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Photo-Ageing of a Thermoplastic Aromatic Polyurethane in Contact with Artificial Sweat

Claude Dubois,[1*] *Joël Vebrel,*[2] *Valérie Rigny-Bourgeois,*[1] *Yves Grohens*[3]

[1] EA 473 LRC CEA M-07, UFC, 16 route de Gray, F-25030 Besançon Cedex, France
[2] LCMI, UFC, 16 route de Gray, F-25030 Besançon Cedex, France
[3] L2P/LBCM, UBS, rue St Maudé BP 92116, F-56321 Lorient Cedex, France
E-mail: claude.dubois@univ-fcomte.fr

Summary: An artificial photo-ageing cell was adapted in order to study the behaviour of polymers partly immersed in artificial sweat. The goal was to select polymers and to transform them into objects that come in contact with the skin. The polymer studied in this paper is a thermoplastic aromatic polyurethane (TPU) with the following characteristics: soft, transparent, lightly yellow coloured and hypoallergenic. The ageing of this polymer was studied with or without the presence of light stabilizers, and with or without sweat.
The physico-chemical changes in the TPU were analysed step by step during ageing. The differences in mass variation between the different ageing modes (with or without sweat; with or without stabilizers) provided information on the hydrolytic action of the sweat. The chemical changes that occurred around the irradiated or immersed surfaces were studied by IR-ATR spectrometry in order to characterize the photo-oxidation and hydrolytic effects as well as their coupling. The morphological modifications of the polymer were recorded by differential scanning calorimetry.

Keywords: durability; photo-ageing cell; photo-oxidation; thermoplastic aromatic polyurethane; sweat

Introduction

Poly(vinyl acetate), PVC and silicone are currently being used to manufacture nose plate-glasses. These polymers are in contact with skin, so they must be soft, transparent, non-coloured or light-yellow coloured, hypoallergenic and easily injected into small moulds. Other polymers have been studied for this kind of application. To this end, an artificial photo-ageing cell has been adapted to study their changes when partly immersed in artificial sweat. A previous study was carried out using an ethylene-vinyl acetate copolymer, EVA, that resisted photo-oxidation and hydrolysis well and particularly when stabilized.[1] The main changes consisted in an increase in crystallinity of the polyethylene phase mainly due to thermal effects.[2] Next, a thermoplastic aromatic polyurethane was placed under the same constraints in order to estimate its durability. That is the aim of this paper.

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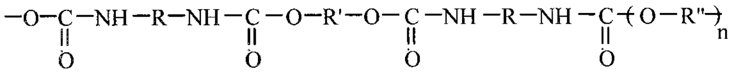
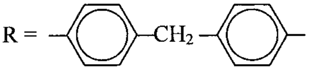
Experimental

The thermoplastic aromatic polyurethane (TPU) resulted from the reaction of 4,4'-diisocyanato-diphenylmethane, oligo(oxybutane-1,4-diyl) and butane-1,4-diol. Its structure is as follows:



$$-O-\underset{\overset{\|}{O}}{C}-NH-R-NH-\underset{\overset{\|}{O}}{C}-O-R'-O-\underset{\overset{\|}{O}}{C}-NH-R-NH-\underset{\overset{\|}{O}}{C}\left(O-R''\right)_n$$

n = 15 - 30



R' = $(CH_2)_4$ R'' = $(CH_2)_4O$

The samples (20x20x3 mm) were irradiated with UV-visible light in a Suntest CPS Heraeus cell adapted for the study of their behaviour when partially immersed in artificial sweat (Figure 1).

