

INFLUENCE OF DEGRADATION MEDIUM ON THE PARTIAL DISSOLUTION OF POLYESTER TEXTILE SAMPLE

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ABSTRACT

Polymer degrades due to significant changes in its chemical structure, physical properties or appearances under specific environmental conditions. When polymer is exposed to solutions, swelling and dissolution govern the degradation process. Swelling or partial dissolution is characterized by the occurrence of cracks or stress fracture in the polymer fiber. In this study, the chemical resistance of polymer textile sample to partial dissolution or swelling was examined. The sample was exposed to solutions of different pH levels (NaHCO₃-Na₂CO₃ buffer with a pH of 10.47; distilled water with a pH of 7.0 and HOAc-CaAc buffer with a pH of 4.67) for 142 hours. After soaking, this was the surface characteristics were examined with the use of a Scanning Electron Microscope.

Although indications of the formation of cracks were found, negligible weight loss was observed. This implied the slow reactivity of the sample to the solution. The onset of polymer degradation accelerated as the test reagent deviated from neutrality either way.

I. INTRODUCTION

Whenever dirt is imbued in our fabric materials, soaking with detergent overnight is the best way to get rid of it. The washing cycle renders the material weak and feeble. Deterioration of the physical attributes and aging is essentially due to the combined action of sunlight and air. As the material interacts with the environment, chemical, physical and biological changes manifest itself and are concretely observed and measured through various means.

Polymers can be destroyed by a variety of environmental agents. Their desirable properties have led to their continued demand for applications in severe conditions that include high temperatures, high-energy radiation, chemically or biologically active environment and extreme mechanical stress. Polymers may deteriorate further by swelling and dissolution¹.

Thermal degradation occurs due to heat during processing or severe temperature applications. Thermally induced degradation is characterized by the breaking up of main polymer chain backbones, reverting back to the original “mer” or monomer (referred to as depolymerization). It also involves elimination of pendants or side groups along the polymer chain to give a highly unsaturated compound without substantial scission. Furthermore, sunlight is recognized as an important factor in the deteriorative aging and weathering process which occurs in commercial polymers. The energy of UV light and possibly the visible components of sunlight are sufficient to rupture chemical bonds. The absorption of energy and its transfer to the bond to be broken is described as the photo-physical aspect of photo-degradation. The first chemical step is usually homolytic bond scission to form free radicals and conjugated double bonds. Although all polymers degrade at high temperatures in the absence of air, degradation is almost always faster in the presence of oxygen. Oxidative degradation in commercial polymers is manifested during melt processing at high temperatures during service²

When polymers are exposed to liquids, the main forms of degradation are swelling and dissolution. With swelling, the liquid or solute diffuses into and is absorbed within the polymer. Microscopically, the small solute molecules fit into and occupy positions among the polymer molecules forcing the macromolecules apart such that the specimen expands or swells³. Examples of such phenomena include the expansion of a rubber band when placed in toluene or the swelling of wool and cotton fibers when soaked in water or exposed to humid air.

Other than cotton, rayon or wool fabrics, thermoplastic polyester, a synthetic fiber with high tensile strength made by the esterification of ethylene glycol and other organic compounds, comprises the bulk material in clothing and textile products. This includes polyethylene terephthalate (PET) and polybutylene terephthalate (PBT).

The useful life of a polymer is dependent not only on the weak links in the material but also on its surroundings. In the clothing and textile industries, their aesthetic value is of prime consideration. Degradation must therefore be carefully monitored in order to evaluate the usefulness of polymers in different applications.

In the characterization of polymer degradation, reliable techniques are required to predict the susceptibility of the material. Existing analysis should be able to monitor chemical, physical and mechanical changes brought about by the processing and use of the polymer as well as handling of the waste⁴.

To fully describe the events taking place during degradation, the early changes can be monitored by the observation of new functional groups in FT-IR spectra. Any changes in molecular weight is monitored using size exclusion chromatography (SEC) and the formation of degradation products is identified using gas chromatography (GC), mass spectroscopy (MS) or liquid chromatography (LC). Scanning Electron Microscopy (SEM) and Differential Scanning Calorimetry (DSC) are techniques employed to qualify the morphology and crystallinity of the polymeric material⁵.

