Polymer Testing 65 (2018) 281–296

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material Behaviour

Effect of outdoor exposure on the moisture diffusion and mechanical properties of epoxy polymers

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ARTICLE INFO

Keywords:
Epoxy polymer
Thermoset
Outdoor exposure
Moisture diffusion
Glass transition temperature
Plasticization
Vitrification
Fractography

ABSTRACT

Specimens of epoxy polymers of four compositions based on 2,2 di-(4-hydroxyphenyl) propane cured by a cycloaliphatic amine hardener were exposed during 3, 6, 9, and 12 months on an open bench in a moderately warm marine climate of Gelendzhik. In the initial state and at various stages of exposure the moisture diffusion coefficient and maximum moisture content of flat rectangular specimens-coupons are determined for drying and humidification at a temperature of 60 °C. Properties of polymers in three states have been studied: after a stop of climatic tests without conditioning and after additional stages of humidification and drying using stress-strain tensile tests, dynamic mechanical analysis, optical microscopy, fractography. After the exposure in the climatic conditions, different amounts of moisture accumulate in the specimens depending on relative air humidity and precipitation amounts in different year seasons. At the drying stage, moisture transfer obeys Fick's second law. At the humidification stage, a change of mass of specimens depends on sorption of moisture and desorption of hydrolysis products. Tensile strength decreases after the climatic action and differs by a value of 20–66% for the dried and moistened specimens. A method of dynamic mechanical analysis revealed processes of post-curing and destruction depending on the polymer composition and duration of exposure. The humidification also affected a failure mode of specimens. In the initial state and after different exposure times in open climatic conditions after the humidification on fractographs an area of a mirror zone corresponding to plastic fracture increases. After drying, an area of a rough (relief) zone increases. It is shown that in order to obtain reliable information about mechanisms of climatic aging of epoxy polymers it is necessary to compare the properties of controlled specimens taking into account the moisture content to determine a degree of reversible plasticizing action of moisture against the background of irreversible changes.

1. Introduction

Use of epoxy resines and polymer composite materials (PCMs) in engineering, construction, various branches of industry forms a need to study the properties of these materials under the influence of temperature, moisture, solar radiation and other aggressive climatic factors. Totality of physicochemical and structural transformations in the polymeric materials after their stay in the natural conditions is united by a term “climatic aging”. Regularities of climatic aging of polymers and PCMs have been considered in many works, for example, in Refs. [1–16].

The most important factor of the climatic action is moisture. The good properties of epoxy resins are strongly affected by humidity in the environment. Indeed, water in the polymer acts as a plasticizer decreasing the mechanical properties and damaging the chemical structure of the matrix for hydrolysis reactions. This effect is a heavy drawback in many industrial applications (aeronautical, shipbuilding industries, wind turbine blades, etc) [4,7–9,12,16–18].

Features of the temperature-humidity action on the properties of epoxy polymers were considered in Refs. [15,17–30]. In review [17] the separate and combined action of temperature and humidity on the glass transition temperature, yield stress, and thermal stresses of adhesive joints is considered. The action of low and high temperatures is considered. To assess the moisture transfer in adhesives, Fick's laws are usually used. The properties at the interface of adhesive-substrate and in volume are studied. Two types of water are considered: free and bound. It is mentioned that the glass transition temperature T_g of a glassy, very crosslinked polymer is higher than that of a more ductile amorphous polymer. The effects of degradation are analyzed. Plasticization by moisture reduces the yield stress and strain to failure. With

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https://doi.org/10.1016/j.polymertesting.2017.12.007
Received 24 August 2017; Received in revised form 16 November 2017; Accepted 5 December 2017
Available online 06 December 2017
0142-9418/ © 2017 Published by Elsevier Ltd.

the humidification, T_g also decreases, which affects the properties of the adhesives, especially at the high temperatures. It is noted that the combined action of temperature and humidity has not yet been well studied.

In paper [18] two epoxy polymers held in water at a temperature of 32 °C are studied and their adhesion parameters are determined. An increase of deformability with growth of moisture content is shown.

The epoxy polymer DGEBA/TETA (diglycidyl ether of bisphenol-A/triethylene tetramine) system was studied in Ref. [19]. The polymer specimens were kept in water at 23, 45, 75 and 90 °C. The moisture content was compared depending on the aging temperature. When measuring the shear modulus, the decrease of T_g was noted in the specimens containing water. Widening of the transition interval from the vitreous state to the highly elastic one is noted because water evaporates during heating in the chamber. With the exposure at 45 °C, 3.6% of water was accumulated, the glass transition temperature decreased from 135 to 88 °C. With the exposure at 75 °C, less water (3.2%) was accumulated and the glass transition temperature decreased less (108 °C).

The moisture saturation of four carbon plastics based on the epoxy polymers after holding at 66 °C and a relative air humidity of 75% during 50 days and after boiling in water during 10 days was studied in Ref. [20]. Temperature dependences of the modulus of elasticity at a three-point bending in a temperature range of 20–300°C during 10 h and, for comparison, the dynamic modulus of elasticity and the tangent of the angle of mechanical losses *tan δ* during 0.5 h are measured. The dependences of T_g on the amount of sorbed moisture are plotted according to the data of static and dynamic measurements and their good correspondence is shown. To assess the reversible effect, the moistened specimens are dried at 53 °C for 7 days and their glass transition temperatures are again determined. Unfortunately, it is not determined how the moisture content changes when the specimens are heated, which is especially important for the initial high glass transition temperatures (160-280°C).

The epoxy glass-reinforced plastic was tested in water at 40 and 60°C for 285 days, followed by measurements of the dynamic modulus of elasticity, loss modulus, and the tangent of the angle of mechanical losses [21]. The plasticization reduces the modulus of elasticity at the room temperature. Antiplasticization and postcuring of the epoxy matrix are discovered.