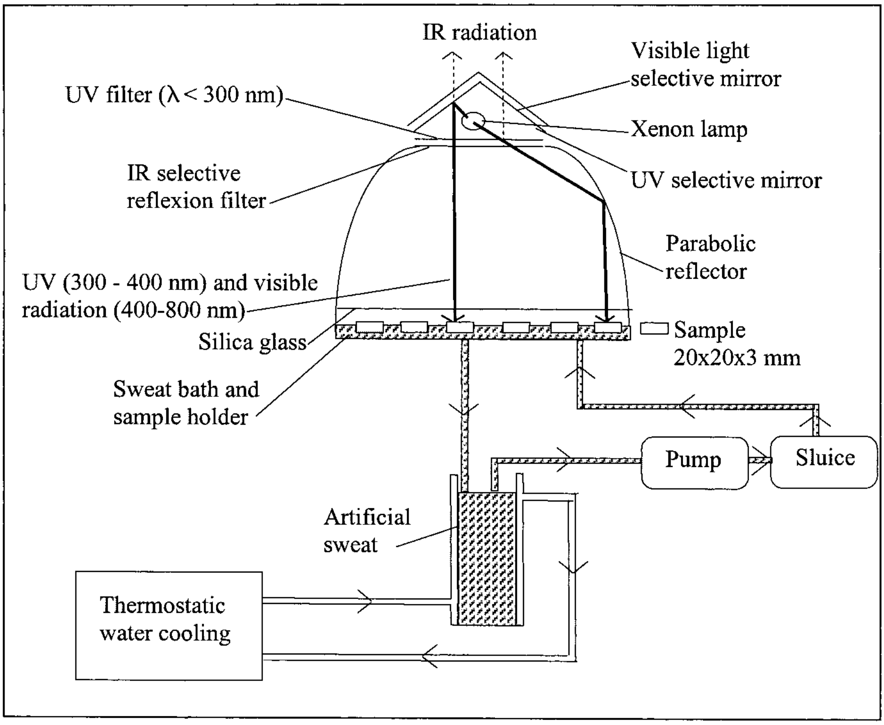


Fig. 1. Cross-section of a Suntest CPS UV-visible irradiation cell with a device that partially immerses the samples in artificial sweat.

Irradiation was carried out using a xenon lamp with a sun-like spectrum in the range of 300 to 800 nm. In an attempt to distinguish between photo-oxidation and hydrolysis effects, irradiation was also carried out without sweat. Both configurations are summarized in Figures 2a and 2b, respectively.

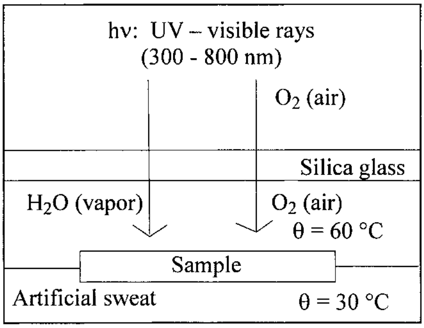


Fig. 2a. Irradiation/immersion in sweat.

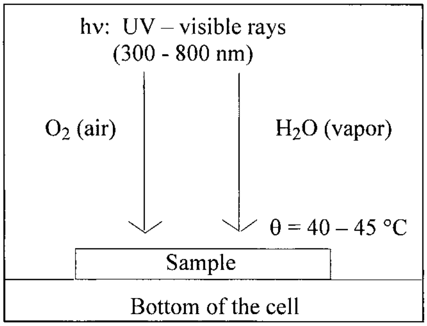


Fig. 2b. Irradiation without sweat.

Chemical composition of the artificial sweat is given in Table 1.

Table 1. Chemical composition of the artificial sweat. (pH = 5.5[a]).

Chemical	Na^+	K^+	Cl^-	Lactic acid.	NH_3	NaOH[b]
Concentration (mol L^{-1}) x 10^{-3}	53.0	11.1	49.0	20.0	4.1	

[a] pH for human sweat 4 - 7 [3]

[b] for pH adjustment

Moreover, the ageing of TPU in both configurations was studied with or without the presence of two light stabilizers:

- UV absorber: 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole;
- antioxidant : pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate).The physico-chemical changes in the aged TPU were analysed using three methods:

- Weight loss: Mettler: ± 0.01 mg;
- Differential scanning calorimetry: furnace Mettler DSC 30, processor TC 10; thermograms were recorded at temperature increases of 10 K min^{-1}.
- IR ATR: Bruker spectrometer ISF 48 (crystal KRS 5, incident angle 45°, penetration depth ~ 8 μm ($1/\lambda = 700$ cm^{-1}) to ~ 2 μm ($1/\lambda = 3500$ cm^{-1}).

