % of all the PET produced worldwide.[25] Unfortunately, irresponsible usage of this non degradable thermoplastic over the last few decades has led to its accumulation in the environment. [26, 27] Of all thermoplastics, the practice of recycling PET is most common, but only a small fraction of it is practically recycled, because of the higher cost of the recycled product.[28] It is thus highly desirous to adopt technically & economically feasible routes towards recycling of PET into industrially important products.

Primary and secondary recycling of PET involves thermal reprocessing of the polymer which reduces its molecular weight substantially, [29] thereby setting up an upper limit on the maximum number of recycling steps. There is abundant academic and practical studies on tertiary recycling of PET, whereby it is converted into basic chemicals,[11] by processes like glycolysis,[30] aminolysis,[31] hydrolysis,[17] alkalolysis,[11, 32] and alcoholysis, out of which only the former two have reached the level of commercial maturity.[11, 33] Glycolysis leads to formation of oligomers, having potential as raw material for preparation of unsaturated polyesters,[34] alkyd resins[35] and polyurethanes.[36-38]

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At present, polyester polyols used for the preparation of flexible polyurethane foams are essentially derived by reacting low molecular weight diols e.g. Diethylene glycol (DEG) with adipic acid (AA) in the presence of glycerol.[39] For rigid PU foam applications, the polyol is obtained by the reaction of AA with ethylene glycol (EG) or diethyleneglycol (DEG) in the presence of phthalic anhydride.[37] Interestingly, such polyols can also be derived by transesterification of PET, which in turn can be further reacted with aliphatic diacids for preparation of either type of PU foam, depending on the type of spacer employed. The polyester polyol obtained from PET is expected to render advantageous characteristics to the final product, particularly in terms of better mechanical properties, high thermal stability, resistance to major chemical solvents due to the presence of aromatic phenyl group.[40] Thus, synthesizing polyols by transesterification of PET waste is a process of preserving natural resources, and this in fact is the driving force for the present study.

It was previously reported that the time and energy requirements for PET glycolysis can be significantly lowered by using microwave as an alternate energy source and the reactivity was inversely proportional to the molecular weight of the diol. [41] Although complete glycolysis of PET was achieved with DEG, the polyurethane foams obtained there from was rather rigid. By reacting the glycolysed polyol with suitable diacids, it is possible to introduce spacer molecules, with increased flexibility. In this context, the reaction of glycolysed PET with AA has been reported to form polyols, which inturn leads to flexible foams. [37] However, literature is scarce on the effect of soft segment chain length of the diacid on the final foam properties. We hypothesize that a higher molecular weight diacid, like sebacic acid (SA) can be used to increase the flexibility of the aromatic polyester polyol based foam further.

In this report, we propose a combination of microwave-assisted PET depolymerisation process, which was used to prepare low molecular weight oligomers, followed by polycondensation with aliphatic diacids to prepare polyols with desired properties. We also hypothesise that it should be relatively easy to adopt chemical recycling for recycled PET grades, which have been subjected to a few thermal processing steps. In this regard, we have demonstrated the potential of this process for recycled PET grades. The polyols have been used as a raw material for production of flexible foams, where the rigidity was increased by varying the amount of isocyanate in the composition.

2.1 MATERIALS

Disposed off PET bottles were collected, washed, dried and cut into small pieces (6 mm x 6 mm) after removal of the polyethylene caps and the polypropylene label. Zinc acetate dihydrate [Zn $(CH_3COO)_2. 2H_2O$, Merck] with a purity of 99% was employed as the trans-esterification catalyst. Adipic acid (CDH), sebacic acid (CDH), p-toluene sulfonic acid (PTSA) (CDH), potassium acetate (CDH), diethylene glycol, glycerol (CDH), diphenylmethane 4, 4'-diisocyanate, a mixture of di- and triisocyanates (MDI) (Merck) and dibutyl tin dilaurate (DBTL) (Merck) were used without any further purification. Double distilled water was used throughout the course of this work.

2.2 METHODS

Typically the following three steps were employed during the project work:

I.   Microwave aided glycolytic depolymerisation of PET
II.   Polyesterification of the glycolysed product with different diacids to obtain APP
III.   Preparation of foam from both aliphatic and aromatic polyester polyols

2.2.1 MICROWAVE AIDED GLYCOLYSES

A domestic microwave oven (LG) with a magnetron source for microwave generation (2.45 GHz, maximum power: 900 W) was used for performing glycolytic experiments. PET pieces (10 g) together with requisite amount of DEG and zinc acetate (0.5 % w/w PET) were introduced into a loosely stoppered reaction flask which was placed in the microwave reactor. The

experiments were performed at different molar ratio of PET: DEG:: 1:2, 1:4 and 1:6 in the presence of glycerol (5 % w/w) and was allowed to proceed at 450 W for extended time periods, leading to the formation of a viscous liquid, which did not solidify on cooling. After predetermined periods, the reaction mixture was filtered through a copper wire mesh (0.5 × 0.5 mm pore size), and the remaining unreacted PET flakes were weighed to estimate PET conversion % as follows.

$$\text{PET conversion (\%)} = (\frac{m_{PET, Initial} - m_{PET, Remaining}}{m_{PET, Initial}}) \times 100 \ \text{………………………..1}$$

where, $m_{PET, initial}$ refers to the mass of PET initially taken for the experiment and $m_{PET, remaining}$ refers to the mass of solid PET flakes which remained unreacted in the reaction medium. For comparison purposes, glycolysis was also performed at 180-190 °C in an oil bath, under inert atmosphere in a four-necked round bottom flask, connected to a reflux condenser, N_2 gas inlet, thermometer and stirrer, the concentration of reactants being same. The results in terms of PET conversion were compared with those obtained under microwave irradiation.

