

A Novel Method to Understand Polyester POY Ageing by Topo Chemical Reaction



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INTRODUCTION

Polymer degradation is a major problem for all manufacturers and users of textile material. It is inevitable, since it begins as soon as any textile article is produced and continues through out the life time of the article until it is finally rejected as useless. It may arise for a variety of reasons. Slater (1991) describes that the process of degradation in textile materials involves changes in the molecular structure (involving the main-chain, side chain, substituent groups or molecular bonds of any kind) that bring about changes, usually adverse in nature in any physical or chemical property of the fibres of which the textile material is made. These changes may include deterioration in Physico-mechanical properties (such as strength, abrasion resistance, tactile response, colour etc.). Degradation is a pervasive change in the textile structure that is inevitable and universal. Degradation, it must be emphasized, cannot be avoided completely. Its progress can be decelerated but not halted totally. Thus its impact may be felt economically, aesthetically, or physically, depending on the type of degradation takes place.

The causes of degradation may be summarised as follows:

1. Inherent molecular factors
2. Degradation as a result of processing conditions
3. Degradation as a result of storage etc.

The degradation mechanisms may be mechanical or photo degradative or thermal or chemical in nature. Degradation may manifest itself in a variety of ways. The most obvious ones that are apparent, either visually or by potentially destructive changes are those in structural or mechanical properties, surface morphology or thermal or chemical behaviour.

There have been several techniques described by various research workers to assess the degradation phenomena. These include the following:

- i. Mechanical - property changes
- ii. Chemical changes
(viscosity, degree of polymerisation and molecular weight, chemical analysis and reactivity)
- iii. Thermal methods
- iv. Instrumental techniques
(Ultra-violet spectroscopy, infra red spectroscopy, gas chromatography, gel-permeation chromatography, optical and electron microscopy etc).

It is evident from the above, that degradation although, an undesirable aspect, can serve a useful purpose. These may be divided into three categories : the production of new substances, analytical uses (characterization and thermal analysis) and property modification.

AGEING PHENOMENON

Ageing is a basic feature of the glassy state, and is found in all glasses whether polymeric, monomeric, organic or inorganic. In all glassy materials, ageing proceeds in a similar way.

Many years ago, scientists established that amorphous solids are not in thermodynamic equilibrium at temperatures below their glass transition temperature T_g . Such materials, therefore, are to be regarded as solidified supercooled liquids. This non-equilibrium state appears to be unstable because volume relaxation studies in these materials reveal that they undergo slow processes which tend to establish equilibrium. Thus, it indicates that even below T_g molecular mobility M , that is, internal brownian motion is not totally absent. This gradual approach to

equilibrium affects many properties of the material. These properties change with time, and the material is said to undergo ageing.

Ageing can be defined as a process in which amorphous solids below their T_g , while tending to attain equilibrium, exhibit changes in their physical properties with the passage of time.

There are two types of ageing phenomena namely Physical ageing and Chemical ageing

Physical ageing

Physical ageing is a gradual continuation of the glass formation that sets in around T_g (Fig.1). During ageing all those temperature dependent properties such as creep etc., change drastically and abruptly at T_g . These temperature dependent properties change in the same direction as during cooling through the T_g range; the material becomes stiffer and more brittle and it affects creep, stress relaxation rates and dielectric constant, etc. Physical ageing does not involve any chemical reaction.

Chemical ageing

Chemical ageing is a process in which chemical reactions take place and the material undergoes changes due to this chemical reactions. Thermal degradation, photo-oxidation can be considered as examples of chemical ageing.

FREE VOLUME CONCEPT

Ageing effects can be studied very easily by using free volume concept. This is the basic and obvious idea that the transport mobility of particles in a closely packed system is primarily determined by the degree of packing of the system or by its inverse measure (ie) free volume. With

increasing degree of packing, this mobility decreases at first slowly, but later on at (Figs.6.2 and 6.3) an even increasing rate. At a critical degree of packing, the mobility steeply falls to zero. Fig.2 shows an amorphous polymer which is cooled from a temperature T_0 above T_g to a temperature T_1 below T_g after which it is kept at T_1 . Since above T_g a polymer behaves as a rubber or a fluid even at very small strains its segmental mobility must be large, and so its free volume V_f must also be large. When a polymer is cooled V_f and M decrease simultaneously. Since free volume is made up of voids and since molecules attract one another, the existence of free volume represents an increase in internal energy of Δ_o with respect to the zero free volume state. Free volume actually exists because it is also accompanied with an increase in entropy Δ_a . The changes in V_f are brought about by a redistribution of the voids. The rate of this process is determined by the segmental mobility M . So we have the following loop scheme : V_f determines M , while M determines rate dy/dt at which V_f changes;

$$\underbrace{V_f} \text{ =====> } M \text{ =====> } \frac{dV_f}{dt} \text{ ----- (1)}$$

The above equation implies that the volume - relaxation process is basically nonlinear and is essential for an understanding of glass transition and ageing. Below a certain temperature M becomes so small that V_f almost stops decreasing with temperature. Mobility M no longer changes rapidly with temperature, though it continues to decrease slightly because of the attendant decrease in thermal activation.

