Chapter 4

Degradation and Recyclability of Poly (Ethylene Terephthalate)

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Additional information is available at the end of the chapter

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1. Introduction

The physical and chemical properties of polymers depend on the nature, arrangement of chemical groups of their composition and the magnitude of intra or intermolecular forces i.e primary and secondary valence bonds present in the polymer. Degradation process occurs due to the influence of thermal, chemical, mechanical, radiative and biochemical factors occurring over a period of time resulting in deterioration of mechanical properties and colour of polymers. The degradation occurs due to changes accompanying with the main backbone or side groups of the polymer. Degradation is a chemical process which affects not only the chemical composition of the polymer but also the physical parameters such as colour of the polymer, chain conformation, molecular weight, molecular weight distribution, crystallinity, chain flexibility, cross-linking and branching. The nature of weak links and end groups in the polymers contribute to stability of polymers. The degradation process is initiated at the terminal units with subsequent depolymerization. For example paraformaldehyde with hydroxyl terminal starts to degrade at about 170°C whereas the same polymer with acetyl terminals decomposes at about 200°C [1]. Replacement of carbon main chain with hetero atoms like P, N, B increases the thermal stability e.g. PON polymers containing phosphorus, oxygen, nitrogen and silicon.

The exposure of polymeric materials to environmental factors over a period of time will lead to deterioration of physical, chemical, thermal and electrical properties. The degree or measurability of deterioration of these properties depends on the extent of degradation, nature of chemical processes involved during the degradation. Degradation can be considered as a type of modification of polymer chain that may involve the main chain back bone or the side chain or groups. The modification could involve rupture of primary valence bonds leading to lowering of molecular weight, crosslinking, cyclisation and thus this type

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of cleavage could be irreversible. There could be degradation involving secondary valence bonds within the polymer chain e.g. hydrogen bonds in proteins which are influenced by heat, pH changes , chemical agents etc. and such type of degradative process could be reversible. Since degradation is a chemical process it affects not only the chemical composition of the polymer but also various physical parameters such as chain conformation, molecular weight, molecular weight distribution, crystallinity, chain flexibility, crosslinking, branching, colour of the polymer, haziness etc. Different polyester compositions exhibit wide variation in their response to degradative agents depending on the nature of the repeating units, chemical composition and structure e.g branching, size, shape, crystallinity.

2. Poly (ethylene terephthalate)

Poly (ethylene terephthalate) known by the trade names Mylar, Decron , terylene, Recron, has high crystalline melting temperature (260°C), and the stiff polymer chains in the PET polymer imparts high mechanical strength, toughness and fatigue resistance up to 150-175°C as well as good chemical, hydrolytic and solvent resistance. Poly (ethylene terephthalate) fiber has a very outstanding crease resistance, good abrasion resistance and can be treated with cross-linking resin to impart permanent wash and wear properties [2-4]. The fiber can be blended with cotton and other cellulosic fibers to give better feel and moisture permeation. Thus the fiber is used for applications such as wearing apparel, curtain, upholstery, thread, tire cord filaments, industrial fibers and fabric for industrial filtration.

The polymer is also used for making blow molded bottles for soft drinks, beers, spirits, other food-products and pharmaceuticals. This is because of the outstanding barrier properties of poly(ethylene terephthalate) . The film applications include photographic, magnetic, X-ray films or tapes , metalized films and electrical insulation. PET also finds use as an engineering plastic where it replaces steel, aluminum and other metals in the manufacture of precision moldings for electrical and electronic devices, domestic and office appliances and automobile parts. In the engineering applications the polymer is reinforced with glass fiber or compounded with silicones, graphite or Teflon to improve strength and rigidity. The polymer reinforced with glass fiber are rated for continuous use at temperatures up to 145-155°C. The properties and usefulness of the final polymer depends on controlling its structure by control of the process parameters during the polymerization and subsequent processing of the product.

The polymer is generally obtained by melt ◎phase polymerization to get resins of inherent viscosity in the range of 0.5-0.7 dL/g. For getting polymer with higher molecular weight i.e. inherent viscosity greater than 0.7 dL/g, solid state polymerization (SSP) is carried out. The latter process involves heating of solid low molecular weight melt-phase polymer below its melting point but above its glass transition temperature (Tg). It is very difficult to polymerize higher IV polymer in the melt-phase because of the thermal degradation reactions occurring simultaneously and competing with the poly condensation reactions.

Polyethylene terephthalate (PET) is a semi crystalline polymer possessing excellent chemical resistance, melt mobility and spinnability [2-4]. The polymer is composed of repeating units as shown in the Figure 1. Each unit having a physical length of about 1.09 nm and a molecular weight of ~200. When it is produced from the reaction of terephthalic acid and ethylene glycol, it is capped on the left by H- and the right by ◉OH. Polymerization is thus accompanied by the production of water which is removed under elevated temperature and vacuum. Accordingly the presence of water in the molten state will rapidly depolymerize the structure so that thorough drying of the polymer prior to melt spinning of fibers is necessary.

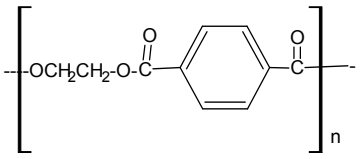


Figure 1. Structure of PET

The aromatic ring coupled with short aliphatic chain makes the polymer a stiff molecule as compared to other aliphatic polymers such as polyolefin or polyamide. The lack of segmental mobility in the polymer chains results in relatively high thermal stability. A textile grade polymer will have an average number of 100 repeat units per molecule so that the extended length of the typical polymer chain is about 100nm with a molecular weight about 20,000. Higher levels of polymerization produces higher strength fibers but the melt viscosity and stability of the melt to even tiny amounts of moisture causes hydrolytic degradation. The measurement of average degree of polymerization is done either by molten viscosity (by measuring the pressure drop through a calibrated orifice) or the viscosity of the diluted polymer in an appropriate solvent [3]. The latter is measure of polymer chain length known as Intrinsic viscosity or IV and the value for a typical fiber grade polymer is 0.6 dl/g in 60/40 w/w mixture of phenol and tetrachloroethane solvent [2-4]. The IV in the latter solvent is related to M_v (Viscosity average molecular weight) of the polymer by the Mark Howink equation (Equation 1) .

$$\left[\eta\right] = 7.44 * 10^{-4} \left(M_v\right)^{0.648} \tag{1}$$

It is very difficult to polymerize higher IV polymer in the melt-phase because of the thermal degradation reactions occurring simultaneously and competing with the poly condensation reactions. Thus during processing the polymer is subjected to temperatures in the range 280-300°C, which results in various types of degradations. The main degradations that can occur include thermal degradation, oxidative degradation and hydrolytic degradation. Radiation induced or photo degradation leading to free radical reactions and enzymatic catalysed reactions leading to logical degradation are also possible. In addition to these there can be chemical degradation reaction of polyester initiated by specific chemicals like glycol, ammonia or amines or other such reagents. Besides these there can be weathering ageing which could be the combined effect of exposure to temperature, moisture, chemical, UV and

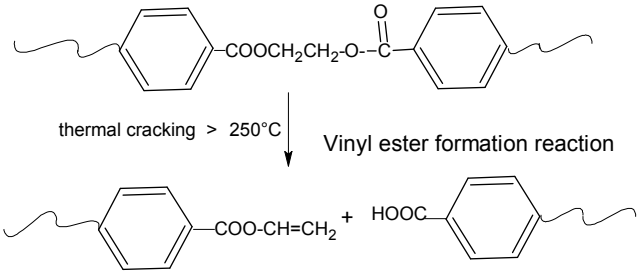
visible light and other conditions such as exposure to grease, oil. Polyester can also undergo stress induced degradation reactions when subjected to mechanical stress. The degradation of polyester can lead to several changes in the articles made out of the polymer. These changes include discoloration, chain scissions resulting in reduced molecular weight, formation of acetaldehyde and cross-links or gel formation and fish-eye formation in films. The thermal and thermo oxidative results in poor processibility and performance characteristics in the products. Discoloration is due to the formation of various chromophoric systems following prolonged thermal treatment at elevated temperatures. This becomes a problem when the optical requirements of the polymer are very high, such as in packaging applications.