2.2.2 SECONDARY RECYCLING: MULTIPLE EXTRUSIONS

Studies were performed to investigate the effect of multiple extrusions on the intrinsic viscosity of PET, which is expected to affect its reactivity towards glycolysis. For this purpose, approximately 15 g of PET was loaded into the plastometer barrel of an MFI instrument (International Equipments) (Figure 2.1) and extruded under a load of 2.16 kg at 260 °C and the extrudate was loaded into the plastometer barrel for re-extrusion. This process was repeated several times (10) and the effect of extrusion cycles on the intrinsic viscosity of the sample was

measured, before being subjecting the degraded PET to glycolytic experiments. The thermally degraded PET will be referred to as RPET in the subsequent text.

Figure 2.1: Melt Flow Index Tester (International Equipments)

2.2.3 POLYESTERIFICATION OF GLYCOLYSED PRODUCTS

The DEG glycolysed product was reacted with two different difunctional carboxylic acids, namely AA and SA (hydroxyl: acid ratio:: 1:1). For comparison purposes, aliphatic polyester polyols were also prepared by reaction of AA and SA with DEG under similar conditions. Esterification catalyst, PTSA (0.1 %), based on the moles of diacid, was introduced in steps into a reaction kettle (500 mL capacity) containing the glycolysed product and the diacid. The reactor was equipped with a stirring assembly, a thermowell and a dean stark apparatus. The reaction was initially heated to 170 $^{\circ}$C and maintained for a period of 3 h, after which the temperature was increased to 200 °C. The reaction was allowed to proceed at 200 °C till the required acid

number (< 30) was achieved. Water formed as a result of the esterification process was collected and quantified.

2.2.4 PREPARATION OF POLYURETHANE FOAMS

In order to assess the effect of the aromatic phenyl group on the properties of PU foams, both aromatic as well as aliphatic polyester polyols were reacted with isocyanates to prepare polyurethane foam. For this purpose, weighed amount of the polyol, silicone oil surfactant (2% w/w polyol), DBTL catalyst (1% w/w polyol) and foaming agent (water) were mixed in a flat-bottom teflon beaker and stirred mechanically for 1 min. Requisite amount of MDI, calculated according to the following formula was added and stirred vigorously, which led to the formation of a viscous liquid. This was poured into cylindrical Teflon molds (60 mm diameter, 36 mm length) and allowed to foam within.

$$m_{iso}.n_{eq,iso} = [m_{H_2O}.n_{eq,H_2O} + m_{poly}.n_{eq,poly}]i_{NCO} \qquad \ldots\ldots\ldots\ldots 1$$

where m_{iso}, m_{H_2O} and m_{poly} refer to the mass of polyisocyanate, water and polyol respectively and $n_{eq,iso}$, n_{eq,H_2O} and $n_{eq,poly}$ are the equivalent number of polyisocyanate (7.4 mmol/g), water (111.1 mmol g^{-1}) and polyol (estimated from the hydroxyl number) and i_{NCO} is the desired NCO index (1.05) maintained for the preparation of flexible PU foam formulation.[42]

Under similar conditions, polyisocyanurate foams (PIR) were also prepared, where the NCO index was increased to 2. In addition, the PIR formulation also contained requisite amounts of potassium acetate, which reportedly catalyses the rate of trimerisation of isocyanate.[37] The process of foam formation was monitored by measuring characteristic parameters including cream time, gel time and tack-free time.

The polyurethanes and polyisocyanurates were designated as PETPU and PETPI followed by the acid used for its preparation, i.e. AA and SA for denoting adipic acid and sebacic acid respectively. For example, the polyurethane foam derived from glycolysis of PET followed by esterification with AA will be referred to as PETPU-AA and the isocyanurate foam derived from the same will be referred to as PETPI-AA respectively in the subsequent text. The naming of polyurethanes and polyisocyanates derived from aliphatic polyols follows similar naming pattern where DEG is used instead of PET.

2.3 CHARACTERISATION TECHNIQUES

The viscosity-average molecular weight of PET was determined by solution viscometry. Samples were dissolved in a mixture of phenol and 1,1,2,2-tetrachloroethane (60/40 w/w) under heating, and the intrinsic viscosity [η] was measured using Ubbelohde suspension level viscometer at 25 °C. The viscosity average molecular weight of PET was calculated using the following equation [43].

$$[\eta] = 75.5 \ x \ 10^{-3} mL/g \ M_v^{0.685}$$
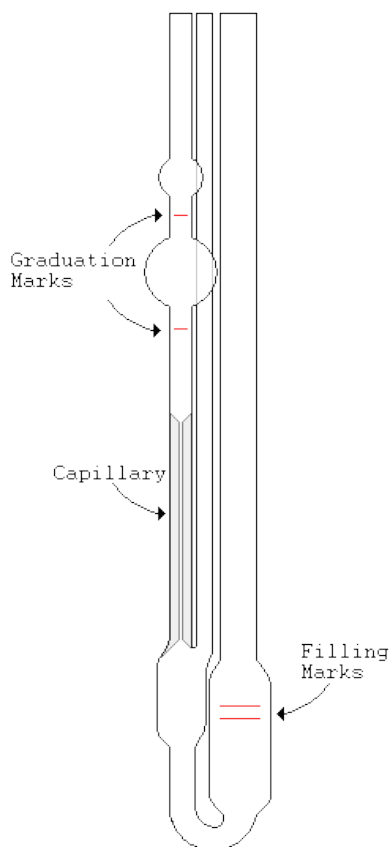
Figure 2.2: Ubbelohde suspension level viscometer

The intrinsic viscosity of the glycolysed polyols was determined in methanol at 25 °C. The Hydroxyl number (HN) was determined using acetic anhydride, as per test method A, described in ASTM D 4274 – 99. For the purpose of acid number determination, the solution was titrated against standard methanolic KOH solution in acetone medium, as per the procedure reported previously. [41]

Thermal characterization was performed using Perkin Elmer Diamond STG-DTA-DSC (Figure 2.3) in N_2 atmosphere in the temperature range of 50-800 °C. A heating rate of 10 °C/min and sample mass of 5.0 ± 0.5 mg was used for each experiment.