Water sorption at 80 °C of twelve variants of nanocomposites based on diglycidyl ether of bisphenol-A (DGEBA) was studied in Ref. [22]. The water content changed from 2.4 to 4.8%. The analysis shows that the water sorption occurs according to Fick's diffusion model. After 3670 h of exposure, *tan δ* is studied in the wet and dry specimens. The moisture reduces T_g of polymers and increases the peak width of *tan δ*.

Dynamic mechanical tests of epoxy polymers are carried out after the exposure in distilled water at 70 °C [23] and after the thermal humid action [24,25], and the dependences of T_g on the amount of sorbed moisture are determined.

Surfactants of organic clay nanoparticles (the organoclays) are introduced into the compositions of the epoxy resins of diglycidyl ether of bisphenol A (DGEBA)/with the hardener 4.4 diaminodiphenylsulfone (DDS). Moisture sorption isotherms are measured at 30 °C for different activities of water vapor and with the exposure to water [26]. With the addition of surface active particles, the equilibrium moisture saturation increases due to the increase of free volume. This is proved by measuring the density. It is supposed that water molecules interact with the polymer, plasticize it and form clusters. The *tan δ* curves show a double peak in both samples. It can be explained in terms of free volume and epoxy-water interactions. The rupture of the hydrogen bonding between polymer chains by water molecules would produce an increment of the chain mobility during the glass transition region and therefore a higher free volume of the material. In all similar studies [19–26], there is a general drawback: an estimation of the plasticizing effect of moisture is not rigorous, since the moisture is evaporated from the specimens during the DMA measurements, and because of this the shape of the *tan δ* curve is distorted.

The epoxy resin DGEBA (DER 331) cured with the diamine hardener DDS with varying degrees of curing (from 65 to 100%) is studied in Ref. [27]. The moisture saturation of the dried specimens is carried out at 35 and 75 °C. At 35 °C, the limiting moisture saturation increased, depending on the degree of curing from 1.3 to 2.8%, and was explained by the increase of the content of free water molecules. On the contrary, at 75 °C, the content of bound water decreased from 2.9% to 2.1%. While humidifying, the decrease of T_g was observed. With the moisture saturation at 75 °C the effect of postcuring was revealed by the *tan δ* double peak. On the graphs of the dynamic modulus of elasticity versus temperature, one can clearly see the increase of the modulus in the highly elastic state as the degree of curing increases.

The addition of various diluents to the epoxy resins affects their properties and changes the value of the limiting moisture saturation [28,29]. The presence of reactive diluent 1,4-butandioldiglycidylether in the tetraglycidyl-methylenedianilin epoxy resin reduces the equilibrium moisture saturation by 35%. Nanoadditives (carbon tubes, nanofibers, graphene-like particles) were also introduced into this polymer. The moisture promotes swelling of the polymer matrix. This swelling reduces internal stresses that occur at high curing temperatures. It is stated that during thermocycles, the moisture can freeze and destroy the matrix. With thermal spikes, the moisture can become vapor and destroy the composites. The nanoadditives slightly changed the value of the equilibrium moisture saturation. The dynamic mechanical parameters of the curves of dry and moistened polymers are studied. In the composition with the excess hardener content, another *tan δ* peak is detected. It is shown that in the presence of nanofillers a microphase of binder with lightened molecular mobility is formed, which is proved by the presence of the additional *tan δ* peak.

With the exposure of polymers in the full-scale climatic conditions, the moisture acts as the plasticizer and initiator of the hydrolysis of epoxy structures, and this factor of influence is partially reversible. The effects of surface erosion manifest in combination with solar radiation, rain, and wind [2–5]. According to [1], the moisture causes a significant deterioration of the mechanical properties of glass-reinforced plastics due to the active influence on glass fiber, especially at increased stresses. In the epoxy glass-reinforced plastic with treatment of fiber by a silane agent, it was found by a method of Fourier transform infrared spectroscopy that a number of groups of ethane, benzene, toluene, ethylbenzene, phenylpropane, methanol, ethanol and other residues increased with the increase of exposure time. It is proved that in the surface layers of glass-reinforced plastic T_g of the epoxy matrix decreased significantly more than in the inner layer.

After 20 years of operation of an airplane Boeing 737-200, a fragment of a horizontal stabilizer made of carbon fiber reinforced plastic was studied [30]. Changes of the epoxy matrix over 48,000 flights were estimated by the methods of Fourier transform infrared spectroscopy and dynamic mechanical analysis. It is shown that the chemical changes of the epoxy matrix are similar to ones during the aging at 120 °C for 1 year. The increase of T_g was discovered with a rise of *tan δ* peak temperature.

The epoxy polymer DGEBA (the diglycidyl ether of bisphenol A) cured with the amine hardener DETA (Diethylene Triamine) as well as a unidirectional glass-reinforced plastic based on it was studied in Ref. [15]. The aging under laboratory conditions happened during 8 weeks at a temperature of 45 °C and ultraviolet source irradiation with a wavelength of 340 nm with a power of 0.77 W/m^2. The thermal humid aging was performed separately during 6 weeks at 70 °C and a relative humidity of 85%. The full-scale exposure in Vietnam lasted 76 weeks with a total radiation of 6424 MJ/m^2 with the relative humidity of 82% in the temperature range from 22.6 to 29.8 °C. After UV irradiation in the chamber and full-scale exposure, the effect of polymer degradation in the surface layer of the specimens by the decrease of T_g was discovered, whereas with the thermal humid action this effect did not appear. The photodegradation of epoxy polymer in the surface layer

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