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Effect of water on the behaviour of adhesives modified with thermally expandable particles

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ABSTRACT

In this work, the water diffusion in Thermally Expandable Particles (TEPs) modified adhesives was measured and the residual strength of water saturated and desorbed TEPs-modified adhesives was assessed. Bulk specimens were used to measure the diffusion coefficient of water in a TEPs-modified adhesive and tensile dogbone specimens were used to measure the stress-strain curves as a function of water uptake. In addition, the glass transition temperature (T_g) of aged and unaged TEPs-modified adhesives was measured, and the fracture surfaces of failed tensile specimens were examined using a scanning electron microscopy (SEM). It was observed that the moisture uptake increases as a function of TEPs content. The tensile properties (i.e. strength and elastic modulus) of the TEPs-modified adhesive tend to decrease with increasing water content, which recover after desorption at the same temperature as the initial environmental conditioning.

1. Introduction

Adhesives have become the method of choice for many structural joining applications. However, one disadvantage of adhesive joints is the permanent nature of the bond. Several techniques exist for controlling debonding in adhesive joints [1]. One option is the use of thermally expandable particles (TEPs). It has already been shown that with the right amount of TEPs, a bond can be dismantled rapidly with local heat [2,3]. However, one of the concerns associated with this technique is the effect of water on the adhesive properties as the particles can create a path for an increase of water diffusion.

It was shown that the success of the concept of using TEPs with adhesives depends on the combination of the TEPs and the adhesive system [4,5]. The resulting properties of the TEPs-modified adhesive systems are influenced by the mechanical, physical and chemical properties of the used TEPs and adhesives. The TEPs-modified adhesives should keep their properties as close as possible to the unmodified adhesives or in acceptable limits in order to fit the strength requirements for a given application [5]. Moreover, the adhesive is susceptible to water absorption from the surrounding environment and this affects the mechanical properties of the adhesive, leading to reduction in the performance of the structure.

It is known that moisture is absorbed by the polymers/adhesives in two different ways: as free water (which occupies the free spaces of the adhesive and is responsible for plasticization) and as bound water, (which forms single or multiple hydrogen bonds with the adhesive's polymer chain, resulting in swelling of the adhesive, plasticization and consequent decrease of strength and glass transition temperature (T_g)) [6]. If the water uptake is done at low temperatures, as soon as the adhesive is dried, the mechanical properties of the adhesive are usually recovered [7]. In addition, the absorbed water can act as a crazing agent, continuously decreasing the mechanical strength of epoxi adhesives with exposure time in water [8]. Water absorption into a polymer may also leads to chemical changes such as chain scission and hydrolysis. However, plasticization is considered reversible upon drying, while crazing, chain scission and hydrolysis are irreversible.

Gravimetric methods are usually used to measure the water uptake of an adhesive. This method consists simply in subjecting a plate of bulk adhesive to an ageing environment, such as distilled water, a salt solution, air with a particular relative humidity, or other environments compatible with what the adhesive will be subjected in its service life, such as toluene for example [9], and measuring the weight change over time with a precision scale.

It was shown in the literature that the water uptake behaviour of structural adhesives depends greatly on the environmental conditions [7]. In general, the equilibrium mass uptake increases with environmental moisture. Some authors [9,10] have measured the equilibrium moisture uptake of epoxy adhesives and have found that it remains

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constant with environmental temperature, while others found significant differences on the equilibrium moisture uptake when subjecting the adhesive to warmer environments [11].

The effect of moisture absorption on the mechanical properties of adhesives modified with nano- or microparticles was investigated by several researchers [12–14]. It was shown that absorbed water can attack the matrix/filler interface and cause debonding at the interface [14]. However, as per authors knowledge, there are no studies in the literature about the effect of moisture absorption on the properties of TEPs-modified adhesives.

The main objective of this research was to measure the water diffusion in TEPs-modified adhesives and assess the residual strength of water saturated (wet) and desorbed (re-dry) TEPs-modified adhesives. Bulk specimens were used to measure the diffusion coefficient of water in a TEPs-modified adhesive and tensile dogbone specimens were used to measure the stress-strain curves for unaged, saturated and desorbed specimens. In addition, the glass transition temperature (T_g) of aged and unaged TEP-modified adhesives was measured, and the fracture surfaces of failed tensile specimens were examined using a scanning electron microscopy (SEM).

2. Experimental details

2.1. Materials

2.1.1. Adhesive

A two-component epoxy adhesive Betamate™2098, supplied by Dow Automotive (Dow Europe GmbH, Horgen, Switzerland) was selected for this study. This adhesive, used within the automotive industry, is part of a new generation of crash durable adhesives, which combines high strength with high elongation, was used in previous adhesive studies by the authors [2,3].