II. MATERIALS AND METHODS

In this study, a polyester textile sample is immersed in three test reagents to determine its chemical resistance. Chemical resistance manifests itself through visual effects of failure such as swelling, surface erosion or cracking. These involve the development of stress fracture. Chemical resistance, in general, is the response of a polymeric material to any chemical or physical interactions which lead to polymer degradation. Specifically, microstructural response of the sample in two buffer solutions and distilled water are analyzed using SEM. The influence of some material characteristics or properties towards partial dissolution is discussed.

The first solution involved a conjugate base, sodium carbonate dissolved in distilled water. Sodium bicarbonate was then added to constitute a solution with a pH of 10.47. A second solution was prepared by dissolving calcium acetate in distilled water and then adding enough acetic acid to make up a solution with a pH of 4.67. The final solution used was plain distilled water with a neutral pH of 7.0. The pH of these solutions were computed using the Henderson-Hasselbach equation, a sample of which is shown in the Appendix.

The initial weights of four sets of samples were determined, after which, three were soaked in the different solutions for at least 142 hours. The fourth sample served as the control and this involved no soaking.

After the initial soaking, the samples were air dried and mounted on sample stubs for SEM viewing. The samples were coated with a very thin layer of electrically conductive material (Palladium) using the Ion Sputter Coater to ensure good electrical contact with the ground electrode.

The samples were then viewed through the SEM. The weights of the sample after soaking were also determined to qualify its resistance to moisture. A comparison of the surface characteristics of the three samples was done.

III. RESULTS AND DISCUSSION

Major differences were observed in the three samples soaked with different solutions. In terms of weight loss, however, all three samples showed very insignificant changes in weight. Table 1 shows the changes the weight profile of the samples.

Table 1
Weight Profile of Polyester sample

Solution	Average Weights, g		Average Weight Loss, %
	Initial	Final	
Acidic Buffer	0.1873	0.1870	0.160
Basic Buffer	0.1852	0.1850	0.108
Neutral Solution	0.1832	0.1822	0.546
Control Sample	0.1816	0.1816	0.000

Figure 1 shows a photomicrograph of the original polyester textile sample showing the woven fibers. This was taken using the Scanning Electron Microscope at an operating voltage of 20 kV and a magnification of 54 x. This control sample will serve as the basis for the comparison of the reaction of the other three samples to the different soaking solutions used.

Figure 2, on the other hand is a SEM photomicrograph of the textile fiber sample at a higher magnification (720 x). This clearly shows the surface view of the unadulterated sample with no cracks whatsoever present in the surface.

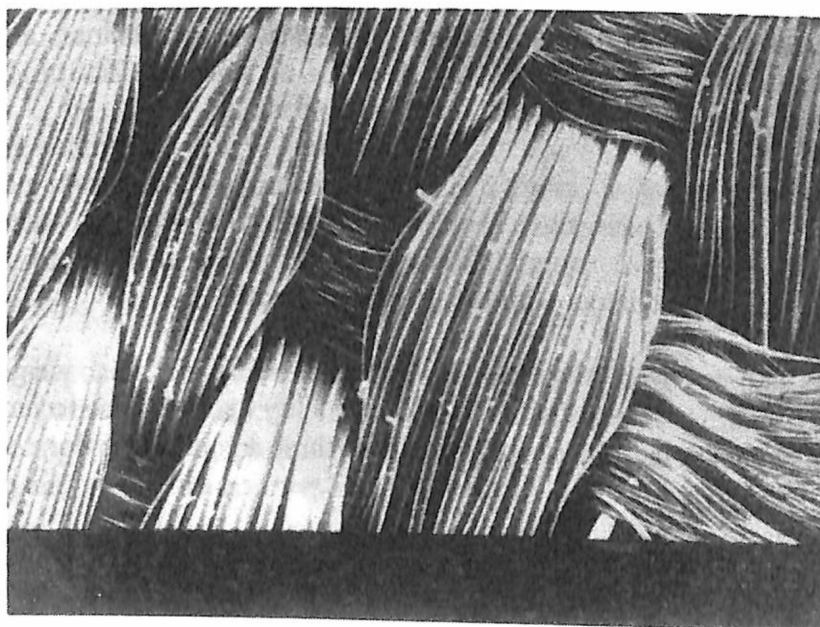


Figure 1. SEM photomicrograph of polyester textile sample showing the unadulterated textile fibers with no cracks. 20 kV, 54 x mag.

