Degradation Process of an Industrial Thermoplastic Elastomer Polyurethane-Coated Fabric in Artificial Weathering Conditions

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ABSTRACT: The aging of an industrial thermoplastic elastomer polyurethane (TPU)-coated fabric, based on a polyether diol and an aromatic diisocyanate, is studied in artificial weathering tests. It is noticed that the degradation of this TPU-coated fabric leads to a weight loss, to the formation of a reticulated layer in sample surface, and to a change of surface relief. The degradation layer and the surface relief have been observed by optical microscopy. The weight loss has been followed with aging time. The main degradation products causing weight loss are volatile. Therefore, they have been analyzed by gas chromatography–mass spectroscopy. The weight loss degradation takes place in the exposed part of the reticulated layer by volatile products emission, which implies the urethane and the polyether bonds. Water is involved in degradation process: without external water supply, weight loss is limited; with a permanent contact of vapor or liquid water, the weight loss rate is constant and depends on aging conditions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2525–2534, 1999

Key words: hermoplastic elastomer polyurethane; artificial weathering; degradation

INTRODUCTION

Thermoplastic polyurethane elastomers (TPUs) are high performance materials, and TPU-coated fabrics now find applications in inflatable structures, conveyor belts, protective coverings, etc. Since many of the new applications are for outdoor exposure, the weathering behavior of such materials is critical.

TPUs are derived from three basic compounds:

- a long-chain polyester diol or polyether diol,
- an aromatic or aliphatic diisocyanate,
- a short-chain diol as chain extender, which in most cases is butanediol.

They are characterized by a segmented structure consisting of flexible segments, the polyester or polyether chains, and hard segments, the urethane groups. It is known that TPUs undergo significant structural changes on weather exposure, which have been found to depend on the structure and the morphology of TPUs.[1–5] These changes lead to a deterioration in physical and mechanical properties,[2,3 6–8] and most published studies have dealt with the processes responsible for degradation and ultimate failure.[9–17]

Consequently, the degradation of TPU has been studied by a variety of analytical methods. We showed in a previous paper[18] that measurement of weight loss may be used to follow weathering of industrial TPU-coated fabrics. We compared artificial weathering of three industrial TPU-coated fabrics in a Weatherometer test with and without water spray with natural weathering

Figure 1   Sketch of the TPU-coated fabric.

carried out in Florida. The loss of weight with time was found a sensitive measure of the degradation due to weathering. Since there is weight loss, either extractable soluble species or volatile products are removed and the exposed surface of the TPU-coated fabric is changed.

A preliminary experiment was carried out: samples degraded in the Weatherometer test without water spray were immersed in water for 32 days and weight loss was measured after drying.* The weight loss was 25% at most in the Weatherometer test with water. Thus, the extractable soluble species represents only 25% of degradation products. Therefore the main degradation products are volatile.

For this study, an experimental setting is devised to collect the removed volatile compounds during the aging process of an industrial TPU-coated fabric in artificial weathering conditions. These compounds are studied by gas chromatography–mass spectroscopy (GC-MS), the weight loss is followed, and the degraded surface is observed by optical microscopy. These analytical methods will lead to the description of the degradation process of the industrial TPU-coated fabric.

EXPERIMENTAL

Material

The industrial fabric studied was black TPU coating based on a polyether diol, an aromatic diisocyanate, and a polyamide fabric, nylon 6/6 (Fig. 1). It was manufactured by the extrusion/calandering method; the fabric was coated both sides. The coated fabric was stored in the form of rolls at room temperature and protected from light. The samples were cut directly from the rolls and the surface was not treated with solvents or additives before weathering.

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* The weight loss represented 25% at most of the measured weight loss in the weatherometer test with water.

Conditions of Weathering

The artificial weathering tests were carried out:

- in the Atlas Weatherometer (WOM), model Ci35A for up to 3500 h. The WOM was equipped with a 2500/7000 watt water-cooled lamp with internal quartz filter and external type S borosilicate filter. It emitted from the UV (250–300 nm) to the IR including the visible range (400–750 nm). The cycle of the WOM test without water (WOMd) was 3.8 h illumination at 70°C and 1 h in the dark at 38°C. The cycle of the WOM test with water (WOMw) was 60 min in the dark at 38°C with water spray, 40 min illumination at 70°C, 20 min illumination with water spray at 70°C, and 60 min illumination at 70°C.
- in a Rayonet apparatus using lamps emitting at 300 nm ($T = 50°C$), without water (Rayd) or with water saturated vapor (Rayh).