Figure 2.3: Thermo Gravimetric Analysis (TGA) Perkin Elmer Diamond

The surface morphology of samples was studied using a Scanning Electron Microscope (Zeiss EVO MA15) (Figure 2.4)under an acceleration voltage of 20 kV. Samples were mounted on metal stubs and sputter-coated with gold and palladium (10 nm) using a sputter coater (Quorum-SC7620) operating at 10-12 mA for 60 s. The average cell dimensions and standard deviations were determined by measuring the diameters of about 20 cells using inbuilt image processing software.

Figure 2.4: Scanning Electron Microscope (Zeiss EVO MA15)

The density of the PU foam was determined by averaging the mass: volume ratio of five specimens per sample following ASTM D1622–98 standard. The average value along with the standard deviation has been reported in the paper. The compressive mechanical properties of the foams were determined using a Universal Testing Machine (International Equipments) (Figure 2.5) as per ASTM D1621–00. Compressive load was applied at a cross-head speed of 3.6 mm/min, till the foam was compressed to ~ 15 % of its original thickness. The compressive strength was calculated based on the "10 % deformation" method as per the standard procedure. At least, three identical specimens were tested for each composition and the average results along with the standard deviation values have been reported.

Figure 2.5: Universal Testing Machine (International Equipments)

FTIR spectra of samples were recorded in the wavelength range 4000 - 600 cm^{-1} using Fourier Transform Infrared (FTIR) spectroscopy on a Thermo Fisher FTIR (NICOLET 8700) (Figure 2.6)analyser with an attenuated total reflectance (ATR) crystal accessory. The isocyanurate content was estimated as the ratio of intensity of the isocyanurate absorption band at 1412 cm^{-1} to intensity of the aromatic absorption band at 1597 cm^{-1}.[37]

Figure 2.6: Thermo Fisher FTIR (NICOLET 8700)

CHAPTER 3

RESULTS AND DISCUSSION

3.1 MICROWAVE ASSISTED GLYCOLYSIS

Detailed characterization of PET used for the present study is presented in the supplementary section. Glycolysis of PET with DEG leads to the formation of liquid oligomers, which do not solidify on cooling. The reaction was followed by monitoring the extent of PET conversion, the variation of which is presented in Figure 3.1. It can be seen that the PET conversion reached a maxima after 30 minutes of irradiation, after which even traces of PET could not be detected in the medium. Under similar PET: glycol concentrations; the reaction took ~ 9 h to reach the same level of de-polymerization.
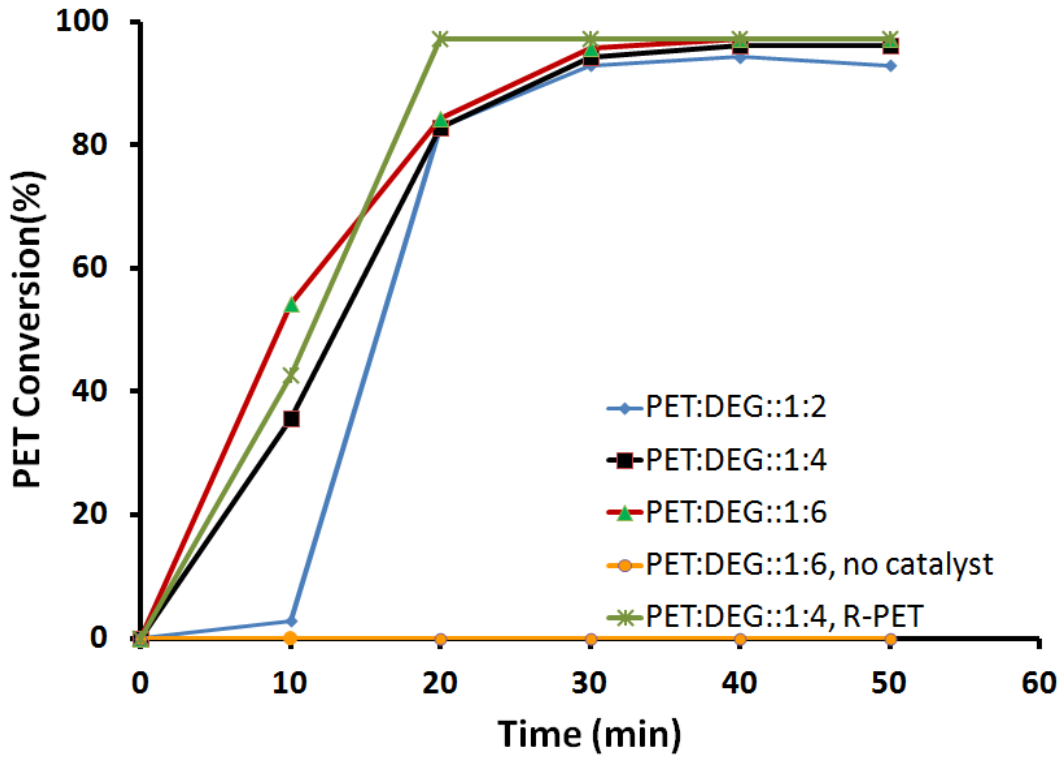
Figure 3.1: Effect of glycolysis time and PET: DEG ratio on the extent of PET conversion, and surface morphology of PET