The initial stage of thermal degradation is a random scission of the in-chain ester linkage resulting in formation of a vinyl ester and carboxyl end groups. Transesterification of the vinyl ester then occurs to give the vinyl alcohol, which is transformed immediately to acetaldehyde. The polyester chain is thus regenerated and an average degree of polymerization maintained. The net result of such a reaction is the replacement of hydroxyl end-groups by carboxylic acid end- groups, producing in the process an equivalent amount of acetaldehyde. Hydrogen atom abstraction may also occur to some extent when impurities in the polymer generate macro-radical sites. These will react with oxygen, producing peroxy radicals and subsequently hydroperoxides, which are themselves thermally and photochemically unstable and will induce further breakdown. The presence of moisture and acid/alkaline impurities will affect hydrolysis. Polyethylene terephthalate is an essentially hydrophobic polymer and hence rate of hydrolysis is thought to be determined by the nature of its chain ends. An increase in the carboxyl end-group concentration will increase the rate of hydrolysis of the polymer. Thermal degradation is degradation induced by elevated temperatures in the absence of oxygen. The chemistry of thermal degradation is different from hydrolytic degradation [6].

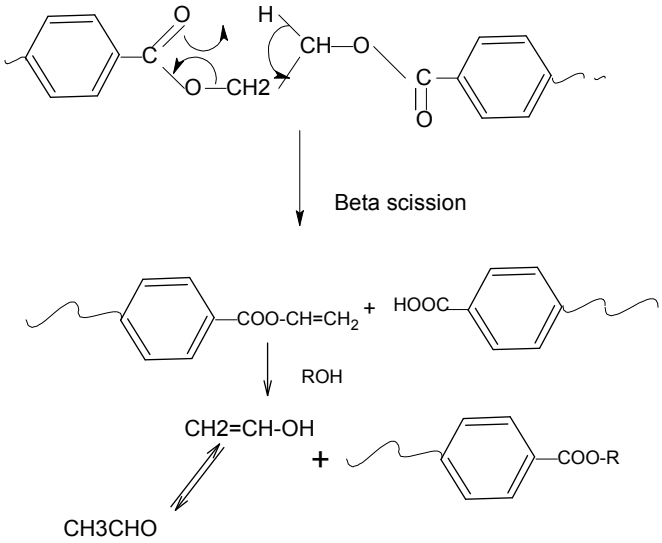
Thermal degradation results in different types of end-groups on the polymer chain. The initial step is the scission of the chain of the ester linkage resulting in a decrease in molecular weight either through random scission at the ester linkages or through chain ends and an increase in carboxyl end-groups. The methylene group which is located at the β position to the carbonyl group is the main point where the decomposition process is initiated. The main side reaction occurring is the β scission of the ester linkage results in the vinyl terminated carboxylate unit and carboxyl-terminated units as shown in Scheme 1.

The formation of acetaldehyde is explained generally through a Mc Lafferty rearrangement involving a six membered transition state occurring through inter or intra molecular hydrogen shifts in the methylene group which is located at the β position to the carbonyl group , as shown below [7] :

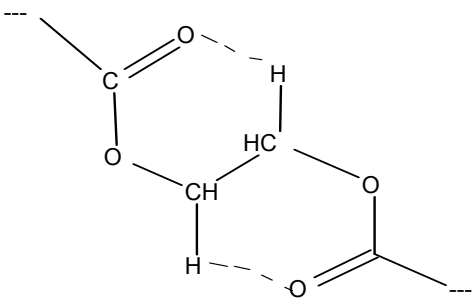
Apart from aldehyde CO, CO_2, ethylene , benzene, biphenyl are also identified as degradation products and the degradation products are analyzed by sub-ambient thermal volatilization analysis (SATVA) and pyrolysis gas chromatographic methods. Mechanism of ethylene formation is explained by the Scheme 3 [8-11].



The mechanism is by beta scission as shown below:

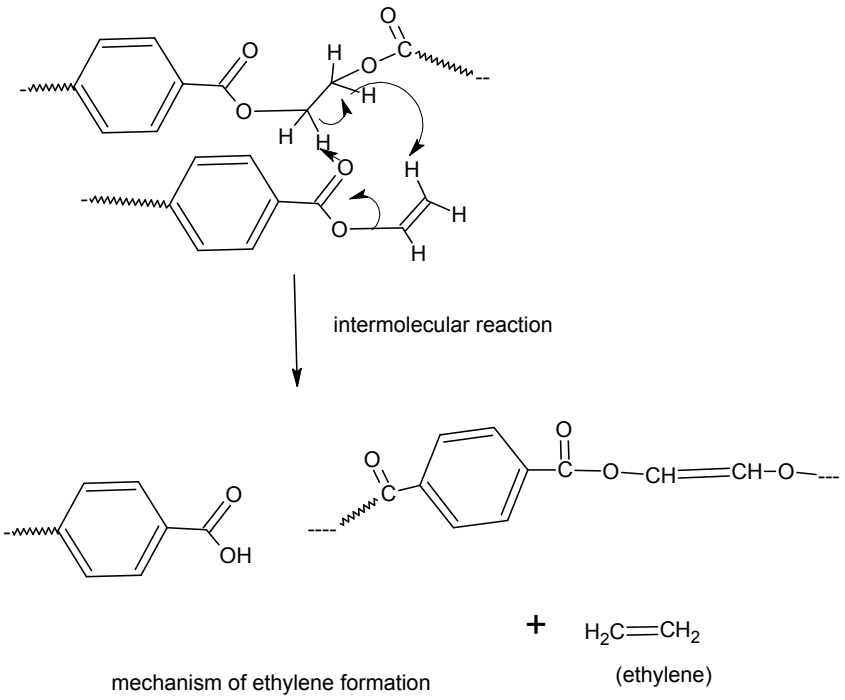


Scheme 1. Mechanism of β ⊚scission followed by acetaldehyde formation



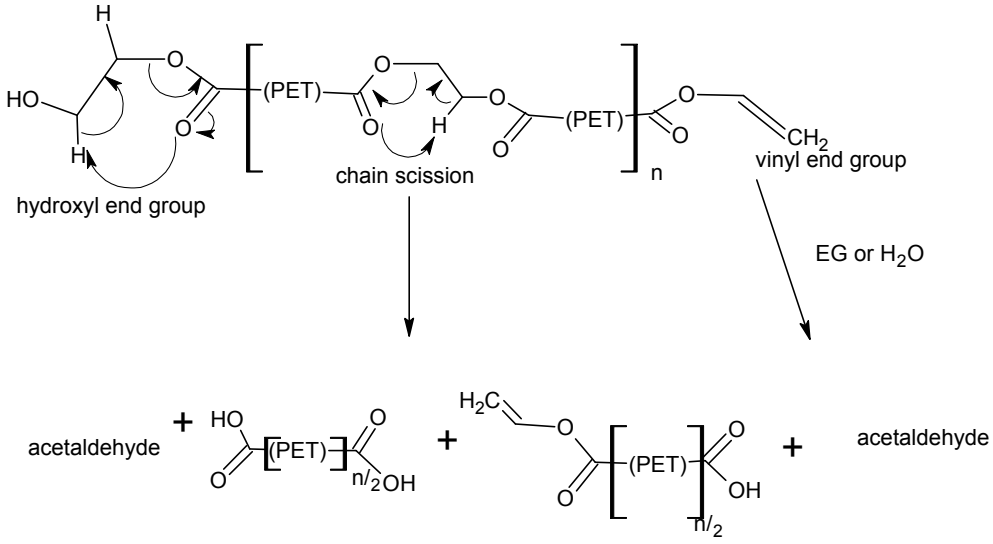
inter or intra molecular hydrogen shifts in PET

Scheme 2.



