ELKEME
HELLENIC RESEARCH CENTRE FOR METALS S.A.

56th km ATHENS-LAMIA NATIONAL HIGHWAY, 32011 OINOFYTA
TEL: 0030 2262 604400 Fax: 0030 2262 604358
www.elkeme.gr email: info@elkeme.vionet.gr

ELKEME is certified acc. to **ISO 9001:2008**
Certificate No.: GR14.1629Q

Customer:	Halcor Tube Plant
Address:	57th km Athens-Lamia National Highway, 32011 Oinofyta
Applicant(s):	G. Hinopoulos
Project Number:	7317
Date requested:	02/07/15
Date completed:	06/08/15

Ref: Comparative Evaluation of Five Plastic Run-Off Tubes in UV-Ageing Resistance

Project Leader: F. Tzevelekou & D. Voulgaris **Report Approval by:** G. Pantazopoulos

Recipient(s): G. Hinopoulos

Copies to: I.Biris, K. Daniilidis, A.Kaimenopoulos, E.Karantinos, E.Kotsampasakis, M. Mariglis, G. Pantazopoulos, P. Sapountzis, D. Skarmoutsos, E. Spiropoulou, S.Theodosiou

Summary

Halcor provided five samples D, E, LS and X of run off plastic tubes used in air conditioning devices for comparative evaluation of UV-ageing resistance.

UV-ageing of the samples was performed in climatic test chamber Vötsch VC 4034 for 14 days; exposure conditions: 100% UV light, no moisture - condensation protection on, at 45^{o}C for the first 9 days followed by temperature increase to 50^{o}C for the next 5 days.

According to visual observations, except sample X, the rest of the tubes consist of a white spiral encapsulated in a transparent polymer. Based on the identification of the as received samples' polymers by FTIR, the samples were grouped as follows:

Group 1: Tubes D and LS have PVC based polymers.

Group 2: Tubes B and E have Polyester based transparent polymer and PVC based spiral.

Group 3: Tube X is Polypropylene

The techniques used for the comparative evaluation of the samples UV-ageing resistance were: 1) Visual observation, 2) Yellow colour determination (CIE-L*a*b* colour system), 3) FTIR analysis and 4) Microhardness measurement.

Specimens for evaluation were taken at 0, 7 and 14 days of UV-ageing test. From the visual observation, yellow colour and FTIR analysis results, the tube samples can be classified from the more to the less resistant to UV-ageing as follows:

$$X \geq B > LS > E > D$$

According to microhardness measurements Polypropylene tube X is softer compared with the PVC based tubes. However, microhardness results were not conclusive in terms of UV-ageing evaluation. That is possibly attributed to inadequate evolution of the ageing in order to affect the hardness of the tubes.

1. Introduction

Halcor provided five (5) plastic samples of run-off tubes, used in air conditioning, for evaluation in UV-ageing. The samples were delivered in the as produced condition (**Figure 1**), no exposure preceded to any environmental conditions.

Except sample X, all the other samples consist of a white spiral encapsulated in a transparent polymer. **Figure 1** illustrates the different spirals' geometries (e.g. spaces between each twist, diameter). Sample X is a light grey uniform tube.

The UV-ageing was evaluated by:

1. Visual observation
2. Yellow colour determination
3. FTIR analysis
4. Microhardness

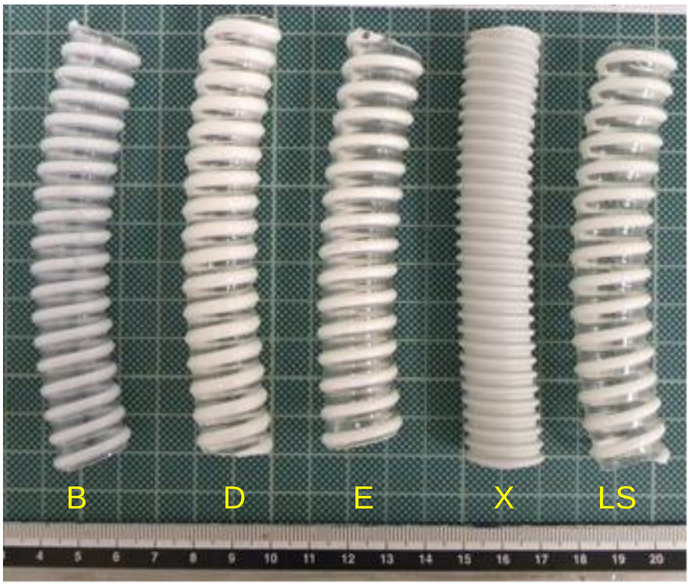


Figure 1: Image of the as received samples.