The viscosity-average molecular weight of PET was determined by solution viscometry, which revealed that the M_v of the PET films decreased from an initial value of 27,431 to 1521 ± 130 after glycolysis for 30 min in the presence of DEG. During the glycolytic process, the reaction products diffuse from the surface, leading to a rough texture as shown in Figure 3.2. It is interesting to note that the glycolytic depolymerisation of PET does not take place in the absence of catalyst, even on extended exposures. From the reaction stoichiometry, a PET : DEG of 1:2 is appears to be sufficient for glycolysis, and as expected the rate of PET conversion increases much rapidly with increase in the PET : DEG ratio, which can be attributed to kinetic factors

[44]. In view of the same, glycolytic reactions with PET (50 g batch) were carried out under a PET: DEG ratio of 1: 4. The HN of the glycolysed products obtained after the reaction of PET with DEG after microwave irradiation for 30 min is 430 ± 15.
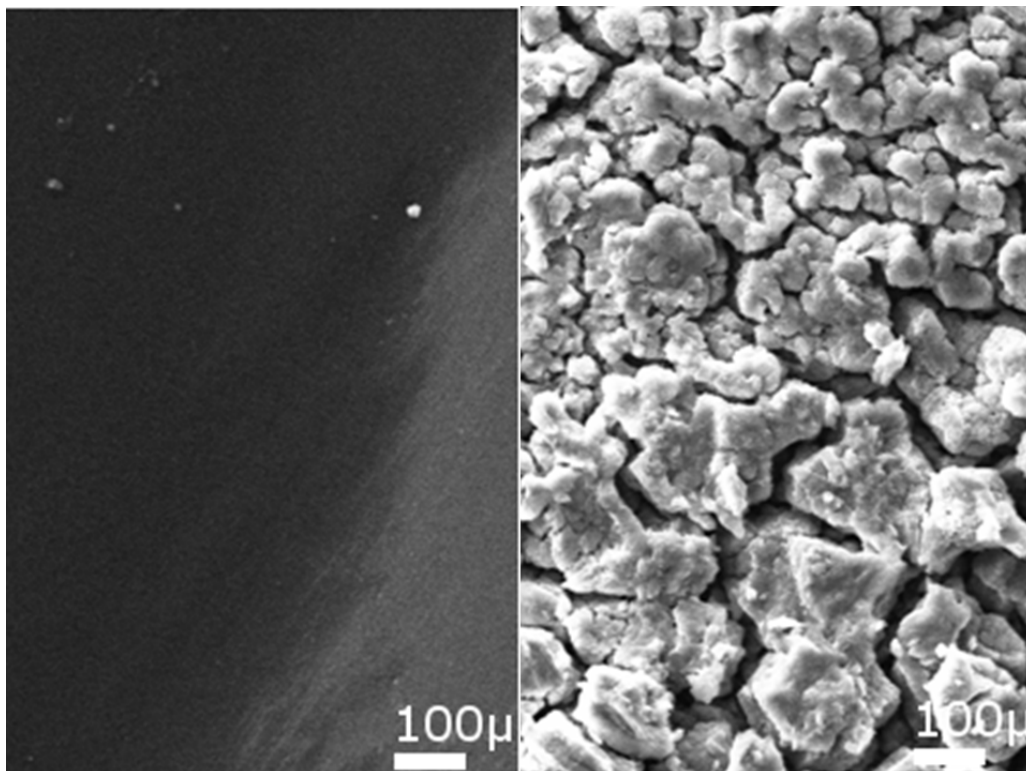
Figure 3.2: Effect of glycolysis on the surface morphology of the PET films a) initial, b) after 30

The FTIR spectra of PET, DEG and glycolysed PET is presented in Figure 3.3 The spectrum of DEG exhibit characteristic absorption bands due to ether stretching (C-O) at ~1050 to 1150 cm^{-1}, with maxima at 1150 cm^{-1}. Characteristic alkyl (R–CH$_2$) stretching at ~2850–3000 cm^{-1} was also observed, along with hydroxyl group absorption ranging from ~3200–3600 cm^{-1}. In comparison, the glycolysed product exhibit absorption at 1715 cm^{-1} due to –C=O stretching, which can be attributed to the presence of ester group, formed as a result of glycolysis of PET

and this peak could also be observed in the spectra of PET. The absorption band at ~3200–3600 cm^{-1} can be attributed to the presence of free hydroxyl groups present in glycolysed PET oligoesters.
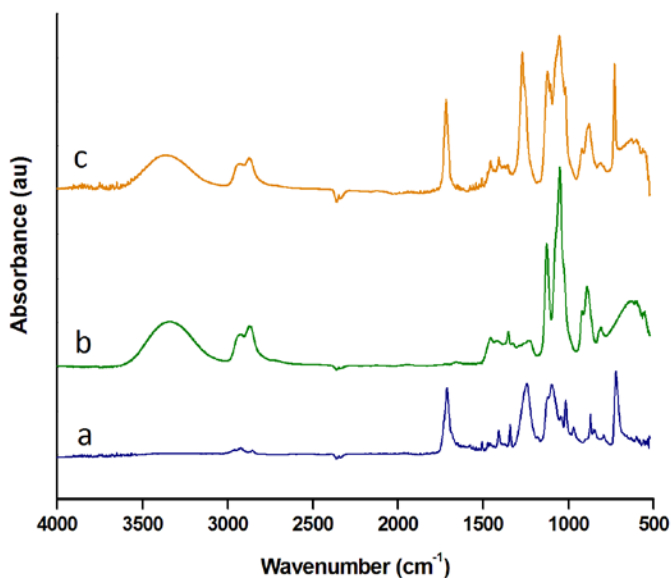
Figure3.3: FTIR spectra a) poly(ethylene terephthalate), b) diethylene glycol, (c) glycolysed