For WOMd, Rayd, and Rayh exposures, the samples were plates of 20×40 mm^2. A sample carrier was devised. It consists of two aluminum plates (thickness 2 mm) with windows (10×30 mm^2) cut in them, which were screwed together. Two quartz plates (thickness 2 mm) were placed between the aluminum ones. TPU-coated fabric samples were squeezed (exposed surface 10×30 mm^2) between the quartz plates and sample carrier was placed straight in a quartz tube. The quartz tube had a three-way tap and was closed by a tight stopper. Figure 2 describes the quartz tube and the sample carrier.

For Rayh exposure, liquid water (200–300 mg) was added in the quartz tube bottom in order to maintain 100% of relative humidity in the tube.

Figure 2   Sketch of the quartz tube and the sample carrier used to analyze the volatile compounds.

Figure 3 Plot of weight loss (mg) with time (h) for 12 mm diameter disk surface of the TPU-coated fabric in the WOMd, WOMw, Rayd, and Rayh.

Analytical Methods

Weight Loss

The weight loss was determined by the difference between the loss of the nondegraded sample and the degraded sample. The samples were

- either plates of 20×40 mm^2 with an exposed surface of 10×30 mm^2 weighed to an accuracy of 0.1 mg on an electronic analytical balance (Sartorius H110).
- or WOMw test plates weighed to an accuracy of 1 mg on a standard balance (Sartorius BA 310P).

The weight loss was expressed with respect to surface area of a TPU-coated fabric disk of 12 mm diameter (113 mm^2).

The degraded samples with water were dried at room temperature up to constant weight and compared in the same conditions to a nondegraded control sample so as to balance humidity variations.

For WOMw exposure, the samples were plates of 70×140 mm^2 with an exposed surface of 50×120 mm^2.

Microscopic Observances

The PMG3 Olympus microscope was used to observe the surfaces and the cross-sections of nondegraded and degraded samples of the TPU-coated fabric.

GC-MS Analysis

The volatile products were analyzed by GC-MS for WOMd, Rayd, and Rayh exposures.

One end of an activate charcoal filled Pyrex tube for GC-MS analysis was bound to a pump (Dräger Quantimeter 1000) and the other to the three-way tap of the quartz tube. The volatile products were adsorbed on active charcoal by pumping.

A control test with the empty sample carrier in the quartz tube allowed us to take the volatile products from the UV-exposed equipment into account. Another control test with TPU-coated fabric in the sample carrier in the quartz tube was placed in a dryer at 70°C. It took into account the volatile compounds from the temperature exposed equipment and from the nondegraded sample.

The Pyrex tube was placed in a thermodesorber (TDAS 5000, Carlo Erba) and heated at 260°C for 3 min after a 10-s purge. The desorbed volatile compounds were carried by helium (1 bar) and condensed in a -110°C liquid nitrogen trap. They were injected at 260°C in a gaz chromatograph (HEGA HR GC 5160, Carlo Erba) and were separated by a capillary column (Poraplot Q, Chrompack $d = 0.32$ mm, $L = 27.5$ m). They were analyzed in a mass spectrometer (HSD 5970 B, Hewlett Packard) monitored by a computer (Hewlett Packard 9000-300) and equipped with a National Bureau of Standard library.

The GC program was 40°C for 6 min to 100°C with a 20°C/min slope and 100°C for 10 min to 240°C with a 20°C/min slope.

The identification was done by comparison of the analyzed products mass spectra to library standards mass spectra and to injected standard mass spectra. The retention times were also compared.

RESULTS

Weight Loss

The weight loss with time is plotted in Figure 3 for the WOMd, the WOMw, the Rayd, and the Rayh degraded samples.

Surfaces

a   b   c

Cross-sections

a'   b'   c'

Figure 4 Surface and cross-section photographs of the TPU-coated fabric nonde-graded (a, a'), 2300 h degraded in the WOMd (b, b'), and 2400 degraded in the WOMw (c, c'). M × 20.

Surface Observance

The degraded surfaces are the same for WOMd and Rayd exposures (Fig. 4).

The degraded surface appears like a network of humps (white zones) and hollows (black zones) from 700 h of aging in WOMd and from 1000 h of aging in Rayd. The word *network* is employed here in the geometrical sense, which means that the degraded surface is a regular distribution of humps on a continuous hollow ground.