2. Experimental

UV-ageing was performed in climatic test chamber Vötsch VC 4034 for 14 days (**Figure 2**); exposure conditions: 100% UV light, no moisture – condensation protection ON, at 45^{o}C for the first 9 days followed by temperature increase to 50^{o}C for the next 5 days. ULTRA-VITALUX® E27/ES, 300W OSRAM Lamp was used. **Specimens for evaluation** were obtained before the test (0 days), at 7 days and 14 days of ageing. **Photos** were captured to **record the appearance** of the samples at 0, 7 and 14 days of ageing.

Surface **colour assessment** was performed with image analysis software (Image Pro-Plus v7.01), using the **CIE-L*a*b*** colour scale. The colour was determined on **surface micrographs** of the specimens captured using an upright Nikon Eclipse ME 600 optical microscope. The specimens were compared per their **b* value** in the blue to yellow colour axis, as shown in **Figure 3**.

A Perkin Elmer **FTIR** Spectrum GX photometer having a Specac Diamond ATR system was used to obtain the **“fingerprint” of the specimens**.

A Tukon 2100 Instron indentation hardness tester was used for the **microhardness** measurements (in MPa) with **Knoop indenter**. 25 g of load were applied for 3 s and dwell time 10 s.

Figure 2: Samples arrangement in the climatic test chamber during the UV-ageing test.

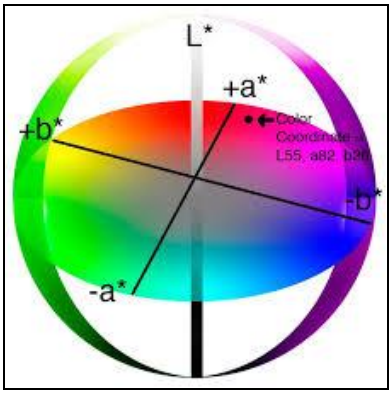


Figure 3: L*a*b* colour analysis.

3. Results

Table 1 presents the identification of the samples' polymers, according to the FTIR analysis. Also the FTIR spectra are shown in **Figure 4**. Hence, there are **three** (3) **groups of tube samples**:

- Group 1: tubes D and LS
- Group 2: tubes B and E
- Group 3: tube X

Table 1: Identification of the polymers.

Sample	Transparent polymer	White spiral
D	Modified PVC	PVC with carbonated salt as a filler
LS	Modified PVC	PVC with carbonated salt as a filler
B	Polyester	PVC with fillers
E	Polyester	PVC with fillers
X	Polypropylene	