Results and Discussion

Without sweat, the weight loss of TPU versus the irradiation time is low and seems to reach a plateau (Figure 3a). Hence, a minor degradation by photo-oxidation occurs in a layer just below the directly and indirectly irradiated surfaces of the TPU. As a result, volatile photo-oxidation products are lost. Under similar conditions, the photodegradation of this TPU is minor compared to those of epoxy or polyester matrixes.[4-5]

Without the presence of sweat, the stabilizers are efficient up to 1500 h of irradiation.

The weight loss is linear versus the irradiation time, and much higher when the samples are partially immersed in artificial sweat (Figure 3b). The large difference in the loss of degradation products is due to strong hydrolysis of the immersed part, which is indirectly photolysed and photo-oxidized (dissolved O_2). The hydrolysis does not occur when the stabilized and non-stabilized TPU samples are immersed in sweat in the dark at 50 °C (weight increase of 0.6-0.7 % due to water absorption).

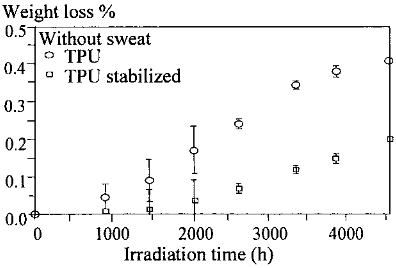


Fig. 3a. Weight loss without sweat.

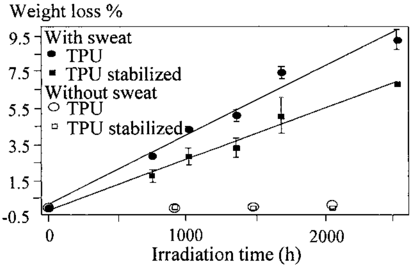


Fig. 3b. Weight loss with sweat.

The differential scanning calorimetry records the enthalpic transitions in the bulk of the new or aged polymer. The comparison between the recorded thermograms can be summarized as follows:

- The thermograms are identical for stabilized and non-stabilized TPU after the same time exposure (with or without sweat). Thus, the photo-oxidation and hydrolysis do not reach the bulk and are limited just to a layer below the directly and indirectly irradiated surfaces.
- The fresh TPU thermogram presents three transitions:[6] the glass transition at -36 ±5 °C due to the partial mobility of the soft segments; the endotherm EI at – 75 ± 3 °C due to

the H-bond breaking between the soft and hard segments; and the endotherm EII due to the melting of the hard phase, or H-bond breaking that occurs inside this phase.

- In the aged TPU samples, only EI increases with temperature in a similar way both with and without sweat (95 °C for 2700 h; 99 °C for 4220 h). In fact, soft- and hard-phase separation takes place in the bulk by thermal effects because similar temperature increases are observed for EI when the TPU is immersed in sweat in the dark at 50 °C.

IR ATR spectrometry was carried out as follows: (Crystal KRS 5, incident angle of 45°: penetration depth of ~ 8 µm ($1/\lambda = 700$ cm^{-1}) to ~ 2 µm ($1/\lambda = 3500$ cm^{-1}). The analysed layer is very thin compared to the largest thickness of the irradiated samples (~ 3000 µm).

The IR spectrum of the fresh TPU presented characteristic bands similar to those recorded in previous studies.[7-8] Due to low concentrations of stabilizers (less than 0.5 %), their vibrational bands were not recorded.