The humps are roughly parallelepiped right-angled and have the following approximate size, height (H), length (L), and width (l):

$$H \approx 10 \ \mu m, L \leq 60 \ \mu m, \text{ and } l \leq 40 \ \mu m$$

In between each hump, the width of the hollows is $\approx 25 \ \mu m$.

In WOMw, the degraded surface appears like a network of humps (black zones) and hollows (white zones) from 500 h of aging. The humps have a rounded form of 5–20 μm diameter and a height between 2 and 4 μm. The width of the hollows is lower than 2 μm.

In Rayh, the degraded surface is a network like in WOMd and in Rayd. The length and width of humps are the same as in WOMd and in Rayd for the same aging times but the height is less than 4 μm. The width of the hollows is $\approx 5 \ \mu m$.

The surface observance shows that the degradation of the TPU-coated fabric leads to the appearance of a network of humps and hollows. The network depth and size are more pronounced for aging without water in spite of less weight loss.

Cross-Section Observance

The cross-section observance shows that aging leads to the formation of a degradation layer on the sample surface (Fig. 4).

This layer appears from 100 h of aging for the four exposures. Its thickness increases and remains the same after 1000 h of degradation. For example, the variation of the layer thickness with aging time is given in Table I for WOMd and WOMw exposures. The observed error is $\pm 3 \ \mu m$.

The degradation layer comes off the surface when degraded samples are placed in dimethyl-formamide (DMF), which is a TPU solvent. This

Table I Variation of the Degradation Layer Thickness with Aging Time for WOMd and WOMw Exposures for the TPU-Coated Fabric

Aging Time	Degradation Layer Thickness (μm)
WOMd (h)	
100–700	16
$\geq$ 1000	33
WOMw (h)	
100	9
300–500	16
$\geq$ 1000	28

layer is reticulated as it remains insoluble in numerous organic solvents whether hot or cold.

Analysis of Volatile Compounds During Sample Aging

Analysis of control tests shows that no volatile compounds are produced from the equipment under UV and temperature exposures and from the nondegraded sample under temperature exposure. The analyzed volatile compounds are thus characteristic of the photooxidative degradation of the TPU-coated fabric. They are the same for the three exposures and are given in Table II.

The chromatogram in Figure 5 shows the volatile products for the TPU-coated fabric degraded 500 h in Rayd.

For Rayh exposure, the volatile compounds are the same as the ones for aging without water but in larger amounts, except for the water-soluble products (for example, alcohols); their faster emission leads to a faster weight loss rate (Fig. 3).

Consequently, water vapor accelerates the degradation process without alteration.

Analysis of Volatile Compounds During the Degradation Layer Aging

The degradation layer was isolated in the shape of shavings in DMF. The shavings were placed between the two quartz plates and degraded in the quartz tube in Rayd exposure. The analyzed volatile compounds are the same as the ones emitted during aging of the whole samples. The degradation of the TPU-coated fabric is thus developed from the exposed part of the reticulated layer.

DISCUSSION

The aim of this discussion is to relate the results in a same coherent physicochemical process.

Proposition for the Formation of the Degradation Layer

Although the degradation layer has been quoted before this work,[6] no reticulation mechanism appears in literature. By analogy with other polymers, the following schemes could be proposed.

The photooxidation of poly(vinyl chloride) (PVC) leads to a radical, —$CH_2C^{\bullet}ClCH_2$—, which reacts according to the mechanism presented in Figure 6.[19] The alkoxy radical induces the formation of reticulation points. By analogy with PVC, it could be possible to propose the mechanism in Figure 6 for TPU. The last radical would cause the reticulation points of the degradation layer.

Table II Volatile Compounds Analyzed During the Aging of the TPU-Coated Fabric for WOMd, Rayd, and Rayh Exposures

Retention Time (min)	Identified Compounds	Retention Time (min)	Identified Compounds
2.3	Carbon dioxide	22.3	2-Methylpropene
4.5	Ethylene	23.1	Butane
6.2	Ethane	24.2	Acetonitrile
13.0	Propene	25.4	2-Propenal
13.7	Propane	26.2	2-Propanol
14	Methylchloride	26.4	Methylacetate
15.4	Methanol	27.2	1-Propanol
18.6	Ethanal	27.8	2-Methyl-2-propanol
21.9	Methylformiate		

Figure 5 Chromatogram of the volatile compounds of the 500 h degraded TPU-coated fabric in the Rayd.

The polyether photooxidation[19] leads to the formation of an alkoxy radical (Fig. 7). This latter could eventually induce reticulation points in TPU because the flexible segments of TPU are based on polyether.