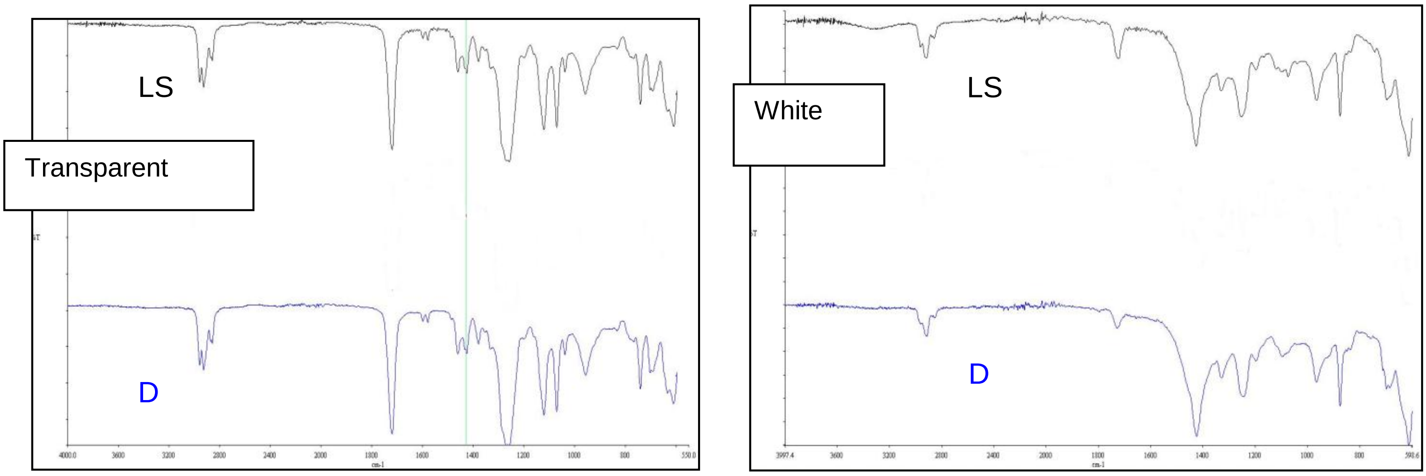


Figure 4 *(continued)*

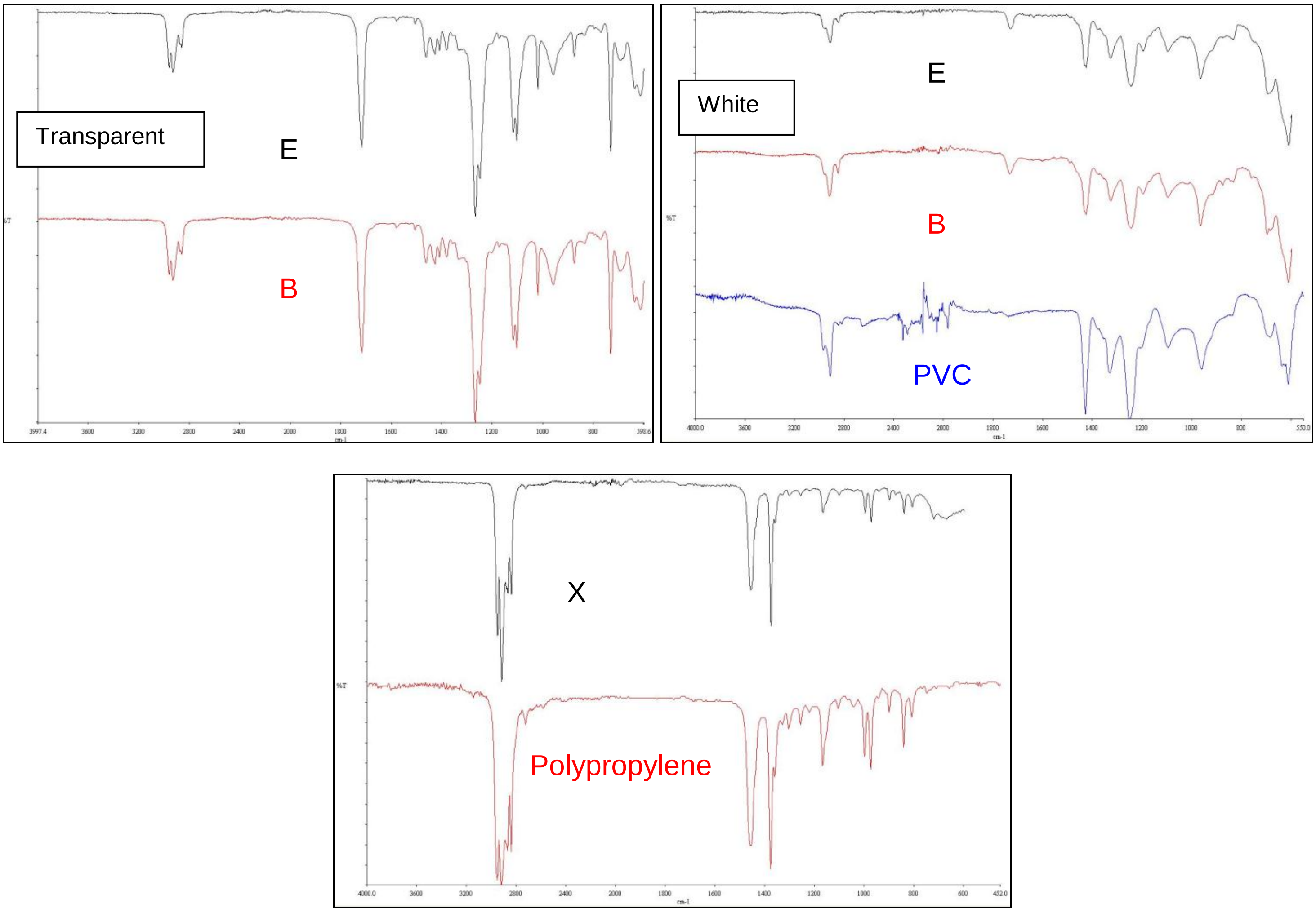


Figure 4: FTIR spectra of the tube samples.

3.1 Visual observation

The appearance of the tube samples after 0, 7 and 14 days of UV-ageing is shown in **Figure 5**. The comments from the visual observation are the following:

- Samples D and LS turned to **yellow after 2 and 7 days respectively**.
- Sample B became yellow after **14 days** of ageing, while sample E started to change colour (yellow) after **7 days**.
- Sample X **did not change colour** within the 14 days of testing. It seems that the grey colour of the tube hides a possible development of yellowing.

Polymers develop a yellowing during the photo-oxidative ageing, which is due to radicals' reactions **[1]**, **[2]**. It is mentionable that all the PVC based samples were sticky in touch, indicating migration of the additives to the tubes' surfaces.

