

Ageing mechanism of *ortho*-phthalic anhydride unsaturated polyester resin

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Abstract

This paper presents the accelerated ageing test results of a durability study on polyester and analyses the ageing mechanism of this material. Pure resin specimens were cast and exposed in a xenon arc lamp ageing cell or a thermo-oxidation ageing cell, or were subjected to natural exposure ageing in the western China exposure zone. The chemical groups, morphology, Yellowness Index (YI), gloss, and mechanical performances of the specimens have been investigated. The results showed that the specimens turned yellow, some cracks appeared on their surfaces, and their mechanical strengths first increased and then decreased during the course of ageing. In the early stages of the ageing period, the polyester undergoes post-cure and physical ageing, whereas after a longer ageing period it undergoes some degree of degradation under the synergistic impact of UV, high temperature, and O₂. The main influencing factor leading to the failure of the polyester is UV irradiation.

Keywords: unsaturated polyester (UP) resin, artificial thermo-oxidation ageing, artificial xenon arc lamp ageing, exposure ageing, synergistic impact.

1 Introduction

General purpose unsaturated polyester, that is, *ortho*-phthalic anhydride-type resin, is one of the most commonly used thermosetting resins, which has the trademark 191#. It is a condensation polymer made from maleic anhydride, *o*-phthalic anhydride, and propylene glycol, to which a certain amount of styrene monomer is added as a thinner/curing agent [1]. Unsaturated polyester resin and its composites are widely used in various fields, such as adhesives, blades for wind turbines, construction structures, boat hulls, etc. Studies on the exposure of



such materials to environmental conditions, for example varying temperature, humidity, ultraviolet radiation, etc., are of the utmost importance in order to assess the impact of these important ageing factors on their mechanical behavior [2]. Reports concerning the ageing failure mechanism of this material have been few in our country [3–5], whereas more detailed studies of this kind of work have emanated from various developed countries [6–12]. The latter studies have been mainly based on the environmental characteristics of the respective countries. The purpose of this work is to establish a database on the resistance to weathering of polymer materials exposed to the environmental conditions of western China and to research the relationship between natural ageing and artificially accelerated ageing for these polymer materials. We describe herein a study on the ageing behavior of UP resin exposed in the western exposure zone or subjected to artificial ageing by simulation of the weather environment of the western area.

2 Experimental details

2.1 Preparation of specimens

General polyester was prepared by mixing resin, cyclohexanone peroxide initiator, and cobalt naphthenate accelerator, and pouring the mixture into rectangular moulds according to GB/T2567—1995. The polyester samples were cured for about 24 h in the moulds at room temperature. The samples obtained were semi-transparent, and their surfaces were smooth and glossy.

2.2 Instrumentation and ageing parameters

An SN-900 xenon arc lamp ageing cell made by Shanghai Lin-Pin Equipment Corporation was used to evaluate the durability performances of the specimens according to GB/T16422.1—1996.

Ageing parameters: exposure intensity $1000 \pm 200 \text{ W} \cdot \text{m}^{-2}$ (monitored by means of an exposure meter); spraying/non-spraying cycle: 18 min/102 min, temperature $63 \pm 3 \text{ }^\circ\text{C}$; 12 h exposure/12 h non-exposure.

An FQRLS-800 thermo-oxidation ageing cell made by Shanghai FuQi Equipment Corporation was used to evaluate the durability performance of the materials according to GB/T7141—1992.

Ageing parameters: temperature: $70 \pm 1 \text{ }^\circ\text{C}$; aeration rate: 50 times/h; wind speed: 0.5 m/s; 24 h continuous exposure.

Natural exposure (GB/T3631—1995)

Exposure areas: for this research, three representative areas in western China were selected, namely LaSa, Tibet; JiangJin, ChongQing; and YuLi, XinJiang, along with one in central China, namely Wuhan, HuBei. Exposure times: 3, 6, 12, and 18 months.



2.3 Testing methods

2.3.1 Mechanical performance testing

2.3.1.1 Dynamic mechanical analysis (DMA) In order to accurately determine the impact of environmental ageing on the viscoelastic behavior of the material, thermal scans were performed on small bars of dimensions ca. 25 mm × 15 mm × 4 mm. The test machine was a Q800 type from TA instruments. The test mode used here was three-point bending under controlled strain. The temperature was set between ambient and 200 °C with a constant frequency of 1 Hz. The preload was set at 0.125 N and the vibrational amplitude was 15 μm. The testing span was 60 mm. Each material was tested in pristine condition for different ageing times.