In polyamides,[19] free radicals $R^\bullet$, derived from degradation, involve the abstraction of hydrogen in the α-position from the amide bound, and leads to the formation of reticulation points (Fig. 8). By analogy with polyamides, it could be possible to consider the hydrogen abstraction in the α-position from the urethane group. It would induce the reticulation mechanism given in Figure 8.

Proposition for the Development and Stabilization of the Degradation Layer

The degradation layer development would happen to the nondegraded part of the surface:

- directly initiated by UV with just sufficient intensity. UV, which goes through the already formed layer, follows the Beer Lambert absorption law: the UV intensity decreases when the layer thickness increases. Consequently, UV could reach a boundary that would be the "nondegraded coating/degradation layer" interface where the UV intensity would be sufficient to cause degradation.
- by the propagation of radical intermediate species initiated by stronger UV in the layers close to the exposed surface. Initiation of intermediate species on surface and their propagation by reactions in the degradation layer thickness follow a radical mechanism. By

means of termination reactions, the concentration decreases when the layer thickness increases. The radical species could thus propagate themselves up to a "nondegraded coating/degradation layer" boundary where the concentration is still sufficient to activate the layer formation.

With these processes, the more the layer thickness increases, the more the layer formation rate decreases. The layer thickness is going to increase progressively up to a certain limit. This limit corresponds to the equality of the formation rate of the layer by the nondegraded part and of the degradation rate of the layer by the outside part. Thus a dynamic process set up and involves a constant thickness of the degradation layer.

Proposition for the Difference Aging Rate for Exposures with and without Water

The curves of weight loss in WOMd and in Rayd show a practically null degradation rate after 1000 h of aging (Fig. 3). The curves of weight loss in WOMw and in Rayh show a constant degradation rate (Fig. 3). Water is thus involved in degradation as a reactant.

The WOMd and Rayd weight loss do not change anymore when water, initially in the sample, may be eliminated. This is confirmed by an insensitive weight loss ($\leq$0.15 mg) of a first dried and 300 h Rayd-degraded sample, whereas the weight loss of the same sample but not dried (containing at least 1% of water) loses 0.5 mg in the same aging conditions.

For PVC

$$-CH_2-\overset{\underset{|}{Cl}}{C}\text{}^\bullet-CH_2- \quad\xrightarrow{O_2}\quad -CH_2-\overset{\underset{|}{Cl}}{C}-CH_2- \quad\xrightarrow{+RH}\quad -CH_2-\overset{\underset{|}{Cl}}{C}-CH_2- \;+\; R^\bullet$$

$$-CH_2-\overset{\underset{|}{Cl}}{C}-CH_2- \quad\xrightarrow{\Delta}\quad -CH_2-\overset{\underset{|}{Cl}}{C}-CH_2- \;+\; \text{}^\bullet OH$$

For TPU

Figure 6 Reticulation mechanism of PVC[19] and possible reticulation mechanism of TPU.

With external water (liquid or saturated vapor) being replaced, the degradation can go on with a weight loss rate almost constant fitted to each exposure. Thus when the degradation processes were said to be the same with and without water, the expression "without water" was actually with water present initially in sample.

Proposition for the Microscopic Appearance of Degraded Surfaces

The degraded surface appears like a network of humps and hollows (Fig. 4). The degradation with weight loss is developed by emission of small mol-

For polyethers

$$-(CH_2)_4-O-(CH_2)_4- \;+\; O_2 \quad\xrightarrow{\Delta}\quad -(CH_2)_3-\overset{\underset{|}{}}{C}HO-(CH_2)_4- \;+\; OH^\bullet$$
$$O^\bullet$$

Figure 7 Reticulation mechanism of polyethers.[19]

For polyamides

$$-CH_2-NH-CO-CH_2- \; + \; R^{\bullet} \longrightarrow -CH_2-NH-CO-CH^{\bullet}- \; + \; RH$$

$$2 \; -CH_2-NH-CO-CH^{\bullet}- \longrightarrow \begin{array}{c} -CH_2-NH-CO-CH- \\ | \\ -CH_2-NH-CO-CH- \end{array}$$

For TPU

$$-CH_2 \langle \bigcirc \rangle NH-CO-O-CH_2-CH_2- \xrightarrow[- RH]{+ R^{\bullet}} -CH_2 \langle \bigcirc \rangle NH-CO-O-C^{\bullet}HCH_2-$$

$$2 -CH_2 \langle \bigcirc \rangle NH-CO-O-C^{\bullet}H-CH_2- \longrightarrow \begin{array}{c} -CH_2 \langle \bigcirc \rangle NH-CO-O-CH-CH_2- \\ | \\ -CH_2 \langle \bigcirc \rangle NH-CO-O-CH-CH_2- \end{array}$$

Figure 8 Reticulation mechanism of polyamides[19] and possible reticulation mechanism of TPU.

ecules from macromolecular chains cuts on the degradation layer surface.