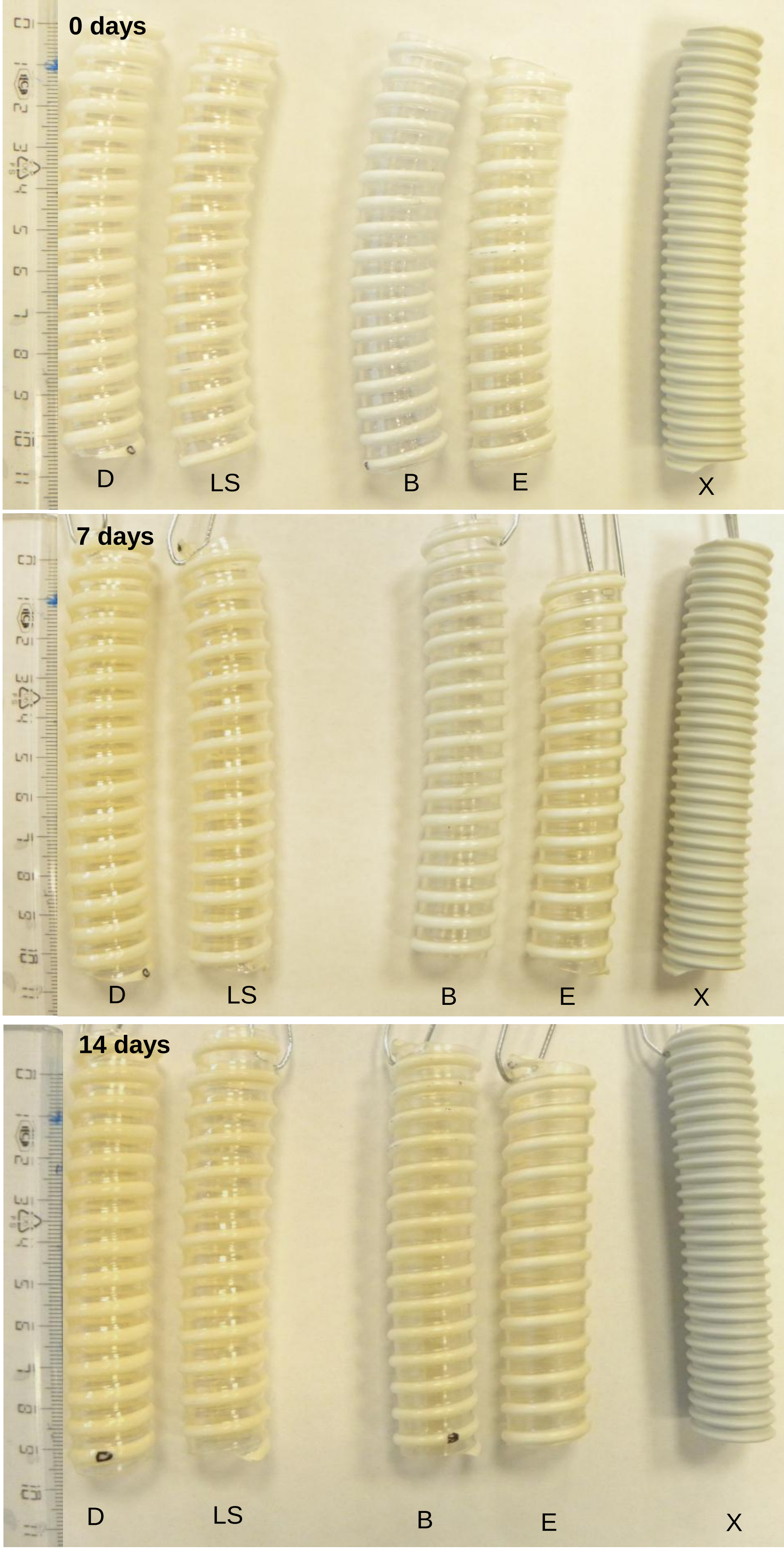


Figure 5: Images of the samples after 0, 7 and 14 days of UV-ageing.

3.2 Yellow colour determination

The b* average values are an expression of the yellow hue. For the samples D, LS, B and E, b* are plotted in **Figure 6**, after 0, 7 and 14 days of UV-ageing. The b* was determined on the spiral areas to obtain the effect of ageing on both polymers of the tubes (transparent material and white spiral). **The changes of b* agree with the visual observation comments**:

- Sample D was the first tube, among the PVC based samples, which developed the yellowing.
- Sample LS and B became yellow after 14 days.
- Sample E started to turn to yellow after 7 days of testing.