When the polymer is cooled to some temperature T_1 below T_g , the mobility M will be small but not zero. Since at this stage V_f is greater than it would be at equilibrium, the volume will continue to decrease slowly. Struik (1978) established the fact that ageing is found in all

glasses irrespective of their chemical nature. He has found out that the mobility will decrease in inverse proportion to the ageing time, t_e ,

$$\text{Mobility, } M = \frac{K_1}{t_e} \quad \dots (2)$$

where k_1 is a constant. Since mechanical relaxation times are inversely proportional to mobility M , the above equation tells us that they increase in proportion to the ageing time. For each increase in t_e by a certain factor, then the relaxation time will also increase by the same factor. The creep will be shifted along the logarithmic time scale. Ageing can be characterised by a double logarithmic shift rate (μ), given by

$$\text{Shift rate, } \mu = \frac{-d \log A}{d \log t_e} \quad \dots (3)$$

where A - shift factor
 t_e - ageing time

Equations 2 and 3 will be valid only if the material is far removed from thermodynamic equilibrium. When equilibrium is approached, μ will begin to decrease, and at equilibrium ageing ceases and μ is zero.

Disappearance of ageing at low temperature

From the free volume concept of ageing, the equilibrium process of ageing occurs at temperature between T_β , highest secondary transition temperature and T_g . Above T_g , the polymeric material reaches its thermodynamic equilibrium very quickly. Below T_g , and during ageing, the free volume V_f , will diminish to a value at which segmental motion is hindered. The changes in V_f brought about by isothermal ageing or by differences in the rate of cooling through the T_g range, will not affect the secondary relaxations.

When a polymer is cooled through the T_{β} range, the polymer segments will lose their flexibility. Above T_{β} , the free volume has already become so small that the motion of the segments is strongly hindered. Hence at temperatures below T_{β} , segmental motion and therefore ageing also, will practically disappear.

As far as ageing is concerned, the processing of plastics by extrusion, injection moulding etc, may be regarded as a quench. Processed plastics are expected to show the same ageing effects.

As the material cools through its T_g range, it changes from a flexible rubbery melt into a rigid glass, just as unoriented polymers. Oriented amorphous polymers will age in the same way as unoriented ones.

MECHANISM OF AGEING

Two types of mechanism were proposed to explain the physical ageing phenomenon. They are:

Densification of non-crystalline fraction

Ageing corresponds to densification of the non-crystalline fraction, in the manner of an amorphous polymer at temperatures just below the glass transition, but shifted to higher temperature by the local constraint on non-crystalline molecular segments exerted by crystal.

Recrystallisation mechanism

Ageing corresponds to delayed recrystallisation of noncrystalline segments generated during constant length heating of drawn polymer to the temperature below T_m . The mechanism relies on the generation of new noncrystalline region by the "stripping-off" of some molecular segments from crystals, by the entropy force generated by

intercrystalline tie segments during heating at constant lengths. During unconstrained heating, these internal forces instead generate shrinkage.

LITERATURE REVIEW

Although a considerable work on study of degradation mechanisms on polymers (nylon, poly propylene, polyester etc.) has been reported, intermation about the use of alkaline hydrolysis of PET partially oriented yarns is scanty in the literature. The thrust of this study is to use weight reduction by aqueous sodium hydroxide as a tool to study the mechanism of ageing.

MATERIALS AND METHODS

Materials

The starting materials were POY of different substrate supplied from POY manufacturers in India. The details are given below.

4 POY's A , B , C & D were selected for the study with respective counts (dtex) 56/96 , 89/34, 140/34 & 178/34

Methods

Storing of the samples

The samples were stored in slack condition at a room temperature for different periods.

Alkaline Hydrolysis

The samples for the respective periods were alkaline hydrolysed as per the method described below

In all the cases of polyester substrates, alkaline hydrolysis was carried out in sealed flasks or beakers at 100°C and 130°C. (1:20 bath ratio, hold time 30 min) as the case may be with mild mechanical agitation on laboratory model HTHP dyeing machine. To terminate the hydrolysis, samples were rinsed in deionized water to eliminate excess alkali and neutralised for 2 min in 0.1% HCl. The specimens were then washed in deionised water until the rinsed water was neutral to litmus paper. The products were then dried in hot oven to a constant weight and cooled in a desiccator.