PET

4.2 MICROWAVE ASSISTED HEATING: ROLE OF DIETHYLENE GLYCOL

The energy associated with the microwave frequency (2.45 GHz, 0.0016 eV) employed for the glycolytic depolymerisation is too small to cleave covalent chemical bonds, which leads us to believe that the enhanced efficiency of the microwave assisted glycolytic process can be attributed to the efficient heating of the medium under the reaction conditions employed, a feature more commonly known as the "microwave dielectric heating" effect. In the present study, DEG plays an extremely important function of an efficient microwave absorber, apart from serving its primary role as a reactant. Due to its exceptionally high loss factor (tan $\delta_{,DEG}$ =

1.2, 30 ^{o}C), [45] it is capable of effectively converting electromagnetic energy into heat, which leads to rapid PET depolymerisation under the experimental conditions employed. However, in the conventional process, the reaction mixture in contact with the vessel wall is heated first, which is then conducted through the medium to the PET flakes. In the latter, the potential of DEG as an effective microwave absorber is not tapped, and this can be used to explain the difference between the observed rates of the two processes.

3.3 POLYCONDENSATION OF GLYCOLYSED PET

The PET glycolysate was esterified with two difunctional acids (AA and SA) over extended periods and the variation in the acid number (AN) and intrinsic viscosity as a function of time are presented in Figure 3.4 (a). As expected, the AN decreases as a result of the condensation reaction and the extent of decrease is higher initially, after which it tends to level off. It has been reported that the catalyst degrades over a period of time and in view of the same, it was introduced in steps, (initially and after 9 h), the total amount remaining same (0.1 % mol). [46] Interestingly, the polyols prepared by polyesterification of glycolysed oligomers with AA exhibit slightly lower AN, which is indicative of its higher reactivity as compared to SA. The polymerization process was also associated with an increase in the viscosity, which was quantified by viscometric techniques, the results of which are presented in Figure 3.4 (b). As expected the polyols prepared by reaction with AA exhibit higher viscosities.
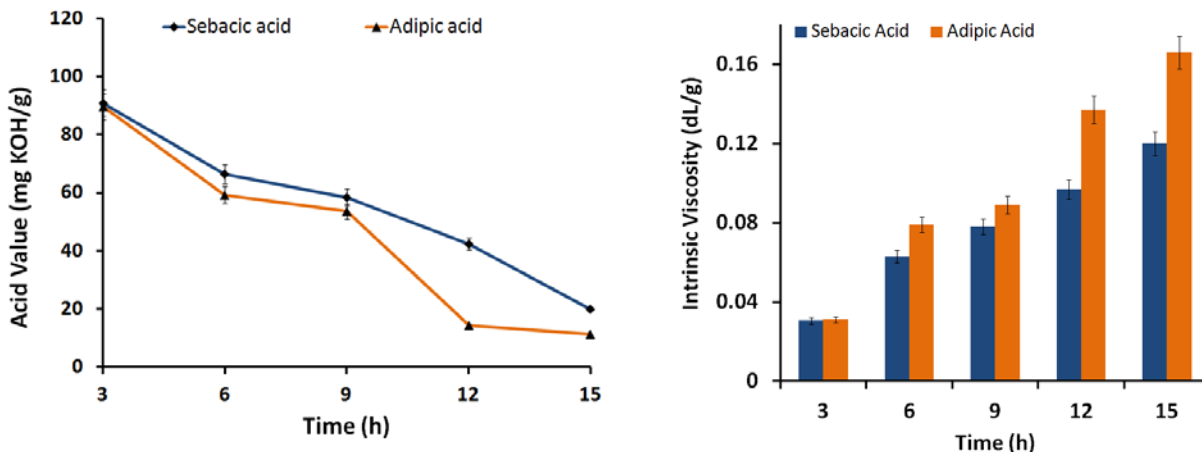
Figure 3.4: Variation of characteristic properties with progress of polyesterification reaction a) acid number and b) intrinsic viscosity

The FTIR spectra of the products obtained post-esterification with acids is presented in Figure 3.5. Characteristic hydroxyl group absorption ($\sim$3200–3600 cm^{-1}) was observed in the spectra of DEG glycolysed PET. Due to polyesterification reaction, the hydroxyl groups are consumed as a result of which the absorption in this region decreases. In view of the similar functional groups, the FTIR spectra of both types of polyols is similar, irrespective of the type of diacid used for its preparation. The hydroxyl number of the polyol decreases from an initial value of 430 ± 15 for DEG glycolysed PET to 20 ± 2 and 28 ± 2 after reaction with AA and SA respectively.
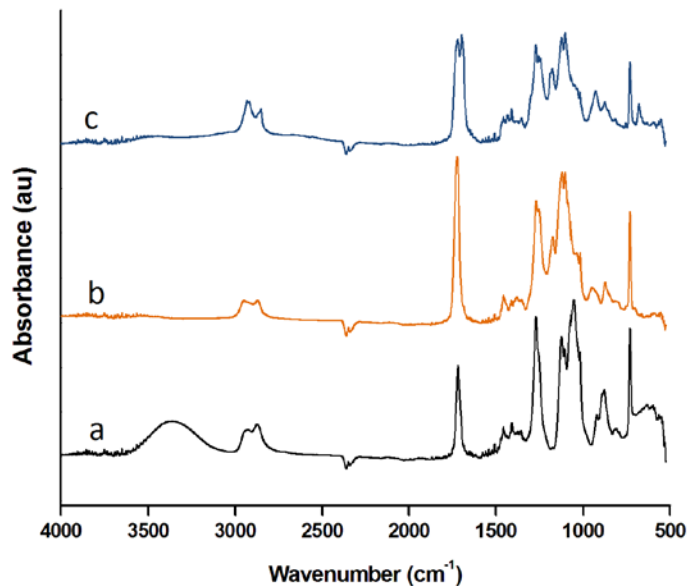
Figure 3.5: FTIR spectra a) DEG glycolysed PET, b) polyol obtained after polyesterification with Adipic acid, and c) Sebacic acid