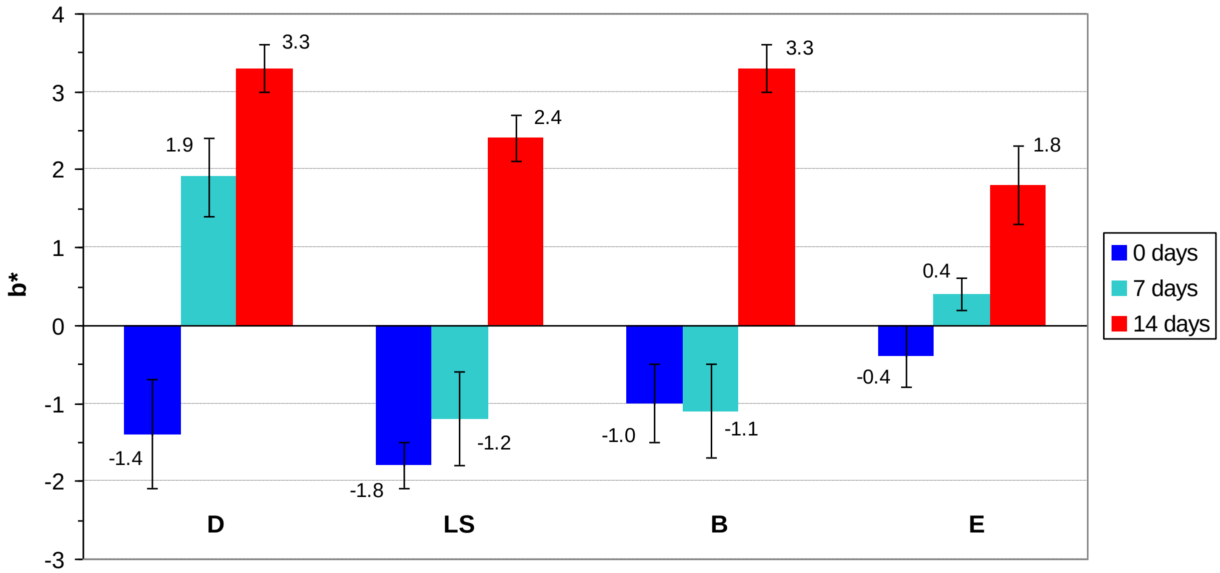


Figure 6: Plot of average b* values of the PVC based tube samples. Error bars: ± 1 σ.

3.3 FTIR analysis

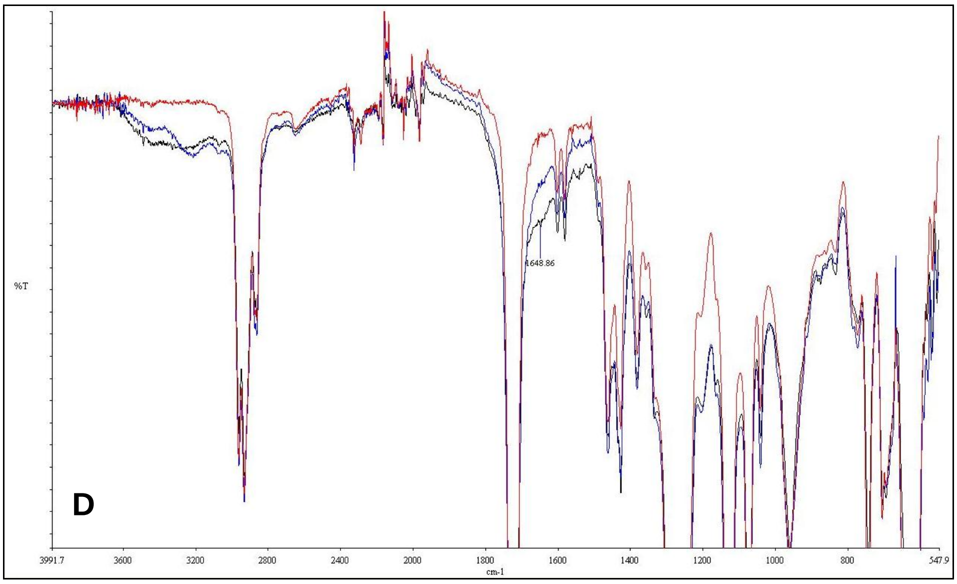
Figure 7 presents the FTIR spectra of the specimens taken from the tube samples at 0, 7 and 14 days of testing. Photo-oxidation reactions of a polymer (**PH**) produce radicals ($P^{\bullet}$) **[1]**. Those reactions can be shown schematically as follows:

$$PH \xrightarrow{hv} P^{\bullet} \xrightarrow{O2} POO^{\bullet} \xrightarrow{PH} POOH + P^{\bullet}$$

Both samples D and LS developed a tailing at 1650 cm^{-1} of the carbonyl group peak (1740 cm^{-1}) due to the **photo-oxidation product** $POO^{\bullet}$ and hydroxy group peaks at 3200 and 3400 cm^{-1}, attributed to POOH. Furthermore, the pattern of those changes agrees with the b* values, meaning that the tube D exhibited the photo-oxidation products at the 7 days FTIR spectrum, while tube LS at 14 days spectrum.

Also FTIR spectra of the tubes B and E show the presence of the POO• and POOH (1680 and 3200-3400 cm^{-1} respectively) in consistency with the respective b* values, tube E at the 7 days FTIR spectrum and B at 14 days spectrum.

FTIR analysis of the **tube X** suggests that also this tube **developed the photo-oxidation products after 14 days of testing**, see the peaks at 1650, 1730, 3360 cm^{-1}. More over, the FTIR peaks at 1580 and 1540 cm^{-1} suggest migration of the additives to the tube's surface.