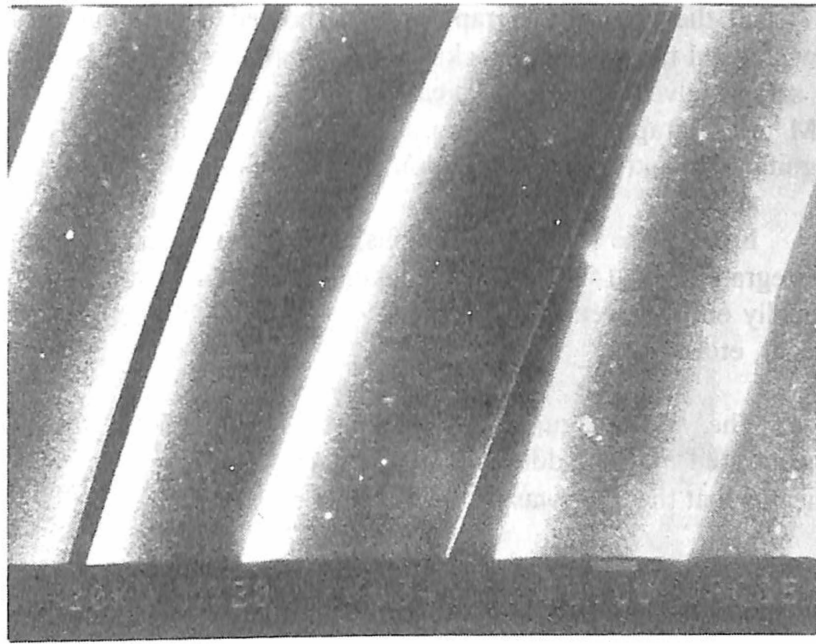


Figure 2. SEM photomicrograph of the same control sample showing the fibers with no cracks. 20 kV, 720 x mag.

The first sample was soaked in distilled water, a medium which was considered neutral because it maintained a pH of 6.7 – 7.0. The sample was viewed through the SEM after 142 hours of soaking and the photomicrographs show almost no difference between this sample and the control sample. Figure 3 shows the photomicrograph of the sample.

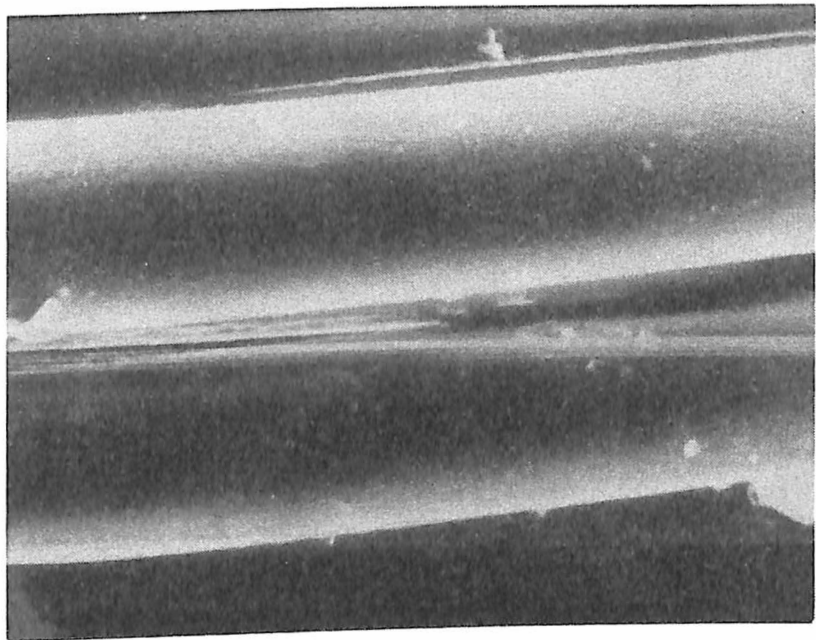


Figure 3. SEM photomicrograph of polyester textile after soaking in distilled water for 142 hours. 20 kV, 720 x mag.