CONDITIONING AND PREPARATION

The experimental materials, prepared as explained above, were conditioned prior to testing at standard atmospheric condition of 65 ± 2% RH and 25 ± 2°C temperature as per IS : 6359-1971.

Determination of weight loss (%)

In all the cases, weight loss was calculated by using the formula:

$$\frac{X_1 - X_2}{X_1} \times 100$$

Where X_1 -Initial weight, X_2 -Final weight

Measurement of density

Fibre density was measured using Davenport Density Gradient Column. The solvents used are a mixture of 450ml of n-heptane and 550 ml of carbon tetra chloride (CCl₄) in the mixing flask and 1000 ml of CCl₄ only in the second flask during the preparation of column. The densities of n-heptane and carbon tetra chloride are 0.68 and 1.68 g/cc respectively. The temperature is maintained at 25°C. Results are the average of atleast 5 replicates.

Measurement of critical dissolution time (CDT)

CDT (time in seconds) was measured as per the Galil method (Galil, 1973). The measured value is an average of 25 replicates.

Determination of Molecular Weight

Average molecular weight of the hydrolysed samples was measured by viscosity method using the equation as suggested by Ravens and Ward (1961).

$$[\eta] = KM_v^\alpha, \quad \dots (4)$$

where $[\eta]$ and $\bar{M}_n$ are intrinsic viscosity of solution and molecular weight of the polyester respectively. A 1% solution of hydrolysed samples was prepared in o-chlorophenol (99% pure). Flow times of polymer solutions and pure solvent were measured at 25°C. The intrinsic viscosity was calculated from the specific viscosity of the solution using Huggins viscosity slope constant as determined by Todd (1954).

Density and CDT measurements

Density and CDT values of hydrolysed samples were measured, as explained in the chapter 4.

RESULTS AND DISCUSSIONS

Weight Loss

It is observed from the Table 1 that the weight loss registers a decreasing trend as the period time increases. This may be due to the basic concept of ageing as densification of noncrystalline regions.

Molecular weight

Table 2 confirms the increase in molecular weight as the storage period progresses. This is obvious as the ageing mechanism involves

recrystallisation of noncrystalline segments and densification of non crystalline fractions.

Density

It is clear from the fact that the fibre density values increases (Table 3) with the ageing period. The results are in agreement with the research studies on polypropylene and nylon ageing.

CDT measurement

The change in the density measurements will directly affect the critical dissolution time. Table 4 the exhibits this fact.

CONCLUSIONS

The ageing mechanism was studied using aqueous alkaline hydrolysis as a tool. The results show that :

- (i) Weight loss (%) decreases as the storage period increases.
- (ii) Molecular weight increases due to recrystallisation of non crystalline regions.
- (iii) Density and CDT values increase as the exposure period increases confirming the densification of non crystalline fractions.

Table 1 Effect of storage period on Weight loss (%)

Code	Duration (In days)				F_{Cal}	F_{Tab}	Remarks
	15	30	45	60			
A	28.52	24.83	20.14	18.29	390	7.82	The ageing effect on weight loss is significant at 1% level
B	25.38	23.23	21.82	19.39			
C	21.42	19.23	17.16	14.28			
D	19.38	16.38	12.89	10.25			

Table 2 Effect of ageing on Molecular weight (Number M_n)

Code	Duration (In days)				F_{Cal}	F_{Tab}	Remarks
	15	30	45	60			
A	18,112.66	18,946.194	19,212.6	21,123.8	182	6.82	Ageing has resulted in the increased molecular weight and is significant at 1% level
B	18,004.33	19,018.92	19,421.7	20,010.7			
C	17,715.89	18,873.50	18,989.5	20,434.2			
D	19,064.49	19,184.28	19,458.5	20,138.2			

Table 3 Effect ageing on density (g/cc)

Code	Duration (In days)				F_{Cal}	F_{Tab}	Remarks
	15	30	45	60			
A	1.3785	1.3789	1.391	1.3923	82	6.82	Increase in density values are significant at 1% level
B	1.3818	1.3822	1.3889	1.4023			
C	1.3780	1.3798	1.3820	1.3898			
D	1.3761	1.3776	1.3790	1.3829			

Table 4 Effect of ageing on CDT (Seconds)

Code	Duration (In days)				F_{Cal}	F_{Tab}	Remarks
	15	30	45	60			
A	27	32	38	46	89.5	6.82	CDT values are significant at 1% level
B	33	37	42	49			
C	36	42	48	52			
D	41	46	49	54			

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