3.4 POLYURETHANE FOAMS FROM POLYESTER POLYOLS

The polyester polyol was reacted with MDI in varying amounts to prepare polyurethane-polyisocyanurate foams, and the foaming process was monitored by measuring the duration of cream time, gel time and tack-free time, the results of which are presented in Table 3.1. The exothermic foaming process initiated almost instantaneously upon mixing of the reagents and the viscous mass continued to expand till the resulting foamed mass solidified due to progressive cross-linking. The isocyanate index for PU formulations is normally varied between 105 - 125, while for PU–PIR foams, it is increased to 180-350. In the present study, the same was maintained at 200 to obtain PIR foams, which were mechanically much stronger as compared to their PU analogues.

The entire process of foam formation is a delicate balance between two reactions. The initial blowing step involves the reaction of the isocyanate group with water to yield a thermally unstable carbamic acid, which decomposes to forms amine, carbon dioxide and heat. This is followed by a gelation step, which involves the reaction of isocyanates with polyol leading to the formation of urethane linkages in the resultant polymer. If the rate of gelation is slow in comparison to the initial blowing step, it amounts to the collapse of the reticular structure. On the contrary, the reverse scenario leads to formation of foams with closed cells, both of which are undesirable, for practical applications. It is in this context that cream time and gel time become critical for industrial formulations. For all practical applications in injection technology, the cream time has to be more than the injection time. The foam should expand and fill the form in approximately the same time as the gel time. The cream time and gel time recommended by reactivity profiles of injection technology are 4–8 and 30–60 s respectively.[47] In the present study, the foam rising (cream time) begins approximately within 15 s of mixing and solidifies completely (tack-free time) within 52-62 s (Table 3.1).

The apparent density of foams, as determined by mass volume ratio are reported in Table 3.1. PIR foams exhibit higher density than PU foams, which was also evident from the smaller cell sizes, as determined from SEM images (Figure 3.6). The average cell size of the foam along with the standard deviations was also determined and is reported in Table 3.1. As can be seen from the SEM images, all the foams possessed cells with almost uniform sizes.

Table 3.1: Characteristics of polyurethane foam derived from glycolysed PET

| Foam	Cream time (s)	Gel time (s)	Tack free time (s)	Density (kg/m^3)	Cell size (μ)	Compressive strength $(KPa)^a$	Young's Modulus $(KPa)^b$
DEGPUAA	15	36	62	225 ± 21	230 ± 21	5.27 ± 0.24	0.5 ± 0.02
DEGPUSA	15	39	60	187 ± 12	322 ± 42	1.35 ± 0.04	0.15 ± 0.01
DEGPI-AA	13	36	63	354 ± 29	198 ± 24	80.76 ± 3.41	102.7 ± 4.3
DEGPI-SA	14	40	67	312 ± 21	296 ± 22	21.4 ± 1.01	27.4 ± 1.2
PETPU-AA	14	33	52	233 ± 18	210 ± 23	18.3 ± 0.97	1.84 ± 0.04
PETPU-SA	14	34	60	198 ± 16	309 ± 31	7.39 ± 0.26	0.73 ± 0.03
PETPI-AA	15	38	61	376 ± 31	196 ± 25	158.86 ± 6.41	189.8 ± 8.34
PETPI-SA	15	36	62	348 ± 26	281 ± 32	122.7 ± 5.22	154.3 ± 7.43

a. Values at 10 % strain
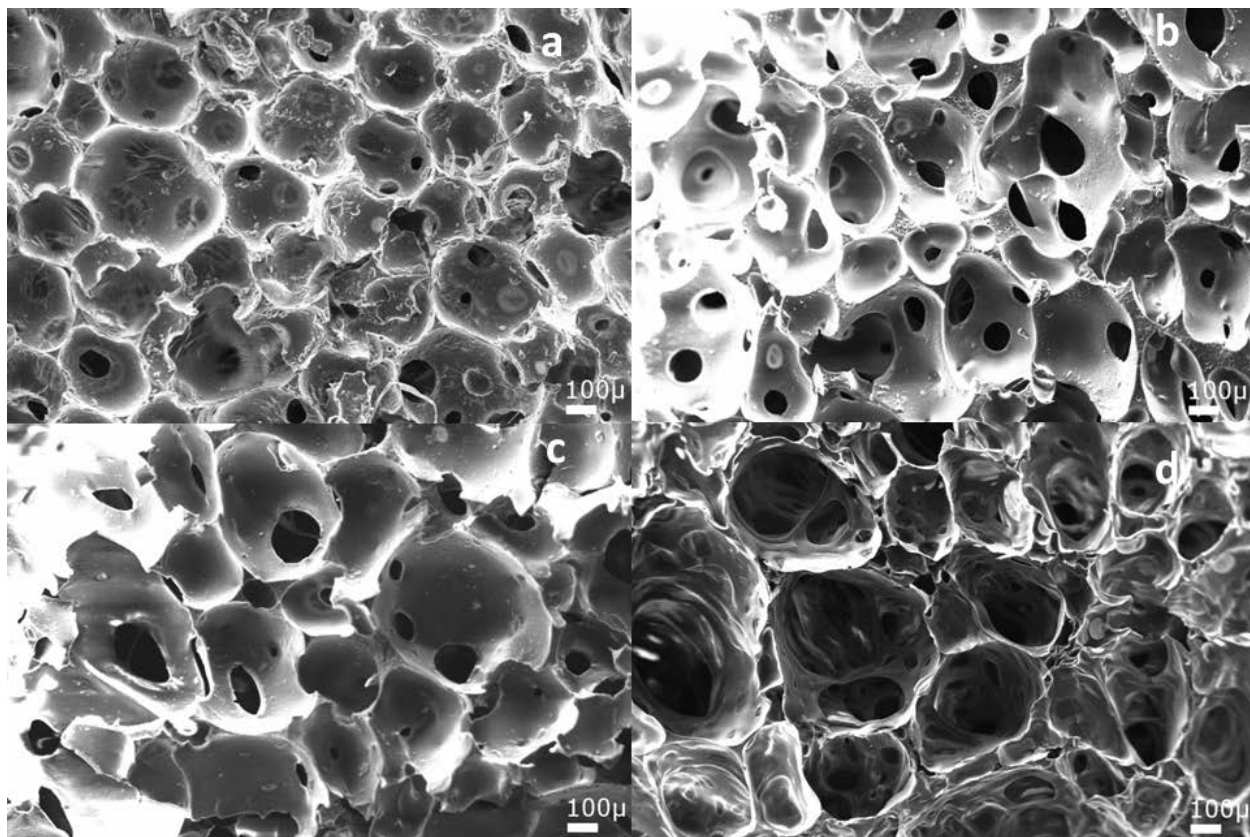
Figure 3.6: Scanning electron micrograph of representative polyurethane foams (a) DEGPU-AA