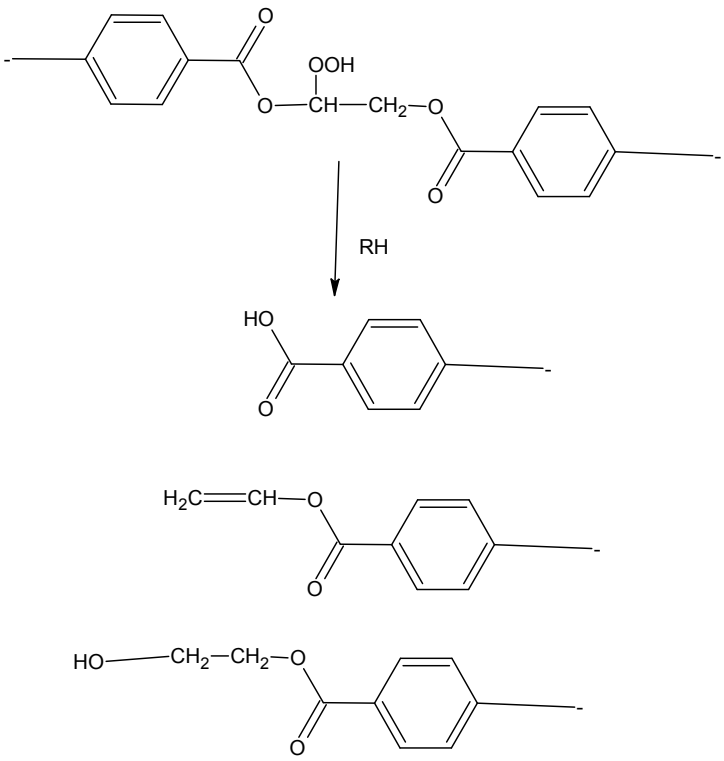
Scheme 3. Mechanism of ethylene formation

The overall degradation and cleavage can be represented by the following scheme 4 [12].



Scheme 4. Overall Mechanism of thermal degradation

The thermooxidative degradation involves the reaction of oxygen at elevated temperatures. This starts with formation of hydroperoxide at the methylene group in the diester linkage of polyester chain. It is not completely understood and is believed to follow free radical mechanism involving formation of hydroperoxides as shown Scheme 5 [13]:



Scheme 5. Thermo oxidative degradation of polyester

Photodegradation of PET occurs on exposure to near ultraviolet light, resulting in both chain scission by analogues of Norrish-type I and II processes shown in the reaction scheme or a photo-Fries-type reaction. This leads to cross-linking there by making the polymer films and fibers, brittle, and discolored. The films also develop crazed surfaces. PET when exposed to UV light degrades rather rapidly leading to deterioration in physical and mechanical properties and develops intense yellow colour [14]. Infrared and gas chromatographic analysis, GPC and colour measurements have shown large changes in hydroxylic region and broadening of carbonyl peaks . These are attributed to perester or anhydride formation. Both hydroxyl and carboxylic end-groups along with carbon monoxide and carbon dioxide are the main products of photodegradation [14]

The rate of degradation under these conditions depends largely on the reaction temperature as well as of the kind and amount of metal compounds used for the tranesterification and

polycondensation catalysts. Thermal degradation of ultra high molecular weight polyethylene terephthalate having IV exceeding 2 dl/g has a greater degradation rate than the conventional PET with IV 0.6 dL/g[5]. The high degradation rate of the higher molecular weight polymer is interpreted by the difference in the terminal group concentrations. Zimmerman et al [15] have shown that rate of thermal degradation in the closed system is about three times higher than that in open system.

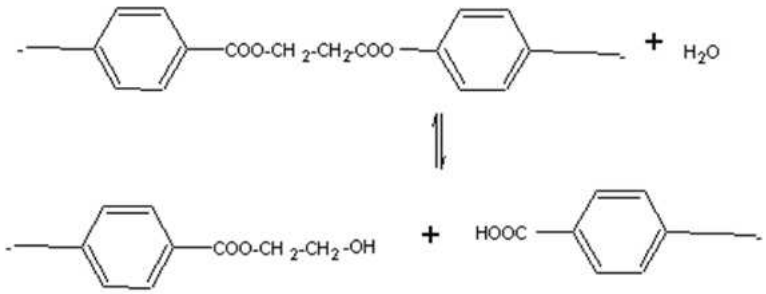
Measurement of carboxyl end-groups is one of the fundamental methods for measuring number average molecular weight of polymers. Pohl has shown as early as in 1954 that hydrolytic degradation of polyester chains can be studied by end-group measurements, which consists of dissolving the sample in benzyl alcohol at high temperature followed by titration using standard alkali [16,17]. There are reports on investigation of degradation using measurements of viscosity, optical microscopy, FTIR and UV methods [18-22]. W. Chaouch et al [23] have investigated the effects of hydrolytic aging of a series of PET vascular prostheses and compared their chemical properties between the virgin prosthesis using nuclear magnetic resonance spectroscopy (1H-NMR) and have used the latter technique to determine the OH group concentrations and the number average molecular weight of the polymer subjected to *in-vitrio* conditions and validated the data using the classical titration and viscosity methods. They have observed that the polyester yarns undergo chain rupture by hydrolytic and oxidative degradation during texturizing.

If moisture is present before the polymer is melted hydrolytic degradation will occur. Each water molecule will break the chain so increasing the total number of chains by one. The effect on average molecular weight will be as shown in Equation (2) [3]:

$$M_n^{'} = \frac{M_n}{\left[1 + x * (\frac{M_n}{1800})\right]} \tag{2}$$

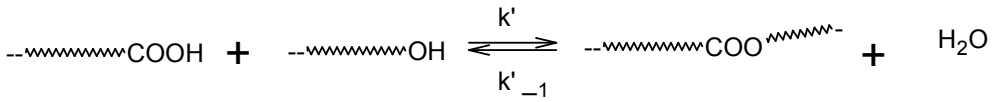
where M_n is the starting average molecular weight, $M_n^{'}$ s the average molecular weight after reaction with water and x is the water content (weight %). This relationship can be used to determine effect of moisture on IV and melt viscosity.

It can be seen from the above relationship that higher IVs produce increased sensitivity of the polymer to hydrolytic degradation. Hydrolytic degradation of polyethylene terephthalate is an autocatalytic reaction, being catalysed by the resulting carboxyl end-group. It is accompanied by an increase in hydroxyl end-groups and there is no discoloration of product and also there is no evolution of volatile products as shown in Scheme 6. This process is known to begin at temperatures ~100 °C. Hydrolytic degradation is reported to be 10,000 times faster than that of thermal degradation in the temperature range 100-120°C [13].