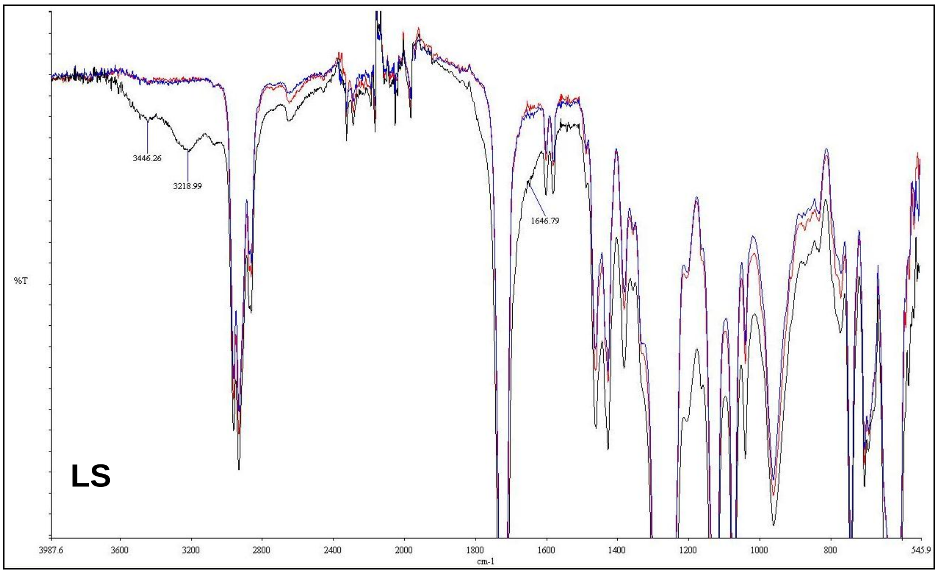


Figure 7 (continued)