2.3.1.2 Static tensile tests Static tensile tests were performed on the polymer material on a WDW-50 universal testing machine according to GB/T2568—2005 at 5 mm/min crosshead speed. Tensile strain was measured by strain gauges attached along the longitudinal axis of the sample. The specimen dimensions were 180 mm × 20 mm × 4 mm.

2.3.1.3 Three-point bending tests Three-point bending tests were performed on the polymer materials on the aforementioned WDW-50 universal testing machine according to GB/T2571. The specimen dimensions were 80 mm × 15 mm × 4 mm. The testing span was 60 mm.

2.3.2 Morphology investigations

The surface morphology of the samples was examined with an XPV-203E optical microscope made by Shanghai Optical Instrument Co. Magnification: 100×.

The glossiness of specimens was assessed according to GB/T1743—1989 using a JKGZ-1 gloss-meter made by Tianjin Jingke precision instrument factory. The angle of the measured light was 60°.

The Yellowness Index (YI) was investigated according to GB2409—1988 using an SP-60 differential colorimeter made by X-Rite Corporation.

2.3.3 Fourier-transform infrared analysis

The KBr pressed-sheet method was adopted, whereby the cured resin was ground to a powder, mixed with KBr (1:50, w/w), and the mixture was pressed into a sheet. A Nicolet 170X Fourier-transform infrared (FT-IR) spectrometer was used for the analysis. Resolution: 4 cm⁻¹; frequency range: 4000–450 cm⁻¹.

3 Results and discussion

3.1 Results

3.1.1 Appearance and morphology

The appearances of the samples changed with time, becoming more yellow by visual inspection in the course of ageing. More specifically, the Yellowness Index (YI) gradually increased.



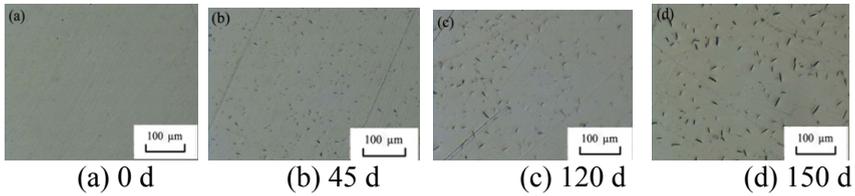


Figure 1: Morphology of the polymers (thermo-oxidation ageing).

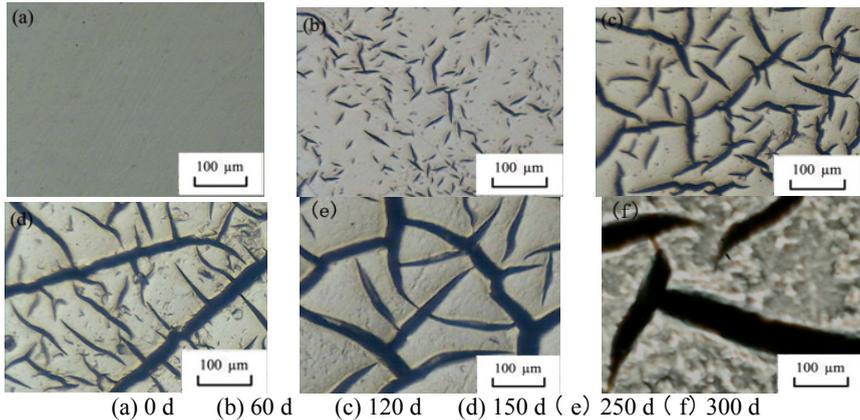


Figure 2: Morphology of the polymers (xenon arc lamp ageing).

Figures 1 and 2 show the morphologies of the specimens after ageing for different times. As shown in Figs. 1 (a)–(d) and Figs. 2 (a)–(f), the surfaces of the polymer display some irregularities and/or cracks. The changes are more obvious for the sample aged in the xenon arc lamp ageing cell.

3.1.2 Gloss

Plots of the gloss of the specimens versus ageing time (chiefly for samples aged under the xenon arc lamp) are shown in Figs. 3 and 4. The gloss of the polymer can be seen to deteriorate, and visual inspection reveals a yellowing with ageing. Natural exposure also led to a deterioration in the gloss of the polyester, with the extent of the change depending on the exposure area (Fig. 4). The changes in appearance were more obvious for the samples aged in the xenon arc lamp ageing cell.

3.1.3 DMA results

In order to obtain a clear view of the impact on the dynamic mechanical performance of the polymer, specimens of pure polyester were aged both artificially and by natural exposure and were then investigated by DMA. Figures 5, 6, and 7 present thermal scans for this polymer.

