

The interplay of physical aging and degradation during weathering for two crosslinked coatings

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Received 25 June 2007; accepted 4 September 2007

Abstract

Polymer molecular relaxation, or ‘physical aging’, is a very important influence on permeability and mechanical properties of any polymer below its glass transition. ‘Physical aging’ occurs as even an unstressed polymer gradually relaxes towards its equilibrium conformation. This and the shorter term response to stress happen over periods much longer than the typical cycle of an accelerated weathering test, thus important properties of a polymeric coating may be affected by the difference in frequency between natural and artificial exposures, in addition to other factors. Further, ‘physical aging’ is affected by chemical changes to the polymer network caused by the degradation during a weathering exposure. In this investigation, purely physical aging was compared with the effect of concurrent chemical degradation by measuring ‘enthalpy recovery’ and mechanical stress relaxation at a variety of temperatures and at various stages during accelerated weathering exposure. The effect of physical aging was quite apparent in both an epoxy-polyamide coating and a polyester-urethane coating. Changes in physical aging behaviour during degradation were different for the two coatings, which points to further reasons for discrepancy between accelerated weathering and natural exposure.

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Keywords: Physical aging; Weathering; Crosslinked polymer; KWW; Cooperatively rearranging regions

1. Introduction

The ultimate goal of weathering studies is to provide a link between the composition of a coating or its constituents and how well it performs its macroscopic function. Many of the protective properties, and somewhat indirectly, the appearance properties of a coating film rely on its mechanical properties and how they fare during its service life. Clearly, abrasion resistance, impact resistance, flexibility, burnishing are directly dependent on mechanical properties. However, corrosion resistance and other protective properties rely on resistance to cracking and appearance properties are spoilt if a coating is cracked, abraded or burnished. Thus, it is necessary to understand how mechanical properties change with exposure.

It is common experience that coatings become stiffer and more brittle during exposure. In addition, it is understood also that crosslink density and molecular weight eventually diminish, although both may increase early in the exposure. It is also common, but not universal, that the glass transition temperature,

T_g , increases gradually during exposure. In order to provide an explanation for the competing increase in stiffness and glass transition temperature with the reduction in crosslink density, one must look further afield than chain scission.

Possible explanations include an increase in hydrogen bonding as the polymer binder becomes more oxidized. However, hydrogen bonds are usually regarded as being only 10–20% as strong as a covalent bond so any increase in stiffness would require a large number of hydrogen bonds to be formed during weathering to counter the loss in covalent bonds.

Another explanation, first put forward as an issue in coating science some years ago [1] is that physical aging of polymers takes place during exposure. This is the process whereby a polymer that is jammed into a non-equilibrium configuration at temperatures below its glass transition gradually relaxes towards equilibrium over timescales of days, weeks or longer. Any glassy polymer undergoes this process, since polymers are only in thermal equilibrium above T_g . Aging is associated with several changes in properties, where perhaps the easiest to visualize is a gradual densification, of about several parts in one thousand, so that the polymer chains get closer to each other. This results in the mechanical modulus and yield stress increasing over this time-frame, as well as other properties changing, e.g. permeability

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decreases, enthalpy and entropy decrease, relaxation times and refractive index increase, etc. There is a very extensive literature [2–4] on how physical aging affects each of these properties and how these properties give insight into the underlying molecular processes in a material. In fact, physical aging has been given as a reason for changes in mechanical properties in weathering in engineering plastics [5].

Physical aging takes place over comparatively long time scales, from days to months, as the molecular configuration of the polymer changes and comes to thermodynamic equilibrium with its environment. Separately, most polymers respond to a stress in a time-dependent way which typically includes an instantaneous component, then a continuum of relaxation times up to days. However, this time-dependent response is assumed to establish an equilibrium of an unchanging polymer to that stress. In fact it has been common to follow physical aging by monitoring how the time-dependent response to a stress changes with aging time [4]. If indeed any of these physical aging processes last for extensive periods, it raises some questions about the very different time-scales in accelerated weathering in contrast to the diurnal and much longer cycles of natural weathering.