The changes in the IR spectra during ageing without sweat are similar, whether the TPU is stabilized or not. The spectra can be summarized as follows:

- They are similar (absorption bands and absorbance) for the directly and indirectly irradiated sides of a sample after the same time exposure;
- New bands form due to photo-oxidation: the OH stretching of alcohol (3500-3400 cm^{-1}) and acid (3000-2700 cm^{-1}), the C=O stretching of peroxyester (1780 cm^{-1}), ester (1750 cm^{-1}), aldehyde (1740-1720 cm^{-1}), acid (1720-1700 cm^{-1}) and quinone imide (1680-1630 cm^{-1}).
- Some previous bands decrease in absorbance: the CH_2 stretching in polyether ($2921_{(as)}$ cm^{-1} and $2851_{(s)}$ cm^{-1}), C-O stretching (1100 cm^{-1}), the C=N stretching (1530 cm^{-1}) and C-N (1310 cm^{-1}), and the NH bending (1310 cm^{-1}).

Thus, the photo-oxidation of this TPU has been clearly demonstrated inside a thin layer just below the surface. After 1000 h of irradiation, the IR spectra remain similar on both sides of the stabilized and non-stabilized TPU samples, which proves that the chemical composition of the thin analysed layer remains mostly constant. This is due to the dynamic balancing of the photo-oxidation reactions and the loss of volatile degradation products. Photo-oxidation probably takes place deeper than the analysed layer. Given the low weight losses, photo-oxidation does not seem to be a significant way of degrading this polymer. Moreover, photo-Fries molecular rearrangements and photolysis occurred inside the bulk (UV absorption: 370 –

400 nm), but were not detected inside the thin layer analysed by IR ATR. The stabilizers slow down the photo-oxidation (lower weight loss), photolysis and photo-Fries reactions.

The changes in the IR spectra during ageing with partial immersion in sweat are similar, whether the TPU is stabilized or not. The spectra can be summarized in the following way:

- They are similar (absorption bands and absorbance) on the directly irradiated side, with or without sweat, for the same time exposure (similar photo-oxidation state);
- The nearly similar IR absorption bands lead to identification of the same chemical functions as those formed or modified by photo-oxidation. Nevertheless, comparing the absorbances recorded on both sides of a sample does not make it possible to quantify the contributions of photo-oxidation (limited by dissolved O_2) and hydrolysis (the greater weight loss proves that hydrolysis by sweat immersion strongly wears away the surface).

Conclusion

The UV-visible irradiation of a thermoplastic aromatic polyurethane partially immersed in artificial sweat leads to photo-oxidation below the directly irradiated surface as well as to strong hydrolysis of the immersed surface, which is promoted by previous photo-oxidation dissolved oxygen) and photolysis reactions. Moreover, separation between the soft and hard phases occurs mainly by thermal effects inside the bulk. Stabilizers slow down degradation and yellowing, but do not stop these processes. Thus, the use of the TPU remains limited for commercial application. The soft, transparent, colourless and hypoallergenic thermoplastic aliphatic polyurethane that was previously selected for a similar study and application was not used because of the difficulties in injecting into small moulds.

[1] V. Rigny-Bourgeois, C. Dubois, M.-F. Mercier, A. Chambaudet, *Angew. MakromoL. Chem.* **1995**, *233*, 59.
[2] C. Dubois, V. Rigny-Bourgeois, A. Chambaudet, *Angew. Makromol. Chem.* **1999**, *266*, 50.
[3] M. Bailly, Ph.D. dissertation of medicine, Université de Franche-Comté, Besançon **1976**.
[4] L. Monney, C. Dubois, A. Chambaudet, *Polym. Degrad. Stab.* **1997**, *56*, 357.
[5] L. Guillot, C. Dubois, L. Monney, A. Chambaudet, *Polym. Degrad. Stab.* **2001**, *72*, 209.
[6] E. J. Woo, G. Farber, R. J. Farris, C. P. Lillya, J. C. V. Chien, *Polym. Eng. Sci.* **1985**, *25*, 834.
[7] K. Knudson, D. J. Lyman, *Polym. Sci. Technol.* **1981**, *14*, 173.
[8] C. P. Christenson, M. A. Harthcock, M. D. Meadows, H. L. Spell, W. L. Harward, M. W. Creswick, R. E. Guerra, R. B. Turner, *J. Polym. Sci. Part B: Polym. Phys.* **1986**, 24, 1401.