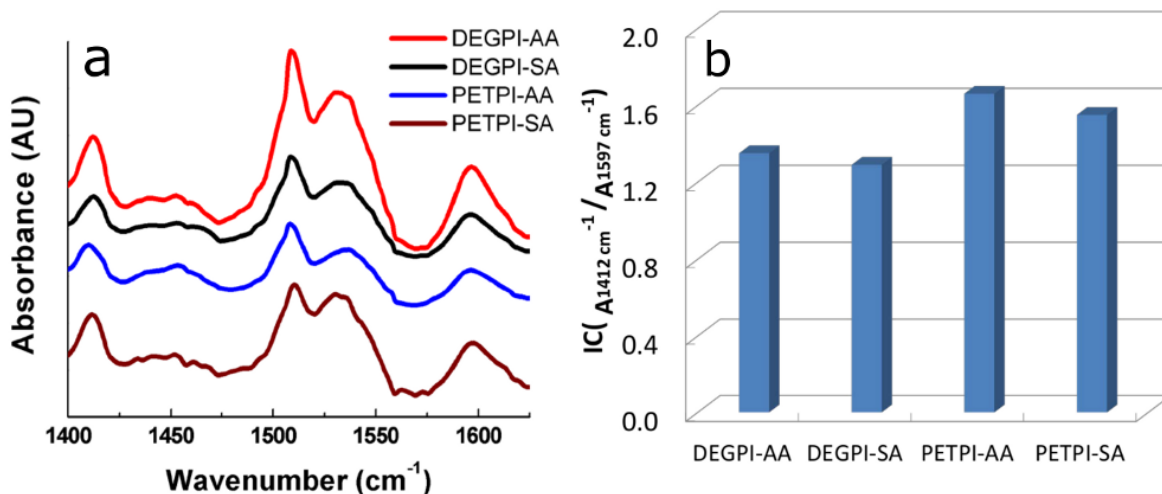(b) DEGPI-AA c) PETPU-AA (c) and d) PETPI-AA

Figure 3.7: (a) FTIR spectra and (b) the representative Isocyanurate content of PIR foam.

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The isocyanurate content was quantified in terms of the ratio of intensity of absorption band at 1412 cm^{-1} to intensity of the aromatic absorption band at 1597 cm^{-1} [37], the results of which are presented in Figure 3.7. The representative FTIR spectra of PIR foams are also presented in the figure. As can be seen, the PIR samples exhibit increased absorption at 1412 cm^{-1} due to presence of isocyanurate groups.

3.5 MECHANICAL PROPERTIES OF FOAMS

The mechanical properties of the foams were evaluated under compression mode and representative stress-strain curves are presented in Figure 3.8. The compressive modulus and strength (at 10% strain) of the foams are reported in Table 1. It can be seen from the figure that all the samples exhibit similar profiles i.e. an initial linear elastic region at low stresses, followed by an extended plateau. This feature is more pronounced in rigid foams with increased isocyanurate content. The observed elastic region arises primarily from the bending of cell struts,

and stretching of the membranes in the cell walls. The subsequent broad plateau is a result of the plastic collapse or cell wall buckling of the foam, which is more commonly referred to as the collapse stress.[48] It is this extended plateau, which endows the foams with their high compressibility and enables them to exert a relatively constant stress up to high strain levels.