Scheme 6.

Suppose we consider the equilibrium reaction [16] shown in Scheme 7



Scheme 7.

k◎is the rate constant for the forward reaction and k◎-1 is the rate constant of the reverse or depolymerization or hydrolysis reaction. The ratio of k◎ to k -1◎ is K, the equilibrium constant for the above reaction.

$K = \frac{k'}{k'_{-1}}$ it is given by equation (3) ,

$$K = \frac{[COO]_E\,[H_2O]_E}{[COOH]_E\,[OH]_E} \tag{3}$$

The values of K are in the range 0.1 to 1, for normal polyester formation. Hence the reversal of polymerization is a faster reaction and it will lead to degradation of the polyester. Under this conditions K is simplified as shown in Equation (4)

$$K = \frac{p\left[H_2O\right]}{M_0\left(1-p\right)^2} \tag{4}$$

where p is the extent of reaction[16] , since X_n=1/(1-p), (X_n is degree of polymerization which is ~90-100 for fiber grade polyester), it can be rewritten as shown in Equations (5) and (6).

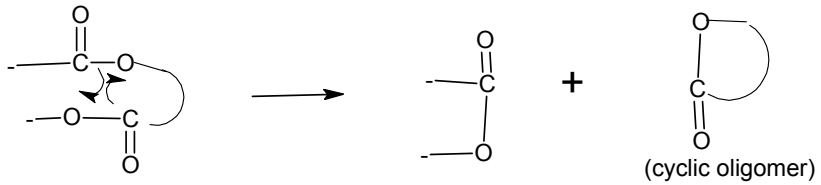
$$K = \frac{p\left[H_2O\right]X_n^2}{M_0} \tag{5}$$

$$X_n\left(X_n - 1\right) = \frac{KM_0}{\left[H_2O\right]} \tag{6}$$

square of X_n is inversely dependant on [H_2O] i.e higher the water concentration the degree of polymerization will decrease much faster.

2.1. Oligomer formation

The other side reaction (shown in Scheme (8)) that can take place is the formation of cyclic oligomers, which can be a major nuisance during melt spinning and dyeing.

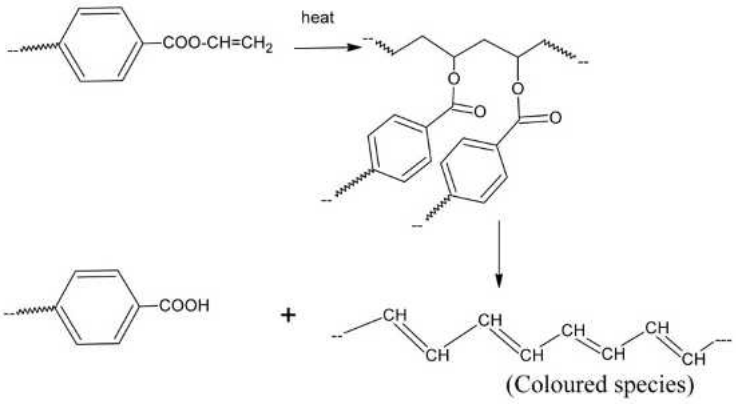


Scheme 8.

The cyclic trimer exudes from the hot polymer surface and coats the spinnerrette plates on the melt spinning units. It can even build up enough to cause breakdown of the thread line. The cyclic trimer exudes form the fibers (which have high surface /volume ratio) during dyeing. The exuded cyclic trimer can float in the bath liquor and contaminate the dyeing equipment [4] depending on the dye bath temperature.

2.2. Causes of discolouration in polyester

The vinyl ester ends also act as cross-linkers and gelling agents. They polymerize and the polymers thermally degrade to give yellow or brown polyenes that discolour the final polymer. The formation highly conjugated species is catalysed by carboxyl groups. The formation of coloured species is followed by increase in more carboxyl terminated species. Hence the product having higher carboxyl value gives more yellowing. The mechanism is given in Scheme 9 [24]:



Scheme 9. Formation of conjugated structures leading to coloured species

The carboxyl end-groups are formed by the random thermal cleavage of the chains and a formation of double bonds.. The carboxyl groups catalyze the hydrolysis of ester groups i.e this can be auto catalytic. Intermolecular reaction leading to increase of acid value, ethylene formation and unsaturated species in the polymer backbone as explained in Scheme 9.

2.3. Experimental studies on degradation reactions

In our experimental studies on thermal degradation of PET having cationic dyeable comonomer units viz. 5-sulphoisophthalate moieties are tracked by measuring the mechanical properties of the textured yarns produced from the partially oriented yarn (POY) spun at different residence times [11]. The surface properties of the POY spun at different times are also examined by SEM studies. The degradation reactions of homopolymer, polyethylene terephthalate (Polyester A.) shown in Figure 2 is compared with that of cationic dyeable polyester containing 5-sulphoisophthalate comonomer units (SIPM) that shown in Figure 3 (Polyester B).

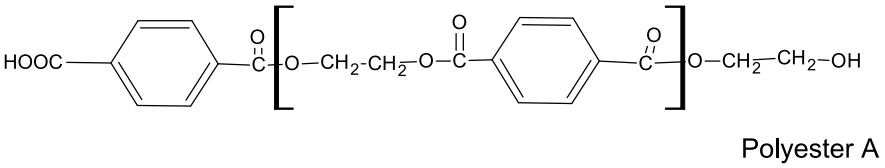


Figure 2. Structure of homopolymer (polyethylene terephthalate)

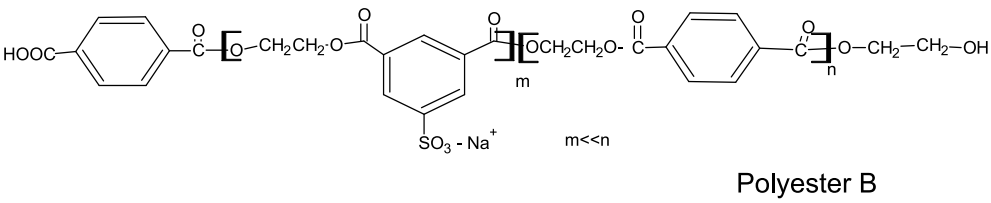
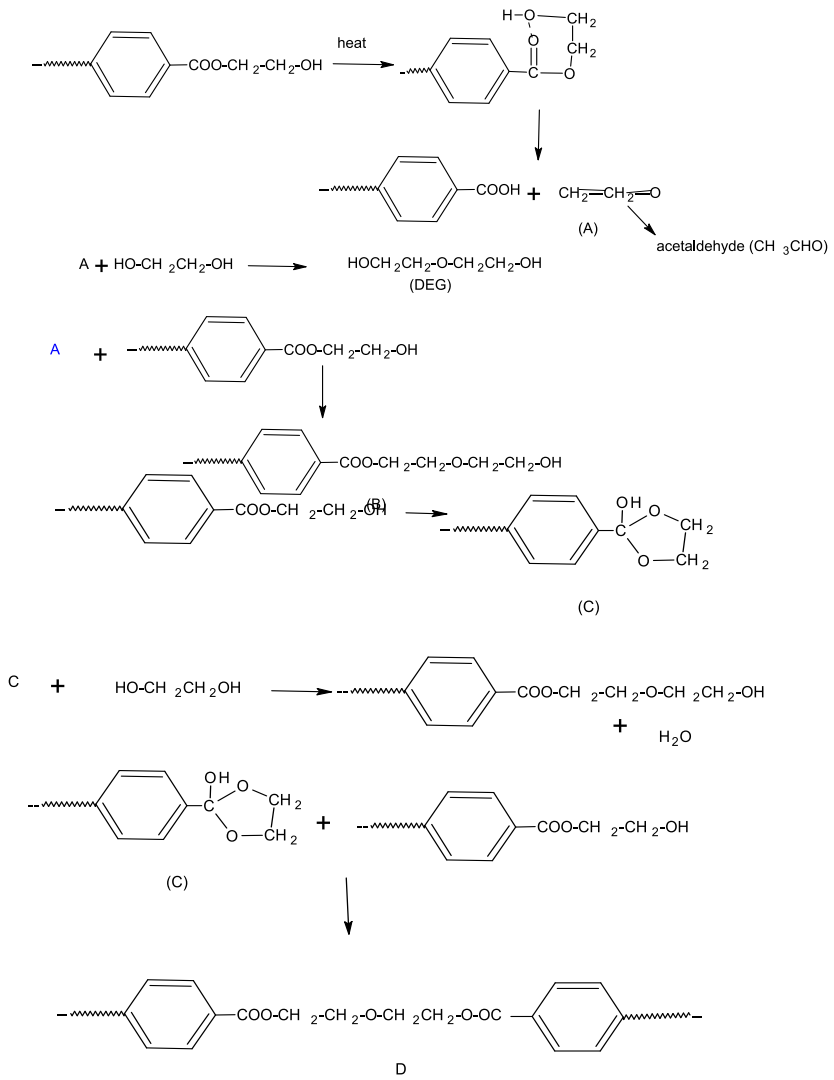