Stress relaxation experiments give a direct measure of the time-dependence of polymer response and also very directly examine the mechanical properties of coating films. Enthalpy recovery measurements by calorimetry are very common in the literature and are a less direct measurement of relaxation, but they have the advantage of being a means of assessing how much the polymer has relaxed from its prior equilibrium above the glass transition (or from its pre-gel state). Prior work on the polyester-urethane coating showed complicated changes during accelerated weathering as crosslink density diminished. The introduction here of a comparison with another polymer is to investigate how variations in polymer structure affect the pattern of concurrent physical aging and network breakdown.

2. Experimental details

2.1. Material and specimen preparation

Polyester-urethane and epoxy-polyamide clear coatings were used in this research. The polyester-urethane is a model for polyurethane coatings used in aircraft topcoats and has been described before [6]. An epoxy was chosen as the other polymer due to the technological significance of this type of polymer, an ability to select a material by its glass transition temperature, and the convenience that they degrade within a reasonable period.

The epoxy selected was a very conventional system of Epon[®] 828 and Epikure[®] 3115 (both from Hexion Specialty Chemicals), typical of a primer polymer. This is a well-known and robust combination, with a higher T_g than either the polyester-urethane or the highest temperature of accelerated weathering cycles used here. As is common practice, this was made using 10% more of the curing agent than the equivalent weights would otherwise indicate.

Coatings were applied either on aluminum panels or on DuPont Tedlar[®] film which enabled easy removal of coatings after weathering to obtain free standing films. Coating thickness of free films was measured with a micrometer and was between 40 and 100 μm .

All polyester-urethane films were cured for a week at ambient laboratory conditions but the epoxy films were better cured at 80 °C for 45 min. Before testing, all samples were subjected to 30 min at 130 °C in order to ensure complete cure and to remove whatever thermal history had accumulated. The completeness of cure was checked by infrared spectroscopy. Depending on the needs of the experiment, samples were kept in a refrigerator or desiccator until needed.

2.2. Sample exposure

2.2.1. Accelerated weathering

Samples for weathering were subjected to Xenon Arc accelerated weathering, using a Q-Sun 1000TM chamber with borosilicate filters, following ASTM D 4587-91 procedure of 4 h at UV light (0.55 W/m² at 340 nm) at nominally 60 (± 2) °C, followed by 4 h water spray (dark cycle) at ambient temperature. Measurements in the weathering chamber with a very thin thermocouple showed that the surface of the coatings reached an average temperature of about 55 °C although the air temperature was 58 °C. Thus, other characterizations were done at 55 °C although 58 °C is the label retained here for temperatures inside the weathering chamber. Weekly removal of samples for testing was done after 2 h into a light cycle to minimize the influence of water during property characterization.

After extended accelerated weathering, both materials became very friable so it was impossible to obtain any mechanical data but calorimetric testing could continue.

2.2.2. Iso-thermal aging

Some films were aged continuously at both ambient temperature and the highest temperature of the accelerated weathering cycle in order to be compared with those subjected to accelerated UV weathering.

2.3. Sample characterization

2.3.1. Enthalpy recovery

At each increment of exposure or thermal history, the state of the polymer was assessed by measuring its enthalpic recovery [2,7,8]. Its current state was assessed by the first increasing temperature scan, see Fig. 1, then it is annealed above its glass transition to eliminate its thermal and aging history (i.e. re-equilibrate it above its glass transition). After a suitable time it was allowed to cool rapidly then another temperature scan was performed to compare to the first. The area between the two curves is a measure of how much the enthalpy changed during its exposure, i.e. “enthalpy recovery”. Temperature scans were from –25 to +130 °C with a heating rate of +5 °C/min on a specimen size of 3–5 mg. The reported value of T_g is that from the inflection point of the change in the heat flow signal in the second heating cycle.

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