International Journal of Adhesion & Adhesives 54 (2014) 191–199

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

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

Mechanical and thermal characterization of a structural polyurethane adhesive modified with thermally expandable particles

M.D. Banea [a,b,*], L.F.M. da Silva [b], R.J.C Carbas [b], R.D.S.G. Campilho [c]

[a] IDMEC, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[b] Departamento de Engenharia Mecânica, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[c] Departamento de Engenharia Mecânica, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal

ARTICLE INFO

Article history:
Accepted 3 June 2014
Available online 18 June 2014

Keywords:
Thermally expandable particles (TEPs)
Adhesive joints
Fracture toughness

ABSTRACT

Thermally expandable particles (TEPs) are used in a wide variety of applications by industry mainly for weight reduction and appearance improvement for thermoplastics, inks, and coatings. In adhesive bonding, TEPs have been used for recycling purposes. However, TEPs might be used to modify structural adhesives for other new purposes, such as: to increase the joint strength by creating an adhesive functionally modified along the overlap of the joint by gradual heating and/or to heal the adhesive in case of damage. In this study, the behaviour of a structural polyurethane adhesive modified with TEPs was investigated as a preliminary study for further investigations on the potential of TEPs in adhesive joints. Tensile bulk tests were performed to get the tensile properties of the unmodified and TEPs-modified adhesive, while Double Cantilever Beam (DCB) test was performed in order to evaluate the resistance to mode I crack propagation of unmodified and TEPs-modified adhesive. In addition, in order to investigate the behaviour of the particles while encapsulated in adhesives, a thermal analysis was done. Scanning electron microscopy (SEM) was used to examine the fracture surface morphology of the specimens. The fracture toughness of the TEPs-modified adhesive was found to increase by addition of TEPs, while the adhesive tensile strength at yield decreased. The temperature where the particles show the maximum expansion varied with TEPs concentration, decreasing with increasing the TEPs content.

1. Introduction

Adhesive bonding is a viable technique for joining a wide range of materials [1]. However, increasing the lifetime, reducing the costs and improving the safety of structures are highly demanded, nowadays. Hence, the development of new technologies and processes for easy recycle, heal or self-heal of bonded structures are becoming of great interest for the industry [2]. If bonds can be broken without damage of the components, recycling is easier. Also, for an environmental friendly disassembly of bonded structures, it is necessary to separate the joint between the bonded components so that the different materials can be reused on a qualitatively high level. One example is the case of the adhesives modified with thermally expandable particles (TEPs), which can be dismounted by heating the joint. However, TEPs might be used to modify structural adhesives for other new purposes, such as: to increase the joint strength by creating an adhesive functionally modified along the overlap of the joint by gradual heating and/or to heal the adhesive in case of damage.

Thermally expandable particles, microcapsules or microsphere, were developed by Dow Chemical Co in the early 1970s [3] and are particles made up of a thermoplastic shell filled with liquid hydrocarbon. On heating them, two transformations occur (see Fig. 1). One is the softening of shell material and the other is the gasification of the hydrocarbon liquid inside it. As a consequence, the shell expands as the gas inside it pushes the softened shell from inside out causing it to grow in size. When fully expanded, the growth in volume of the particle can be from 50 to 100 times. When heat is removed, the shell stiffens and the particle remains in its expanded form. Expansion temperatures range from 70 °C to 285 °C depending on particle and grade [4]. They are commercialized worldwide by the companies Expancel Nobel Industries (Sweden), under the trademark of Expancel [5], and Matsumoto Yushi Seiyaku (Japan), under the trademark of Micropearl [4]. Owing to this unique behaviour, TEPs are used by the industry in a wide variety of applications [6–9]. This innovative idea has been extended to structural adhesives for recycling purposes by Nishiyama et al. [10]. The simple heating of the joint over 100 °C leads to an easy separation of the bonded materials. The adhesive

* Corresponding author at: IDMEC, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal. Tel.: +351 225081750; fax: +351 225081445.
E-mail address: mbanea@fe.up.pt (M.D. Banea).

http://dx.doi.org/10.1016/j.ijadhadh.2014.06.008
0143-7496/

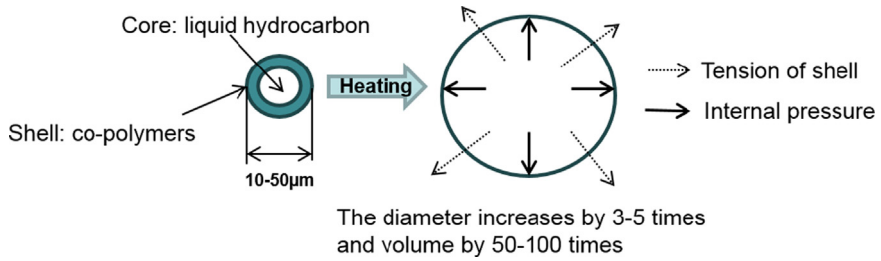

Fig. 1. Model of expansion mechanism.