Figure 3. Structure of 5-sodiumsulphonato isophthalic acid copolymer of PEt

Sulphonate groups present in Polyester B contributes to ionomer interaction and steric hindrance thereby increasing the melt viscosity [25,26]. During the melt polymerization of polyethylene terephthalate (PET) there occurs an unavoidable side reaction due to coupling of the hydroxyl end-groups by dehydration forming diethylene glycol (DEG) units in the chain as shown in the following Scheme 10. [24] In the Scheme 10, the intermediate (A) gives acetaldehyde. The cyclic intermediate shown in Scheme 10 C, leads to both hydroxyl terminated intermediates (B) and polyester having diethylene glycol units in the backbone (D).



Scheme 10. Mechanism of DEG formation

The presence of DEG units depresses the melting point (ΔTm) which is given by the empirical rule based on Vand Hoff equation given by ΔTm = -2.2 m °C (where m is the molar percentage of DEG) . The Tm is measured accurately by differential scanning calorimetry (DSC). The presence of DEG units in the polymer reduces crystallinity, lowers softening point, thermal and hydrolytic stability. About 1 to 1.5 mole % of DEG is always present in PET homopolymer4. Hence DEG content of the polymer becomes an important parameter to be defined. Kinetic studies [11] of polyester containing 5-sulphoisophthalate units indicate that the copolymer degrades faster than homo PET. The rate of degradation depends on the

residence time and temperature to which the molten polymer is subjected Rate of degradation of polymer melts is generally represented [27] by the equation (7)

$$\frac{1}{N} = \frac{1}{N_0} + k_0 \, e^{-E/RT} t \tag{7}$$

where, N and N_0 are the final and initial number average degree of polymerization respectively. Where, k_0 is a constant, E is activation energy, R is the universal gas constant, T is temperature in Kelvin, t is time in minutes.

The degree of polymerization is not an easily measured variable. More commonly, polymer properties are measured in terms of intrinsic viscosity and the degradation equation will have to be written using this variable. The intrinsic viscosity, η can be related to degree of polymerization by the Mark Howink equation given by equation (8).

$$\eta = bN^{\beta} \tag{8}$$

where, η is intrinsic viscosity, b and β are constants depending on the type of polymer.

Substituting equation (7) in equation (8), the rate of degradation of polymer melts can be written as equation (9) , where η and η0 are final and initial intrinsic viscosities

$$\mathbf{1/\eta^{(1/\beta)} = 1/\eta_0^{(1/\beta)} + k_0 (1/b)^{(1/\beta)} exp^{(-E/RT)} t} \tag{9}$$

The activation energies for the degradation are estimated from the kinetic data using the equation (9) are found to be 128.94 kJ $mole^{-1}$ for Polyester A and 59.22 kJ $mole^{-1}$ for Polyester B. These values indicate that the co-polymer is more prone to thermal degradation as compared to the homo-polymer. Holland and Hay [28] have shown by Thermal analysis and FTIR spectroscopy the average activation energy for the β C-H transfer process (loss of 1960,1730 and 1255 cm^{-1} bands in FTIR) was 230±10 kJ $mole^{-1}$ and 250±10 kJ $mole^{-1}$ for PET modified by DEG co polymerization and PET modified with both DEG and isophthalic acid IPA copolymerization respectively. They have also shown that the activation energy for the loss of -O-CH_2-CH_2-OH i.e. ethylene glycol derived end groups (loss of 3440 cm^{-1} in FTIR) was ~ 160±10kJ $mole^{-1}$. Loss of ethylene glycol end-groups leads to the formation of a carboxyl end-groups, which promotes intra-molecular backbiting reactions. The favourable angle of 1,3 structure in the isophthalate unit of the 5- sulphoisophthalate co-monomer unit, facilitates the degradation process easily. The presence of bulky sulphonato group causes disorders in the fine structure of polyester fibre thereby lowering the hydrolytic and thermal stability [29].

Yarn produced with higher residence time has poor mechanical properties The SEM images of the yarn samples indicate that as the residence time in a particular temperature is increased more number of particles of degraded products are formed and they have the tendency to grow larger in size, as shown in figures 4a, 4b and 4c.