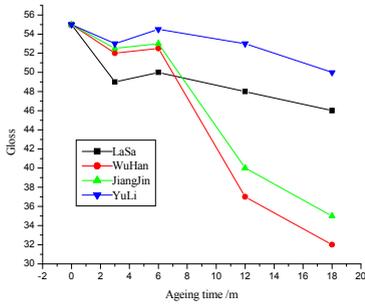


Figure 3: The relationship between the gloss of the polyester with artificial ageing time.

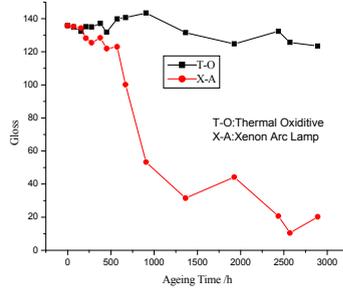


Figure 4: The relationship between the gloss of the polymer with natural ageing time.

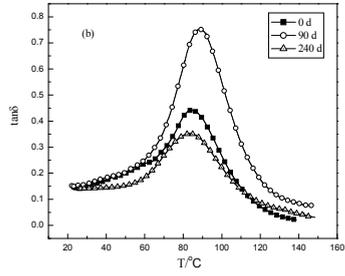
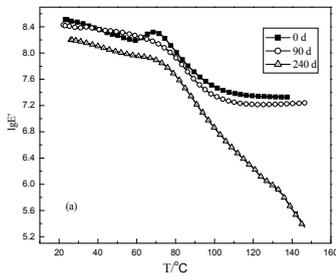


Figure 5: The storage modulus (E') and $\tan \delta$ of the polymer (xenon arc lamp ageing).

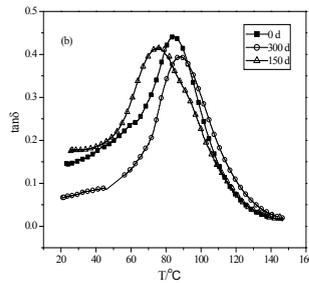
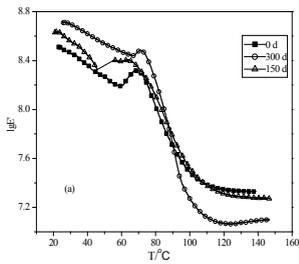


Figure 6: The storage modulus (E') and $\tan \delta$ of the polymer (thermal-oxidation ageing).

Figures 5(a), 6(a), and 7(a) show the relationship between storage modulus (E') and temperature, while Figs. 5(b), 6(b), and 7(b) show the relationship between $\tan \delta$ and temperature. As is evident from the above figures, the storage modulus (E') and the change of glass transition temperature (T_g) of the



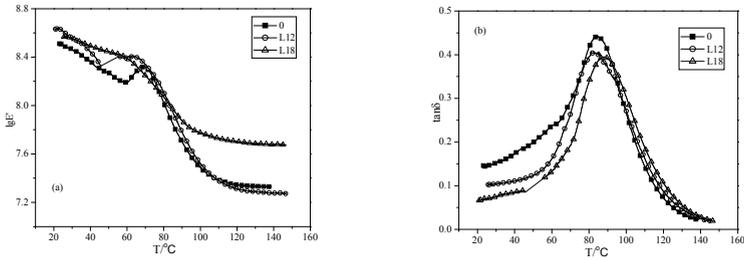


Figure 7: The storage modulus (E')' and $\tan \delta$ of the polymer after LaSa exposure 18 m.

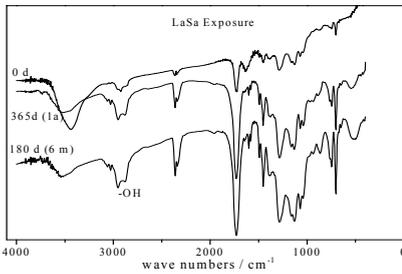


Figure 8: FT-IR spectra of resin aged by xenon arc lamp ageing.

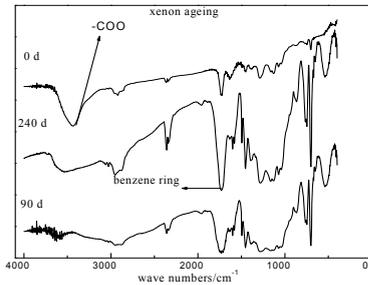


Figure 9: FT-IR spectra of resin aged by natural exposure ageing.