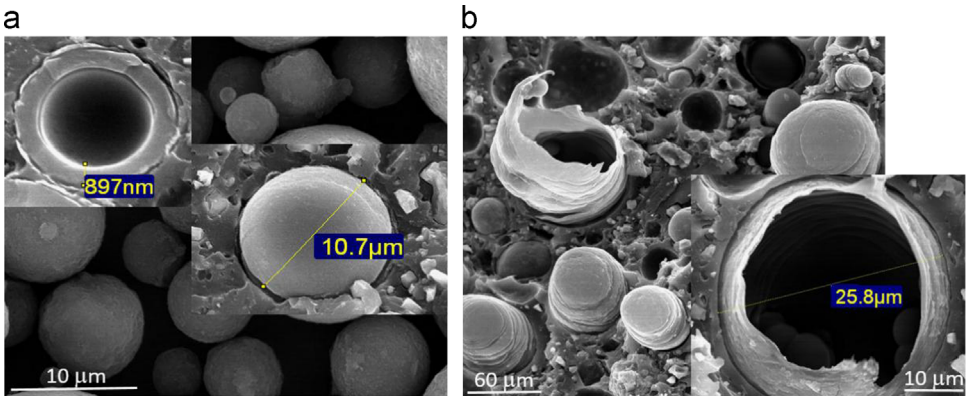

Fig. 2. SEM image of TEPs before (a) and after expansion (b).

expansion may be up to 400% according to the study of Nishiyama and Sato [11]. However the high temperature performance was poor because the particles began to expand around 60 °C and the glass transition temperature (T_g) of the adhesive was lower than the expansion temperature of the particles. High temperature performance is vital for structural applications such as automotive and aerospace. To overpass this problem, Kishi et al. [12,13] used expandable graphite, which begins to expand at 200 °C, with an epoxy adhesive to study de-bond of Carbon Fiber Reinforced Polymer (CFRP) and steel plates adhesive joints and found a good dismantlability at 250 °C. Nevertheless, presently TEPs producers develop particles with higher expansion temperatures [4,5].

Kim et al. [14] used TEPs with a polyurethane adhesive and found that the dismantlement of the joint was possible with microwave treatment for 4 min. More recently, McCurdy et al. [15] used TEPs with three structural adhesives for automotive industry in order to obtain joint dismantling. They found that matching a high performance TEPs with a high performance adhesive is not sufficient to obtain an efficient joint dismantling as there are important implications for joint performance (i.e. joint durability). To conclude, the success of the concept of using TEPs with adhesives depends on the combination of the TEPs and the adhesive system and more research efforts in this area are necessary.

In this study, the mechanical and thermal behaviour of a structural polyurethane adhesive modified with TEPs was investigated as a preliminary study for further investigations on the potential of TEPs in adhesive joints. Tensile bulk tests were performed to get the tensile properties of the adhesive and TEPs-modified adhesive (the Young's modulus, the yield tensile stress and the failure tensile strain). Double cantilever beam (DCB) tests were performed in order to evaluate the resistance to mode I crack propagation of unmodified and TEPs-modified adhesive. In addition, a thermal analysis was done in order to observe the behaviour of the particles while encapsulated in adhesives. Finally, scanning electron microscopy (SEM) was used to examine the fracture surface morphology.

2. Experimental details

2.1. Materials

2.1.1. Adhesive

The adhesive selected for this study was a two-component structural polyurethane adhesive SikaForce®7888 L10, supplied by Sika (Portugal). It cures at room temperature (RT) and is used in the automotive industry. This adhesive is part of a new family of polyurethane adhesives which combines high strength with large ductility. Interest in this class of adhesives is on the rise because of various benefits that they can offer such as: high peel strength, impact resistance, and improved fatigue behaviour [16,17]. Another important advantage is the more stable crack propagation, which can prevent sudden catastrophic joint failure. This permits that damaged adhesive joints can be identified and repaired before total failure, which is a critical point in terms of safety in the automotive industry.

2.1.2. TEPs

Expancel 031 DU 40 particles supplied by Expancel Nobel Industries (Sweden) were selected. The diameter of these particles ranges mainly from 10 μm to 16 μm. The dimensions of the particles before and after expansion were verified through a SEM analysis (see Fig. 2). Data provided by the manufacturer is given in Table 1.

2.1.3. Substrates

Hard tool steel DIN 40CrMnMo7 substrates were used for the DCB specimens, in order to assure an elastic behaviour of the adherends. The mechanical properties of the tool steel DIN 40CrMnMo7 are given in Table 2 (data provided by supplier).

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