The same textile fiber was soaked in the HOAc-CaAc buffer solution (pH 4.67) and the photomicrographs taken showed a different profile. The surface view showed the onset of cracking as illustrated in Figure 4. The cross section of the sample gives a more detailed view of the surface cracks starting to form. A SEM photograph of this cross section was taken at 20 kV and 7200x magnification and is shown in Figure 5.

From these photomicrographs, it is evident that the sample had started to disintegrate after 142 hours of soaking in the basic solution. This condition is normally encountered in the staining of fabrics with household chemicals such as vinegar, etc.

The above figures also show the character of the crack to be more concentrated in the middle part of the fiber. The crack appeared to be rough and indicates that the fiber was probably attacked more rapidly.

The third polyester sample was soaked in the basic buffer solution consisting of NaHCO_3 - Na_2CO_3 at a pH of 10.67. The photomicrographs clearly showed the occurrence of cracks as illustrated in Figure 6. These cracks, however, are notably much smaller than those present in the second sample. The cracks were also found to be significantly smoother compared to the previous sample. Figure 7 shows the cross-sectional view of the same sample.

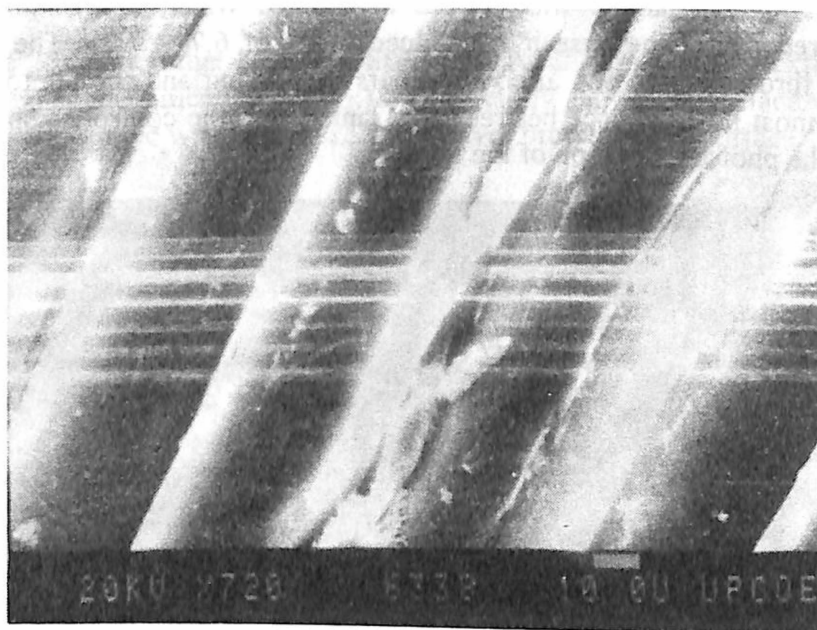


Figure 4. SEM photomicrograph of polyester textile sample soaked in HOAc-CaAc buffer solution showing the cracked fibers. . 20 kV, 720 x mag.



Figure 5. SEM photomicrograph of the cross-section of the polyester textile sample after soaking in HOAc-CaAc buffer solution. 20 kV, 7200 x mag.