The starting point of these small molecules creates molecular empty spaces. These empty spaces are filled by the macromolecule–macromolecule interactions that lead to matter assemblies, only concerning the ultimate part of the degradation layer. These matter assemblies induce conformational changes of macromolecular chains. When chains are extended, the conformational changes are reduced as well as the possibilities of chain movement due to the elastomeric property of TPU.

The competition between connection forces of macromolecules (which can only increase with empty spaces) and the mobility limitation forces (which have a limit) leads to ruptures. The distribution of these ruptures depends on the previous forces. This process results in a limit size of assemblies and let visible microscopic spaces poorer in matter. These poorer spaces will be called "cracks of matter loss."

A picture of this degradation process is the one of a dried land. The land is initially wet and compact. When water evaporates, it creates cracks, which separate land zones being assembled together. The land that is not already dried beyond the cracks, remains compact. In this picture, the evaporated water represents the small

molecules from macromolecular chains cuts represented by the land.

The degradation layer of the UV exposed TPU-coated fabric without external water is presented in Figure 9.

With external water, the water–macromolecule interactions can replace the macromolecule–macromolecule interactions and fill the molecular empty spaces that are created by the emission of small molecules. "Plasticizer" water would avoid important macromolecular assemblies and let the appearance of degraded surface with less relief than in the case of exposure without water.

Figure 9 Sketch of degradation layer of the UV-exposed TPU-coated fabric without external water.

Figure 10 Sketch of degradation layer of the UV-exposed TPU-coated fabric with external water.

The following process can also be considered. The degradation rate of the reticulated layer increases with water. The emission of volatile products is faster and limits the possibilities of conformational changes to the faster matter assemblies. Consequently, the assemblies size would be smaller with water.

The photographs of degraded surfaces in WOMw (Fig. 4) show this distribution of matter assemblies and cracks of matter loss.

The degradation layer of the UV exposed TPU-coated fabric with external water is presented in Figure 10.

Mechanisms for the Weight Loss Degradation

The emitted volatile compounds during the TPU-coated fabric aging belong to the alkanes, alkenes, esters, aldehydes, and nitrile families, except carbon dioxide and chloromethane (Table II). The mechanisms proposed in literature for the formation of these degradation products are quoted here, although the water explicit contribution is not taken into account except where the water total absence is not indicated.

The polytetramethylene glycol photooxidation leads to the formation of formiates.[20] By reducing the formiate chains, an alkoxy radical O=$CHOCH_2CH_2C^{\bullet}H_2$ is formed. The β bond of this radical could be either cut to form methyl-formiate, or cyclized to give γ-butyrolactone.

The urethane bond rupture implies the formation of alcohols, aldehydes, and carbon dioxide.[2,20]

The alkenes come from the urethane group thermolysis.[21,22]

Ethanal, ethane, propane, and butane are thermal degradation products of polyethylene glycol. Their formation is explained by the C—C and C—O bond ruptures.[23]

Acetonitrile comes probably from the urethane groups degradation, which are the only ones with C—N bonds.

The methylchloride formation implies the presence of chlore, which is not announced in the TPU-coated fabric formulation.

The photooxidative degradation of the TPU-coated fabric takes place on urethane bonds and also on polyether groups.

CONCLUSION

The aging of an industrial TPU-coated fabric in artificial weathering tests leads to the following:

- A weight loss.
- The appearance of a reticulated layer in surface, observed by optical microscopy; this layer has a constant thickness by steady formation at the interface "nondegraded coating/degradation layer" and by elimination from the exposed surface.
- A change in the surface relief, observed by optical microscopy.

The weight loss degradation takes place in the exposed part of the reticulated layer mostly by volatile products emission.

The volatile compounds have been analyzed by GC-MS, and showed that both urethane and polyether bonds are responsible of their formation.

The aging processes are the same for exposures with and without external water but with faster weight loss speed with water. It appears that water is the deciding factor of the weight loss degradation process.

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