As expected, the use of higher molecular weight acid i.e. SA, led to formation of foams with lower compressive strength. The initial linear region was used to determine the modulus of the foams, the results of which are reported in Table 3.1. As expected, the modulus of samples prepared using glycolysed PET was much higher, due to the introduction of aromatic phenyl ring in the main chain.
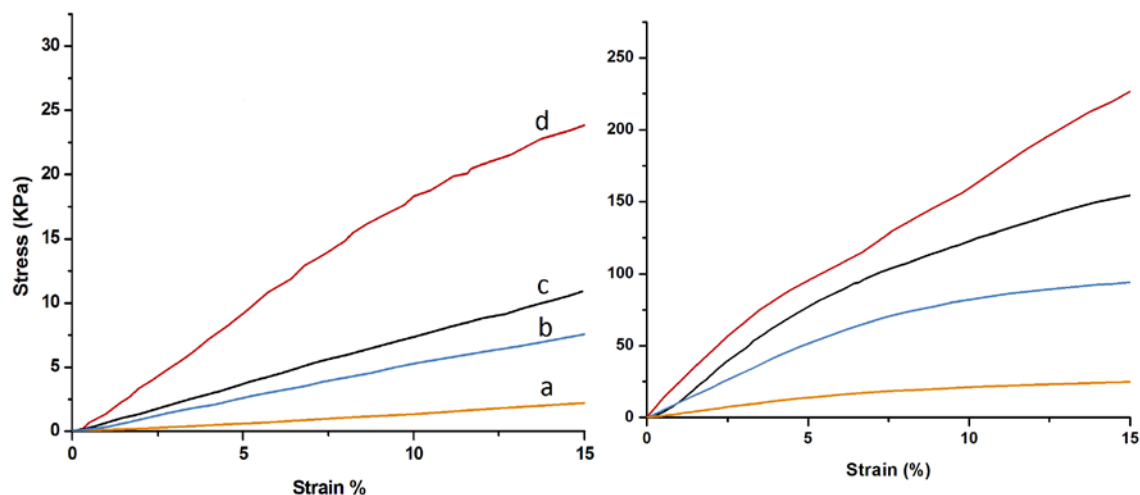

Figure 3.8: Compressive stress-strain relationship for foams in compression mode a) DEGPU-SA b) DEGPU-AA c) PETPU-SA d) PETPU-AA e) DEGPI-SA and f) DEGPI-AA g) PETPI-SA h) PETPI-AA

3.6 THERMAL CHARACTERISATION OF PU FOAMS

In view of the higher stability of isocyanurates in comparison to urethanes, a considerable improvement of thermal stability is expected.[49] The TG trace of polyurethane and polyisocyanurate foams under N_2 atmosphere is presented in Figure 3.9. Interestingly, the thermal degradation profiles was not affected with the type of spacer soft segment present in the polymeric chain and for the sake of brevity, only the TG traces of adipic acid based polyols are presented. As can be seen, the decomposition of PU foams initiates at slightly lower temperature than PIR foams. It can also be seen that the presence of aromatic groups in the foams derived from glycolysed PET lead to higher char yields. The moisture content was highest in PU foams derived from the polycondensation of aliphatic acids and diols (DEGPU-AA), and as expected, the presence of hydrophobic phenyl rings resulted in lower moisture content in foams derived from PET glycolysates.

The thermal decomposition of polymeric materials usually initiates with the cleavage of the weakest bonds in the chain. It has been reported that the decomposition of PU foams starts with the thermal dissociation of urethane linkages, which leaves behind a char ~ 20 % [28]while the PIR foams containing isocyanurate rings are much more stable with a char yield of ~30 % – 50 %. [49] Slightly lower char yields obtained in the present study can be attributed to the presence of higher amounts of aliphatic acid in the composition, which was introduced to achieve flexibility. The studies clearly indicate that all the foam samples could be safely used in service till a maximum of 270 °C, without undergoing any major thermal degradation, and the presence of aromatic rings in the chain leads to enhanced thermal stability.
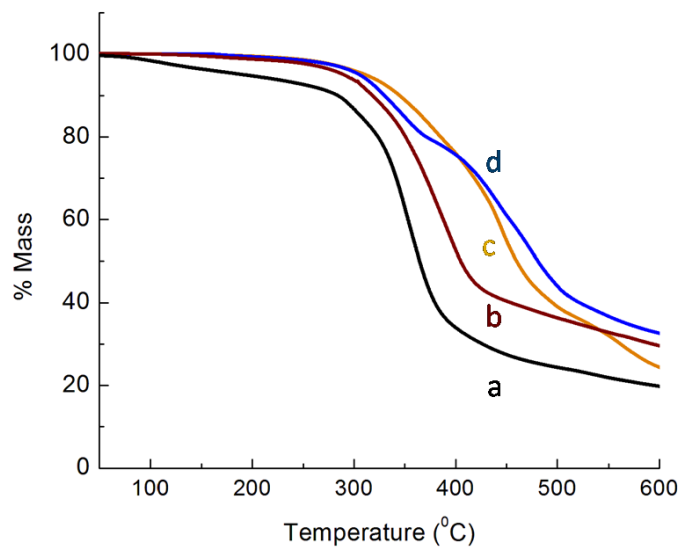
62

Figure 3.9: Thermogravimetric traces a) PUAA, b) PETPUAA, c) PI AA and d) PETPIAA

CHAPTER 4

SUMMARY & CONCLUSION

Discarded PET bottles were glycolyzed with DEG under microwave irradiation in the presence of zinc acetate (0.5% w/w). The reaction time required for glycolysis could be significantly reduced (~30 min) by the use of microwave as compared to the conventional thermal glycolytic process, which requires a minimum of 9 h to reach the same level of depolymerisation. The increased rate of glycolysis under microwave irradiation was attributed to efficient microwave absorption characteristics of DEG. Multiple extrusions of PET led to thermal degradation of the polymer, which resulted in its increased reactivity towards glycolysis. The effect of reaction parameters like PET: glycol ratio and reaction time were optimized to achieve maximum PET conversion. Polyester polyols were prepared by reacting glycolysed PET with difunctional acids like sebacic acid and adipic acid in order to introduce soft spacer segments within the polyester chain. The polyester polyols were used as a raw material for preparation of Polyurethane-polyisocyanurate foams by varying the isoyanate index. The effect of soft segment chain length, and the aromatic phenyl group on the compressive mechanical properties of the foams was evaluated. All the foams possessed cells of uniform dimensions, and the flexibility of the foam was found to be directly proportional to the chain length of the spacer molecule used for its preparation. The use of PET glycolysate as the polyol source led to an improvement in the thermal stability of the resultant foams due to the introduction of phenyl rings within the polymeric chain.

Acknowledgements

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