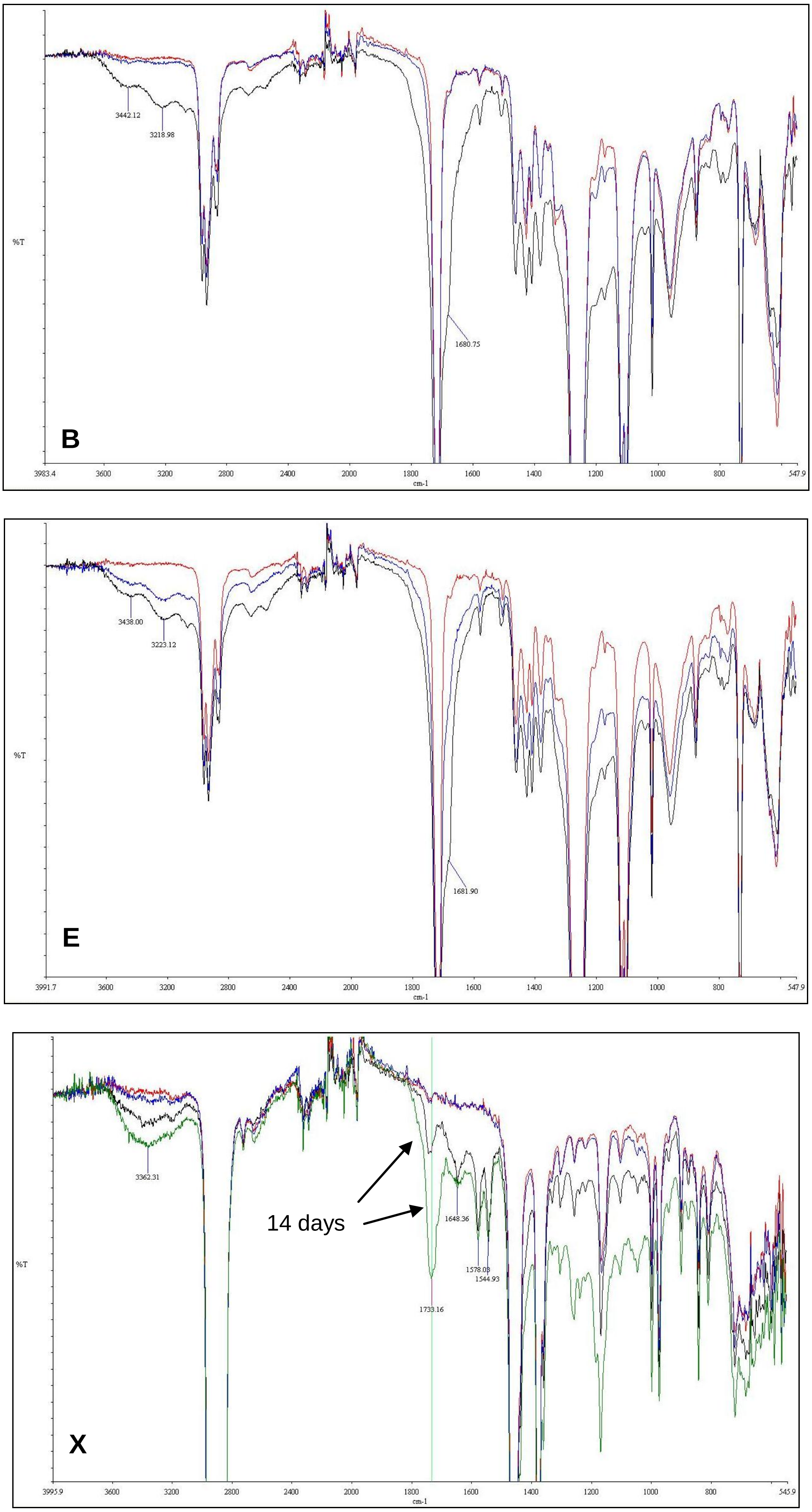


Figure 7: FTIR spectra of the tube samples after 0 (red), 7 (blue) and 14 (black) days of UV ageing.

3.4 Microhardness

Table 2 presents the average values of the microhardness measurements. The Polypropylene tube X is softer than the other PVC based tubes. For the PVC based tubes, the measurements were performed on the transparent part of the tubes. The measurements on the spiral were not consistent due to the curvature.

Based on the findings from the yellow colour (b*) and FTIR analysis, the results of microhardness are not conclusive. Possibly, the progress of the ageing is not enough to affect the hardness of the tubes at the same extent as the properties measured by the other techniques.

Table 2: Average microhardness (in MPa) at 0, 7 and 14 days of UV-ageing, using the Knoop indenter and load of 25 g.

Sample	**Microhardness (MPa)**		
	0 days	**7 days**	**14 days**
D	134	139	133
LS	177	133	138
B	173	174	176
E	137	132	133
X	47	58	62

4. Conclusions

Visual observation, yellow colour (b*) and FTIR analysis revealed a classification of the tube samples regarding the resistance to the UV-ageing, based on the 0, 7 and 14 days specimens evaluation. The sequences from each technique, starting from the more to the less resistant, are the following:

Visual observation: X > B > LS ≈ E > D

Yellow colour: B ≈ LS > E > D

FTIR analysis: X ≈ B ≈ LS > E ≈ D

Thus, an overall sequence is the following:

$$X \geq B > LS > E > D$$

According to microhardness measurements Polypropylene tube X is softer compared with the PVC based tubes. However, microhardness results were not conclusive in terms of UV-ageing evaluation. That is possibly attributed to inadequate evolution of the ageing in order to affect the hardness of the tubes.

5. References

[1] Samuel Affolter, *“Long-Term Behaviour of Thermoplastic Materials”*, Interstate University NTB, Buchs, Switzerland.

[2] Gregory R. Fedor and Patrick J. Brennan, *“Comparison Between Natural Weathering and Fluorescent UV Exposures: UVA-340 Lamp Test Results”*, Q-LAB Technical Bulletin LU 8035.

NOTES:

1. *The type of sample, the date and time, as well as the sampling points are according to customer’s declaration. The results correspond to the sample received by the laboratory.*
2. *Partial reproduction or reprint of the analysis report is not allowed under any circumstances unless there is a prior written permission of the issuing organization.*