2.1.2. Thermally expandable particles

Expancel 031 DU 40 particles supplied by Akzo Nobel Expancel Industries (Sundsvall, Sweden) were selected. The diameter of these particles ranges mainly from 10 to 16 μm. Data provided by the manufacturer is given in Table 1, where T_{start} is the temperature where the particles start to expand and T_{max} is the temperature at which the TEPs reach the maximum expansion.

2.2. Specimens manufacture

The TEPs-modified adhesive was mixed with a Speed Mixer (DAC 150.1 FVZ Speedmixer, Hauschild, Germany) for 60 s at 2500 rev/min. This allows an efficient and homogeneous dispersion, creating visibly bubble-free mixing [16].

Thin sheets of the adhesive modified with different concentrations of TEPs, by percentage weight (0, 10 and 20 wt%), were produced by curing the adhesive between steel plates of a mould with a silicone rubber frame (the silicone ensures the thickness of the adhesive plate of 2 mm), which were pressed (2 MPa) for 24 h at room temperature (RT). From these sheets, bulk tensile specimens (Fig. 1a), water absorption and desorption specimens (Fig. 1b) and T_g specimens (Fig. 1c) were machined. Bulk tensile specimens with reduced dimensions were used, which allowed time efficient production and ageing.

Table 1
Characteristic data for Expancel 031 DU 40 [15].

Particle size [μm]	10–16
T_{start} [°C]	80 − 95
$T_{max.}$ [°C]	120 − 135

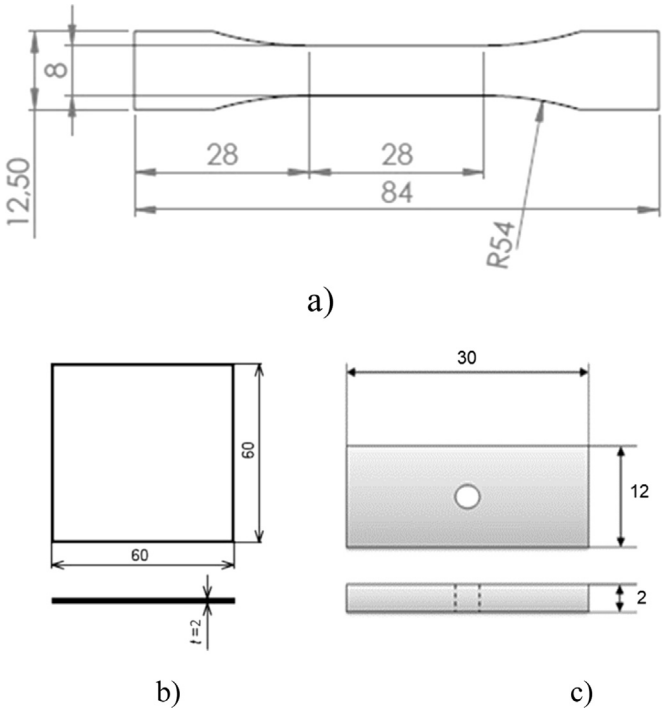

Fig. 1. Test specimen geometry (dimensions in mm): a) tensile, b) bulk water absorption and c) T_g.

2.3. Measurements and characterization

2.3.1. Diffusion tests

Before ageing, the specimens were kept in a desiccator in order to eliminate any water that they might be absorbed from the environment until the specimen's weight was constant. Next, the initial weight of each specimen was measured using a microbalance (Kern-Toledo, Balingen, Germany) with a 0.001 g resolution scale. Subsequently, the specimens were aged in distilled water at 32.5 °C. At least 6 specimens were aged per condition. The weight of the specimens was measured periodically until saturation was achieved.

The water content was calculated using Eq. (1):

$$M_t = \frac{(m_t - m_0)}{m_0} \times 100\% \tag{1}$$

where M_t is the water content, and m_t and m_o are the specimen weight at time t and the initial specimen weight, respectively.

The Fickian diffusion model was used for fitting the water uptake data, as given in Eq. (2):

$$M_t = M_\infty - M_\infty \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} exp\left[-\frac{D(2n+1)^2\pi^2 t}{4h^2}\right] \tag{2}$$

where D is the diffusion rate, M_∞ is the equilibrium water uptake and h is the specimen thickness.

The diffusion rate, D was calculated using Eq. (3) when the equilibrium water uptake was obtained:

$$D = \left(\frac{M_t}{M_\infty}\right)^2 \times \frac{\pi}{16} \times \frac{h^2}{t} \tag{3}$$

Desorption of the specimens was done in a desiccator, at the same temperature used in the absorption procedure. The drying process was performed immediately after the specimens reached saturation. The same weight measurement as water absorption was carried out during desorption, until the weight was constant.