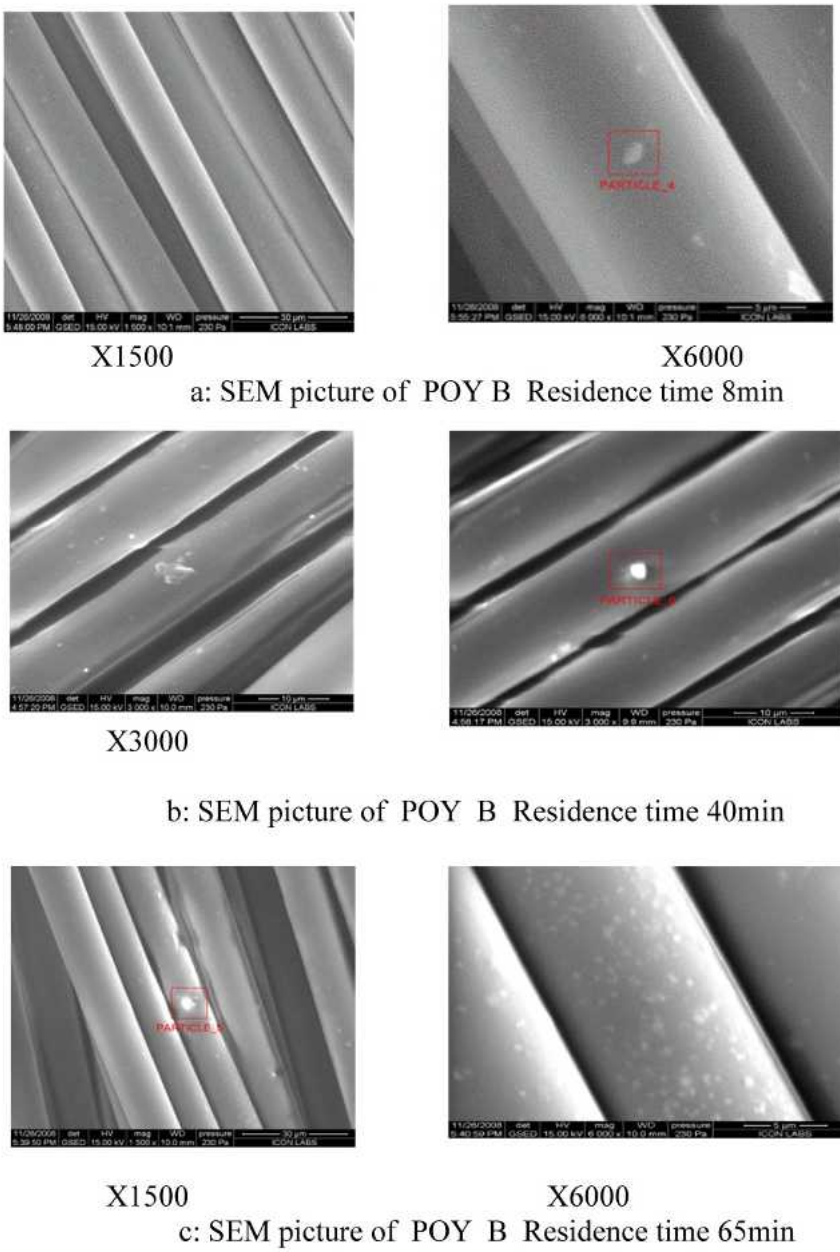
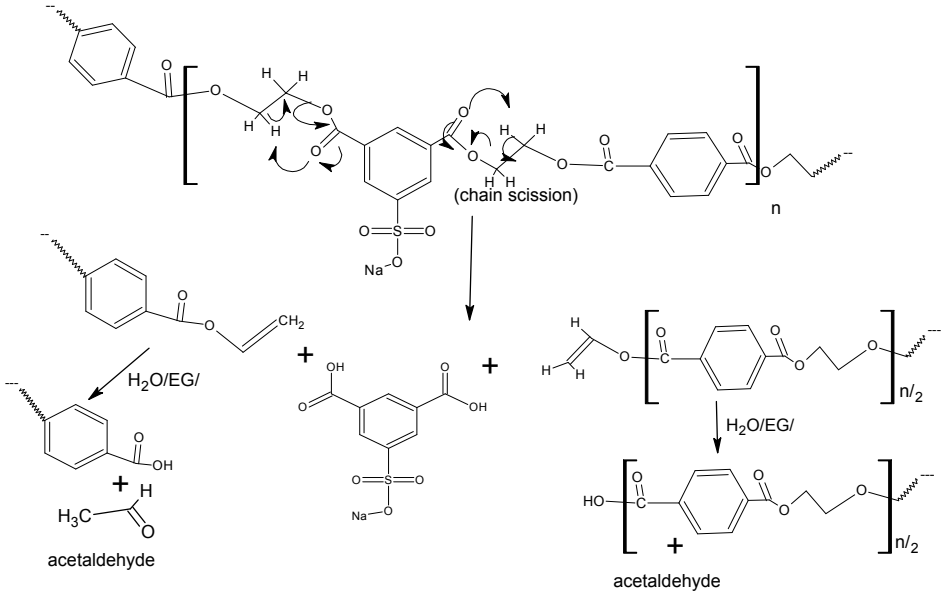


Figure 4.

The degradation results in highly crystalline trimers and oligomers having carboxyl terminals, which occurs by three different routes involving the hydroxyl end-groups or

vinyl end-groups or by the inexhaustible mid chain scission route [7,12]. Based on the mechanism of end-group scission of hydroxyl and/or vinyl end-groups and that of mid chain occurring simultaneously during thermal degradation, the by-product formed has two carboxyl terminals, indicating higher acid value in the resulting product. The proposed mechanism for degradation is given in Scheme 11.



Scheme 11. Mechanism of degradation of polymer containing

The EDX analysis of these particles indicate presence of more organic material (i.e low molecular weight oligomers of larger particle size.) along with some external metallic impurities like Si, Fe, Ti etc. The particles as seen by EDX are organic and are due to more crystalline species. This is separately confirmed by measuring the surface cyclic trimers (shown in Table 1) in the yarn samples produced with different residence times.

S.N.	Residence time (min)	Cyclic trimer (parts per 106 parts (ppm)
1	8	195
2	40	221
3	65	366

Table 1. Amount of cyclic trimer in the polyester Yarn [11]

When the yarn was washed with methanol, some of the particles gets washed off as seen by the SEM of the washed material in Figures 5a and b indicating the oligomers and cyclic trimers get washed off, with methanol. This confirms that the particles seen in the surface are due to surface cyclic trimers.

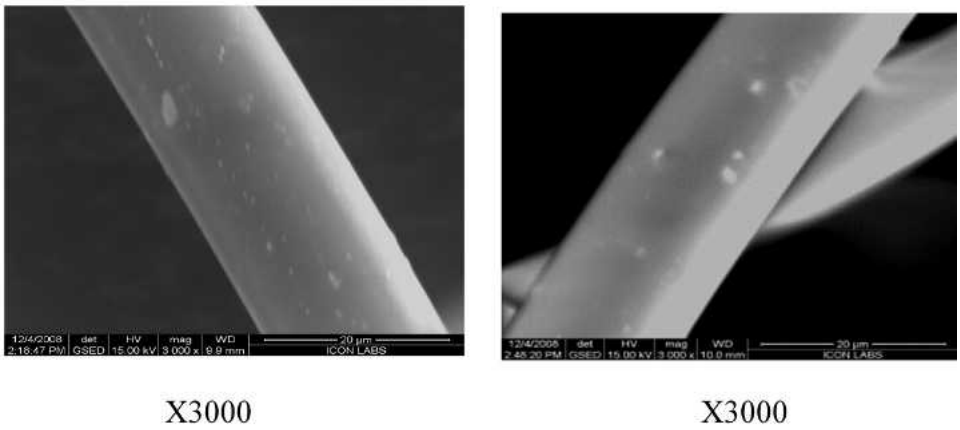


Figure 5. a and b : SEM picture of POY B (residence time 65 min) after washing with methanol.

2.4. Effect of thermal stabilizer on the thermal degradation

Phosphoric acid is added as thermal stabilizer to reduce the extent of degradation. It is reported that phosphoric acid interact with the polycondensation catalysts thereby modifying the catalyst [30-33]. Since the same catalyst catalyses the thermal degradation addition of phosphoric acid mitigates degradation reactions. The mechanical properties of the polyester textured yarn (PTY) produced with different amounts of phosphoric acid is given Table 2.

Quantity of Phosphoric acid added (parts per 10^6g)(ppm)	Tensile strength (g /d)	Elongation (%)
0	2.61	12.6
50	2.84	19.6
110	2.89	20.6
125	2.90	22.1
150	3.0	23.7

Table 2. Effect of phosphoric acid on the mechanical properties of the PTY

The data in Table 2 indicate that addition of phosphoric acid improves the mechanical properties of the yarn. But caution is needed on the amount of phosphoric acid used. Figure 6a and Figure.6 b show the SEM pictures of the polyester yarn prepared with different concentration of phosphoric acid in the polymer. The pictures indicated that when phosphoric acid is 125 ppm it causes more agglomerate formation, indicating that higher amounts of phosphoric acid results in more agglomerate formation which get oozed out to surface.