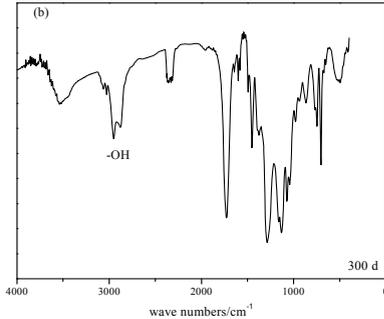
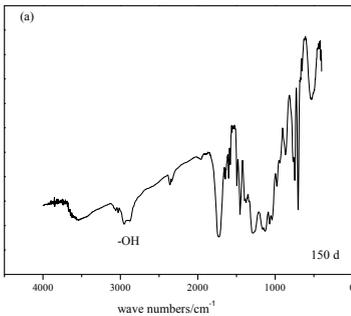


Figure 10: FT-IR spectra of resin aged by thermo-oxidation ageing.

environmentally aged samples of polyester are not the same as those of the pristine material (0 d). T_g increases during the initial stage of the ageing period, but then decreases.

3.1.4 FT-IR spectra

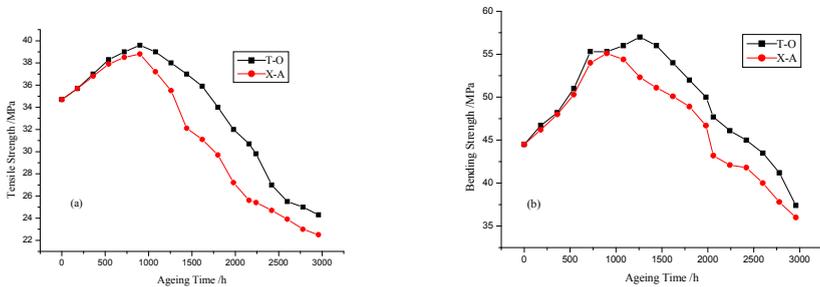
To investigate the microscopic structural changes, the polymer was studied by FT-IR. Salient FT-IR spectra are shown in Figs. 8, 9, and 10.



From Figs. 8–10, it can be seen that the absorption peaks due to the carbonyl ($1720\text{--}1706\text{ cm}^{-1}$) and phthalate ester groups ($750\text{--}790\text{ cm}^{-1}$) are obviously enhanced, while the hydroxyl absorption peaks (920 cm^{-1} , $3300\text{--}2500\text{ cm}^{-1}$) also show obvious changes. After the samples had been aged for about 240 d (xenon arc lamp ageing) or 300 d (thermal-oxidation ageing), the hydroxyl, methyl, and sub-methyl radical absorption peaks had changed, which may be attributed to degradation of the polyester resin.

3.1.5 Mechanical performances

The tensile strength and bending strength test results for the polymer are shown in Figs. 11(a), 11(b), and 12. The mechanical performance shows a trend of an initial increase followed by a decline with artificial ageing (as shown in Figs. 11(a), (b)). Figure 12 indicates that the bending strength of the samples was increased after natural exposure for 18 months. The level of this increase depends on the environmental factors of the exposure areas.



(Note: T-O: Thermo-oxidation; X-A: Xenon arc lamp)

Figure 11: The relationship between the polymer's strength with artificial ageing time.

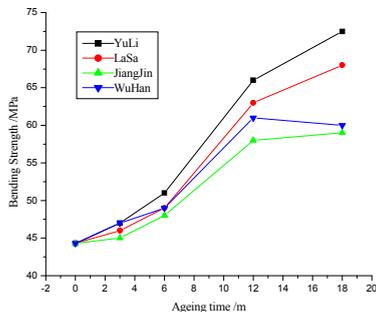


Figure 12: The relationship between the bending strength with natural exposure time.



3.2 Discussion

3.2.1 Appearance and morphology

As shown in Figs. 1 (a)–(d) and Figs. 2 (a)–(f), some irregularities and/or cracks appear in the surfaces of the polymers. This phenomenon becomes more obvious with increasing exposure time. For artificial ageing, the cell temperature was set at 70 °C (higher than the ambient temperature), the polyester had fewer double bonds since these easily react with each other to form a cross-linked structure, and the anhydride and hydroxyl groups underwent dehydration to form carbonyl (—COO) in the molecular chain (—OH peak weakened, —COO enhanced; see the FT-IR spectra in Figs. 8–10). This is a post-cure reaction, and the change may partly alter the chemical constitution of the polyester, leading to internal stress. When this stress reaches a certain level, small cracks will appear in the surface, which become more prevalent during the course of ageing. However, the structure of the polyester did not undergo such changes leading to internal stress, and so although the sample developed some slight irregularities (Fig. 1), no large cracks appeared during thermo-oxidative ageing.