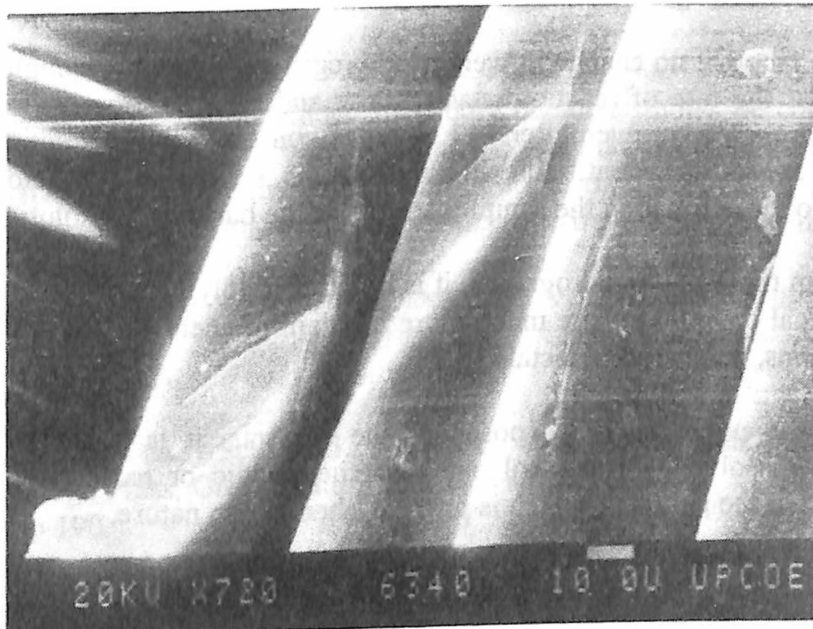


Figure 6. SEM photomicrograph of the surface view of the polyester textile sample after soaking in NaHCO₃-Na₂CO₃ buffer solution. 20 kV, 7200 x mag.



Figure 7. SEM photomicrograph of the cross-section of the polyester textile sample after soaking in $\text{NaHCO}_3\text{-Na}_2\text{CO}_3$ buffer solution. 20 kV, 7200 x mag.

The fact that no change in weight was registered in all the samples soaked suggests that the rate of reaction is very slow and minimal, that no significant deviations are apparent even after 142 hours of contact with the solutions. More prominent cracks are identifiable in the samples soaked in the acidic buffer compared to those found in the samples soaked in the basic buffer solution.

From these photomicrographs, it is noted that polymers, in general, due to their chemical complexity, are much more resistant to chemical attack by acid or basic solutions, compared to metals.

As the polymers are exposed to the solvents, it is either partially or completely dissolved. These solvents, whether acidic or basic accelerate the degradation of the polymer, which is physico-chemical in nature.

The response of the polyester textile fibers to the buffer solutions, in general can be related to permeation which can embrace both absorption and diffusion of the permeating specie into the polymer and the reactivity of the system towards dissolution.

Severe service conditions make the polymer respond differently due to chemical, physical and biological interactions. The chemical resistance of the polymer depends on its crystallinity since crystalline polymers are invariably more resistant than their amorphous counterparts because close chain packing reduces permeability.

In everyday applications, soaking of textile in detergents (a basic solution) removes the dirt as the polymer reacts with the solution. The addition of bleaching agents or chlorox (acid solutions) removes discoloration due to the faster rate of reaction on the fiber. As the exposure time increases (due to frequent washing of clothes), however, the fabric gets weak and feeble and will be eventually too brittle and prone to tearing.

IV. CONCLUSIONS AND RECOMMENDATIONS

The resistance of polymer to chemical attack can be measured by its behavior in acid, basic and neutral solutions. This was done using a polyester textile fiber which was soaked in the three types of media.

The results show conclusively that the acid and basic medium react with the polymer and causes its degradation.

The extent of degradation, however, varies greatly with soaking time as well as the concentration of solution. The kinetics involved in this dissolution process was not studied but will be very useful in the study of polymer degradation.

It is therefore recommended that more detailed studies be conducted on the effect of dissolution time on the sample to establish the kinetic mechanism. Further characterization of physical properties are also recommended. These can include the measurement of the mechanical properties such as tensile strength, breaking strength, etc.

V. REFERENCES

1. Grassie, N. and Scott, G., Polymer Degradation and Stabilization, Cambridge Press, Great Britain, pp 24 (1985).
2. Ibid., p 190.
3. Callister, W., Materials Science and Engineering: An Introduction, 4th ed., John Wiley and Sons, US, (1997).
4. Scott, G. and Gilead, D., Degradable Polymers: Principles and Applications, 1st ed., Chapman and hall, Great Britain, pp 33–36, (1995).
5. Ibid., p. 63.

VI. APPENDIX

A buffer is most efficient in resisting changes in pH when both acid and its conjugate base are present in approximately equal amounts, or $[A^-] = [HA]$. For our purposes, the Henderson-Hasselbach equation is used to approximate the pH of the buffer solutions prepared, and a sample calculation is shown below.

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pH_{(NaHCO_3 - Na_2CO_3)} = (14 - pK_b) + \log \frac{(0.00152)}{(0.00102)}$$

$$pH = 10.47$$