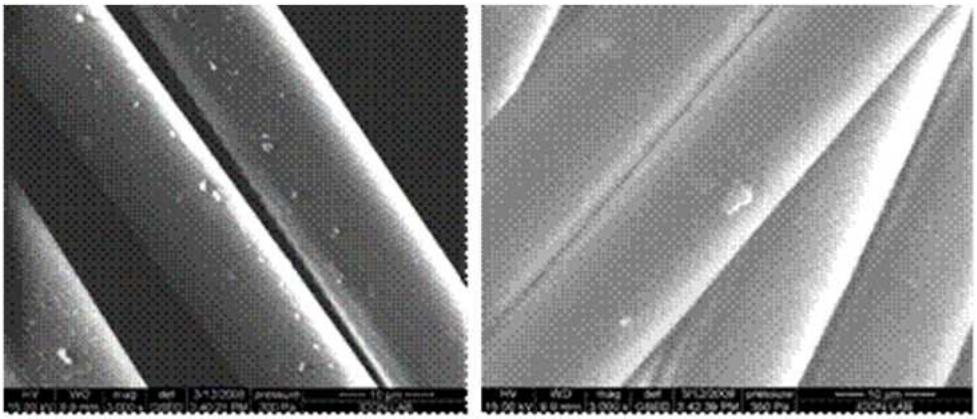
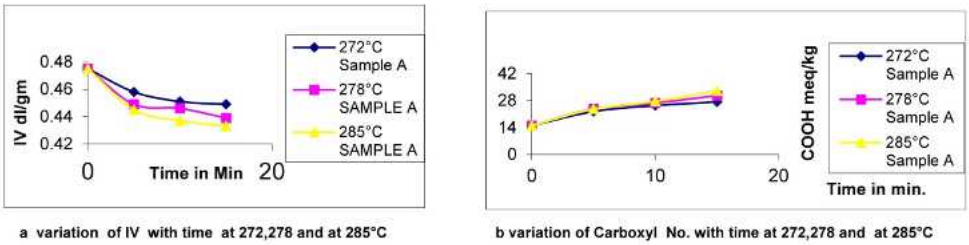


Figure 6. a SEM of polyester yarn with 110ppm H_3PO_4 Figure. 6 b SEM of polyester yarn 125 ppm H_3PO_4

2.5. Degradation studies on penta containing polyester

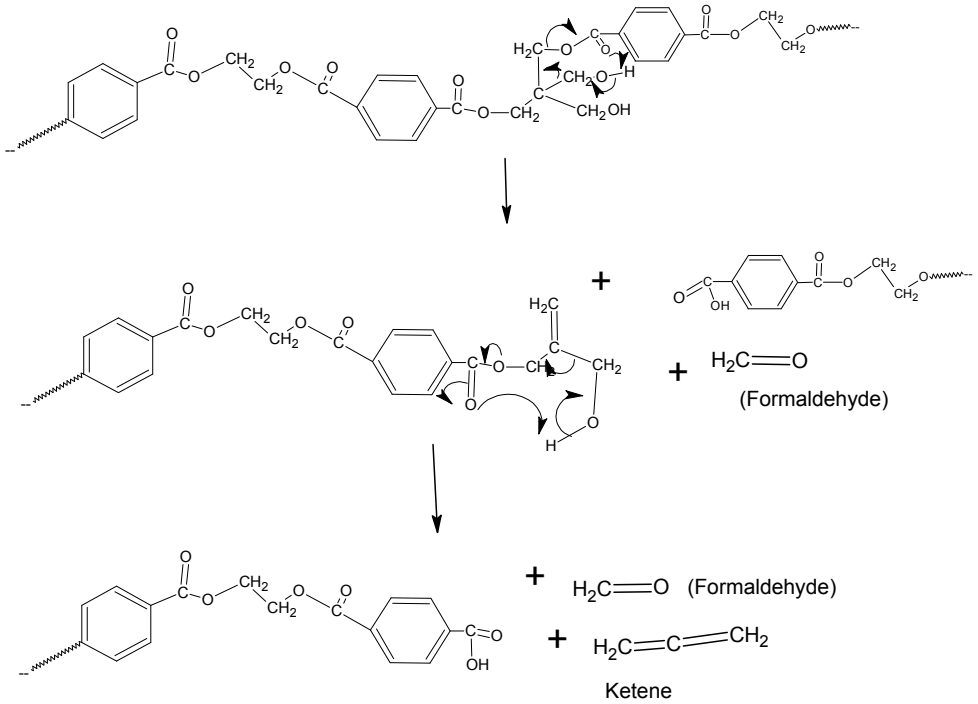
Degradation measurements were done on the polymer containing small amounts of pentaerithritol as a comonomer (to an extent of 0.15 % by weight). Figures 7 a-b, give the variation IV and carboxyl value for the polyester having penta erithritol units (Polymer C), when the dry polymer chips are melted and kept at temperatures 272°C, 278°C and at 285°C, in inert atmosphere at different times. The results indicate a drop in IV by 0.026 units at 272°C compared to 0.042 units at 285°C over the 15 min. & COOH end-group is increased more at 285°C(18 meq/Kg) compared 12 meq/kg at 272°C. Degradation involves the terminal hydroxyl groups having pentaerithritol moieties as shown Scheme 12. This process gets more easily facilitated in presence of alkali. In this process loss of two formaldehyde molecules and a ketene take place resulting in loss of pentaerithritol [34].



a variation of IV with time at 272,278 and at 285°C

b variation of Carboxyl No. with time at 272,278 and at 285°C

Figure 7.



Scheme 12. Mechanism of Degradation in polyester containing penta erithritol moieties

The hydroxyl groups of the partly reacted penta units could become a chain scission source. This results in loss of molecular weight (decrease of IV) and increase in carboxyl terminated by products which is seen by increase in carboxyl value and decrease in IV. The loss of carbon in the samples were seen by EDX analysis in our earlier studies also confirms this mechanism. This also accounts for the loss of pentaerithritol [34]. IV decreases with time reaches an asymptotic behavior because of the result of equilibrium established in the molten polymer. The decrease of IV depends on how the equilibrium is established and how the hydroxyl terminals take part in the Mc Leferty type of fragmentation leading to formaldehyde and ketene loss as shown in Scheme 12. This depends on the residence time the molten polymer was kept at the particular temperature. This gets more aggravated in presence of alkali. Hence pentaerithritol containing polymer degrades more easily in presence of alkali.

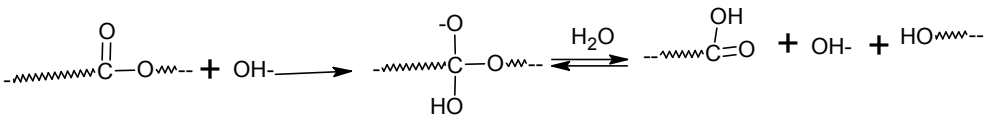
From the degradation results it is clear that the higher residence time and temperature has caused degradation of the chips. The pentaeithritol units having unreached hydroxyl groups could become an easy source for initiating the thermal degradation. The hydroxyl terminals could have also formed due to hydrolysis by the moisture present in the system. It is reported that [16] hydrolytic degradation of polyester causes increase of elongation at break due to more chain scissions excepting samples degraded at higher temperature for more than 20 days in which elongation at break will decrease due to more weak points. Also,

thermal degradation of samples will decrease elongation at break, because of the annealing process.