As shown in Fig. 3, the gloss of the polymer deteriorated in the course of ageing. This change became slow after 150 d (1800 h). For thermo-oxidative ageing, the gloss of the sample hardly changed. Because the ageing process involves a series of complex chemical reactions, this reaction starts at the surface and gradually proceeds to the interior. Clearly, the chemical change leads to the deterioration in the glossiness of the polymer.

The color change occurs because of very many reasons. However, in this work, the presence of metallic ions is the primary reason. Because cobalt naphthenate was used as a promoter, the cobalt ions took part in the reaction and the surfaces of the samples ultimately appeared yellow.

As shown in Fig. 4, the gloss of the polyester changed differently upon exposure in different geographical areas. The morphology of the specimens was much better retained and their changes in glossiness were less than that in the case of samples subjected to accelerated ageing in the laboratory. Indeed, the morphology change of the polymer was not obvious after exposure ageing for 18 months in the chosen areas. This was because the samples subjected to natural exposure ageing endured less accumulative radiation energy and were aged at a lower temperature compared to those subjected to accelerated ageing in the laboratory.

3.2.2 Microstructure

There is a correlation between the chemical structure of 191# resin and the change in its T_g and storage modulus (E'). The values of E' and $\tan \delta$ are related to the chain length of the polymer and its molecular movement. After a short period of ageing, the resin underwent a post-cure reaction, and the molecular chain was lengthened. However, the storage modulus (E') and $\tan \delta$ decreased after prolonged exposure. This may have been due to degradation of the polyester resin. This is supported by the changes in the absorption bands of the respective chemical groups in the FT-IR spectra (Figs. 8–10).



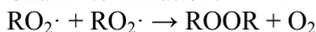
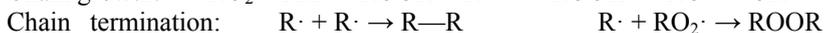
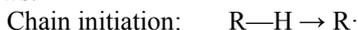
3.2.3 Mechanical performances

From Figs. 11(a) and 11(b), it is evident that the tensile strength and bending strength of the polymer increased in a short ageing period and then decreased after a longer time. Since the test specimens were prepared at room temperature, some of the unsaturated groups had not reacted completely, and these were post-cured at the higher temperature of the ageing chamber or the exposure areas. If the unsaturated groups were converted to saturated groups, the reaction would not proceed. The mechanical performance was seen to reach a maximum value. In the course of the ageing process, the ageing of the material starts from its surface and proceeds towards the interior, as a result of which the strength decreases.

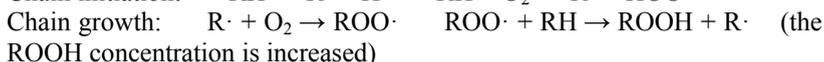
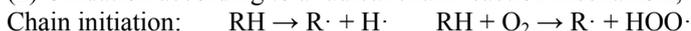
3.2.4 Ageing mechanism

The appearance, the glass transition temperature, and the mechanical properties of the unsaturated polyester are changed under the synergistic impact of UV, heat, and oxygen. From the above trends, the ageing mechanism of the materials may be postulated as follows:

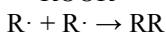
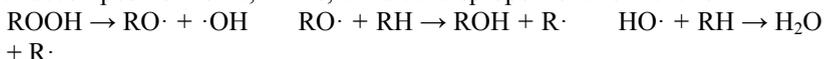
(1) Photochemical reaction according to a free radical mechanism, as follows:



(2) Oxidation according to a radical chain reaction mechanism, as follows:



If the ROOH concentration exceeds a certain level, it will generate a new free radical decomposition route, that is, a radical disproportionation reaction:



4 Conclusions

Two environmental chambers capable of simulated accelerated ageing of polymers have been constructed and tested. One chamber was a thermo-oxidation ageing chamber, providing heat and oxygen, while the other was a xenon arc lamp ageing chamber, providing humidity and UV radiation. Some samples have also been exposed to the natural environmental conditions of WuHan, JiangJin, LaSa, and YuLi. The material aged under the above conditions was 191# (*ortho*-phthalic anhydride-type) unsaturated polyester.

The experimental results have revealed that some irregularities and/or cracks appeared in the surfaces of the samples during ageing, which was accompanied



by a concomitant yellowing. The polymer became stiffer after ageing for about 90 d, which can be mainly attributed to post-curing of the material caused by temperature and UV radiation. However, organic material was ablated from the surface of the sample after ageing for 120 d and its mechanical strength was somewhat decreased; these effects can be mainly attributed to UV irradiation. Its degradation mechanism may involve a radical chain reaction.

Acknowledgement

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