2.6. Effect of pentaerithritol units on alkali hydrolysis of polyester

Adding small amounts of multifunctional monomers results in cross-linking or branching of the main polymer chain [2,3,16]. However, randomly branched (hyper branched) polymers are formed [35] due to high reactivity of pentaerithritol, perfect branching is not achieved and additional linear units are present in the molecule. The extensive branching in the randomly branched polymer prevents crystallisation and results in amorphous material. They are generally brittle with low melt viscosity due to lack of long chains to form entanglements. Partial hydrolysis of branch sites in presence of alkali gives more conducive environment for getting randomly branched or hyper branched structures which are highly amorphous and makes the alkali penetrate the polymer structure easily and degrade it faster. It is known that hydrolysis of PET under room temperature conditions is an extremely a slow reaction. Incorporation of small amounts of pentaerithritol segments in the main chain of PET exerts a profound effect in the hydrolytic susceptibility of PET. Pentaerithritol containing units makes the polymer more susceptible to hydrolytic attack. In contrast, a higher degree of crystallinity hinders the reaction because the crystalline phase is inaccessible to water.

Hydrolytic attack on polyesters involves scission of an ester linkage in the main chain by water. Each chain scission uses up one water molecule and creates one carboxyl group and one hydroxyl end-group. In solid state the hydrolysis process depends on chain mobility and flexibility. A reduction in Tg of the polyester enhances the susceptibility of attack by water . The lower Tg also increases chain mobility and reduces energy required to achieve the transition state. Cagiao et al [36] have shown by wide angle X ray (WAX) studies that initial hydrolytic attack could be restricted to amorphous regions and crystallite edges, although lamellar stacks themselves are attacked. It is also known that chain scission of tie segments between crystallites results in further crystallization of amorphous phase giving rise to apparent increase in crystallinity, which could lead to decrease of tenacity. If the polymer is kept in the aqueous alkali bath for longer time, this becomes more degraded, as Scheme 13.



Scheme 13. Hydrolysis in alkaline medium

The depolymerization and thermo-oxidative degradation results in decrease of IV and a rise in the number of carboxyl end-groups [11]. Similar phenomena are reported for polyester copolymers at higher temperatures [7]. The degradation processes that occur are influenced by the moisture and oxygen present in the system. Polyethylene terephthalate is shown to

give dual slopes of initial fast rate and later slow rate of degradation [37]. The initial rate is attributed to hydrolysis of residual water and the latter slow rate is attributed the thermal degradation initiated by thermal energy. Rate of degradation of polyethylene terephthalate polymer is studied by measurement of the evolved acetaldehyde by Khemani [12]. The degradation causes a decrease in molecular weight either through random scission at the ester linkages or through chain ends.

2.7. Recycling of polyester

The chemical nature of polyethylene terephalate permits easy recyclability by all known recycling methods. Recycling of polyester has become an important process from the environmental point of view and it has given commercial opportunity due to wide spread use and availability of PET bottles, packages and fibers [37-39]. While mechanical recycling is well established, chemical recycling is highly dependent of the manner in which the depolymerization is carried out.

The chemical recycling methods include processes namely methanolysis, glycolysis, hydrolysis, ammonolysis, aminolysis and other processes [40-41]. Chemical recycling of polyethylene terephthalate into yarn through a process where part of the virgin raw materials are replaced by washed post consumer polyester which is partially depolymerized before repolymerization [42]. Controlled hydrolysis of polyethylene terephthalate using dilute HNO_3 as catalyst is shown to produce cation exchange sites based on acidic groups and the acid sites are shown to adsorb heavy metal cations like Cd^{++}, large cationic dye molecules and the acid hydrolysis is shown to be much more efficient compared to neutral and alkaline hydrolysis [43].

Post-consumer PET bottles are generally sorted out at a material recovery facility, compressed into bales, washed and converted to clean dried flake [39]. The feed purity requirements of the intended use of the recycled PET makes recycling more challenging. Generally contaminants are not allowed in fiber or bottle applications due to breakage and aesthetic considerations. During recycling thermal and oxidative degradation products cause yellowing and diminishing of mechanical properties of the product. There are a number of other difficulties which are to be addressed during recycling PET. For example, the presence of ester group in the back bone of the polymer makes the polymer easily degradable with moisture hence recycling process requires special type of drying prior to processing and hence the conventional blow moulders or sheet extruders used for PE or PP couldnot be used in PET applications. PET drying temperature strongly affects the processing characteristics of the PET containing PVC. For example [39] drying at temperatures below decomposition temperature of PVC (120°C 24 hrs) results in clear PET without significant black speck formation upon extrusion but the rheological stability of PET is poor due to the contamination of HCl catalysed hydrolysis reactions. On the other hand, drying at very high temperatures (230°C, 4h) the majority of HCl is getting removed thus improving the rheological stability of the material, although the extrudate shows excessive black speck formation. While recycling PET traces of label adhesives (based on rosin acids

and esters) cause PET to lose clarity and the contamination of impurities such as glue, dirt, paper cause severe deterioration of properties of the recycled polymer. The yet another factor to be considered is the difficulty in getting consistency in the batch-to batch quality of the polymer obtained [39]. It is also not easy to separate contaminants like PVC, PVDC, rosin adhesives, glues, EVA etc which generate acidic compounds which catalyze the hydrolysis of the back bone ester linkages of PET . While physical contaminants like dirt, glass fragments PE are removed the ingrained particulate materials embedded by mechanical abrasion and mechanical grinding during baling, transport and handling are difficult to dislodge. Such impurities pass through the mechanical recycling process and cause stress concentrations (eg.gels, blobs, black specks) that can create problems during fabrication such as excessive fiber breakage during spinning or blow-outs in the wall of blown bottles. Some contaminants such as degraded rubber and wood ash also pass through the extremely fine screens and melt filters and these lead to black specks to the recycled polyester.

State of the art recycling technology by M/s Teijin Limited, Osaka, Japan , has won the Honor award [44]. By this technology, valuable materials are recovered from PET bottles wastes which are crushed, washed and then dissolved in ethylene glycol at its boiling point under pressure of 1 bar to depolymerize to BHET which is later reacted with methanol in an efficient way to produce dimethyl terephthalate and ethylene glycol by ester exchange reaction at the boiling point of methanol.

The recycle value of polyester plastic is found to be second to aluminum and the conditions needed to effect degradation and the extractability of valuable products becomes necessary. New degradation test methods are needed to evaluate the same [37-39].

3. Conclusion

The characteristics needed to understand the wide range of susceptibility of the various agents that facilitate degradation e.g. oxidative, thermal, mechanical, chemical and their dependence on chemical composition and structure of polymers in general and polyethylene terephthalate in particular are discussed. The kinetic studies on polyester containing cationic dyeable comonomer units indicate that the copolymer degrades faster than homo PET . The rate of degradation depends on the residence time and temperature to which the molten polymer is subjected. The SEM images of the yarn samples indicate that as the residence time in a particular temperature is increased more number of particles of degraded products are formed and they have tendency to grow in large size. The degradation results in highly crystalline trimers or oligomers having carboxyl terminals. Addition of phosphoric acid is able to control degradation. The chemical nature of polyethylene terephalate permits easy recyclability by all known recycling methods. Recycling of polyester has become an important process from the environmental point of view and it has given commercial opportunity due to wide spread use and availability of PET bottles, packages and fibers. The effects of contaminants have deleterious effects on degradation and colour of the polymer while recycling of polyester.

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