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Surface modification of thermally expandable microspheres for enhanced performance of disbondable adhesive

Yuchen Lu*, James Broughton, Pat Winfield

Oxford Brookes University, UK

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ABSTRACT

This research successfully improved the compatibility between thermally expandable microspheres (TEMs) and an adhesive system for enhanced performance. TEMs were grafted with poly(glycidyl methacrylate) (PGMA) chains via atom transfer radical polymerisation (ATRP) with activators regenerated by electron transfer (ARGET) or ARGET ATRP technique. The temperature effect on the surface modification of TEMs was investigated for an optimum modification condition. Compared to adhesive incorporating unmodified TEMs, up to 15.8% increase in tensile lap shear strength and 24.0% increase in ultimate tensile strength (UTS) were achieved. Most notably, after environmental conditioning, the UTS of the adhesive system containing modified TEMs was 8.0% higher than the strength of unmodified TEMs before environmental conditioning.

1. Introduction

End-of-life vehicle (ELV) legislations and recycling issues for future multi-material vehicles necessitate the development of new joining solutions that enable rapid disassembly for automotive vehicle maintenance or recycling scenarios [1]. In the search for a disbondable adhesive system suitable for automotive applications, an adhesive system containing thermally expandable microspheres (TEMs) has been identified as one of the most promising approaches with satisfactory disbonding performance observed in previous research conducted within the Joining Technology Research Centre (JTRC) at Oxford Brookes University [2]. TEMs are micron scaled spherical particles comprised of a thermoplastic shell material (2–15 μm thickness) and an encapsulated hydrocarbon core which has a low boiling temperature. At elevated temperature, shell softening and hydrocarbon gasification allows TEMs to expand 30–80 times in volume, which can lead to fracture of the adhesive bond line.

The major limitation of the TEMs approach is the poor compatibility between the TEMs and the adhesive which weakens the mechanical properties and long term durability of the original adhesive system [1,3]. A suitable surface modification technique was selected to especially improve the TEMs/adhesive compatibility while retaining satisfactory in-service disbonding effectiveness. Surface grafting technology is a successful means of producing strong covalent bonds between TEMs and adhesive matrix. 'Grafting to' and 'grafting from' are two common approaches [4]. In the 'grafting to' approach, end-functionalised groups (e.g. hydroxyls, epoxides and thiols) react with a suitable surface to form a covalent bond. However, limitations such as low grafting density or difficulties in the synthesis of suitable functionalised polymers restrict its application. The 'grafting from' approach, in which polymer chains grow from the flat/spherical surface (Surface Initiated Polymerisation 'SIP'), shows wider applicability. Atom transfer radical polymerisation (ATRP) has been demonstrated as a successful SIP technique in various areas including cell adhesion [5,6], drug release [7], anti-biocorrosion coatings [8], and silicon wafers [9].

First discovered in 1995 [10,11], ATRP provides a simple and controlled polymerisation solution with good control of molecular weight, structure and a high degree of chain end functionality. ATRP with activators regenerated by electron transfer or ARGET ATRP offers two major advantages over conventional ATRP technique: a) only ppm amount of catalyst is required which makes the purification or disposal process of toxic components cheaper or sometimes unnecessary, especially for industrial application [12]; b) a higher tolerance to oxygen and a catalyst that can be added in oxidatively stable state [13].

Inspired by the pioneering study conducted by Jonsson and coworkers [14], this study investigated TEMs that were modified by growing poly(glycidyl methacrylate) (PGMA) chains from the surface of TEMs via the ARGET ATRP process. Since each GMA

* Correspondence to: Department of Mechanical Engineering and Mathematical Sciences (MEMS), Oxford Brookes University, Wheatley Campus, Wheatley, Oxford OX33 1HX, UK. Tel.: +44 1865 483 568.
E-mail address: yuchen.lu2015@outlook.com (Y. Lu).

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molecule contains one epoxide group, PGMA chains contain an amount of n epoxide groups (n denotes the degree of polymerisation). Modified TEMs containing epoxide groups can react with the hardeners during the curing process of epoxy adhesive forming covalent bonds and thereby strengthening the TEMs/adhesive composite.

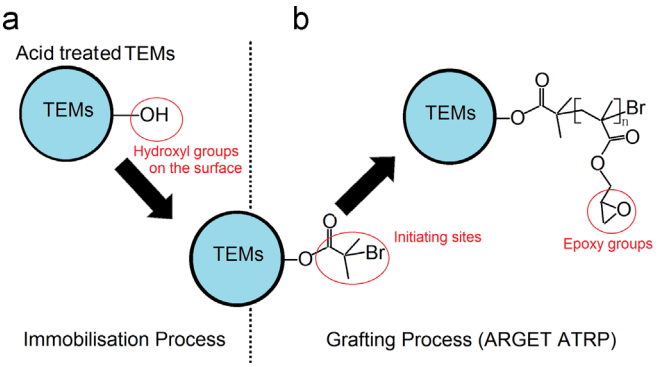

Fig. 1. Schematic illustration of TEMs surface modification process.

Table 1
Chemicals used during immobilisation process.

Chemical name	Function	Quantities	Supplier/grade
Acid treated TEMs	N/A	5 g	N/A
Triethylamine	Reducing agent	5 g	Sigma-Aldrich (≥ 99%)
4DMAP	Catalyst	12.6 mg	Sigma-Aldrich (≥ 99%)
BIBB	ATRP initiator	11 g	Sigma-Aldrich (98%)
Dichloromethane	Solvent	50 ml	Fisher Scientific (≥ 99%)

Table 2
Chemicals used during grafting process.

Chemical name	Function	Quantities	Supplier grade
Immobilised TEMs	Macroinitiator	3 g	N/A
Toluene	Solvent	30 ml	Sigma-Aldrich (98%)
$CuBr_2$	Catalyst	2.52 mg	Sigma-Aldrich (99%)
GMA	Grafting monomer	32.4 g	Sigma-Aldrich (97%)
PMDETA	ATRP Ligand	47.1 mg	Sigma-Aldrich (99%)
L-Ascorbic acid	Reducing agent	50 mg	Sigma-Aldrich (≥ 99%)

2. Experimental test programme

The experimental test programme was divided into three stages: a) surface modification of TEMs; b) investigation of disbonding performance of TEMs/adhesive joints; c) investigation of bulk properties of TEMs/adhesive composite.

2.1. Materials

In this research, 920DU120HEMA grade of TEMs which contains 15 wt% 2-hydroxyethyl methacrylate on the thermoplastic shell material, were kindly provided by Expancel Akzo Nobel. The particle size distribution ranges from 28 to 38 μm. This grade of TEMs starts to expand at around 125 °C and reaches the maximum expansion at around 190 °C [14]. 3M Scotch-Weld 9323, a two component amine cured epoxy adhesive typically used in automotive structural applications, was chosen as the adhesive matrix. This is a standard high strength structural adhesive with a tensile lap shear strength of 30 MPa and high environmental resistance. Information about all other chemicals used in this research was detailed in Section 2.2.

2.2. Experimental procedures

TEMs were modified at different conditions and incorporated into adhesive system for the investigation of disbonding performance and mechanical properties.

2.2.1. Surface modification of TEMs

This surface modification approach is an adaptation of the recent research conducted by Jonsson and co-workers [14]. The whole process was mainly divided into two steps, as illustrated in Fig. 1.

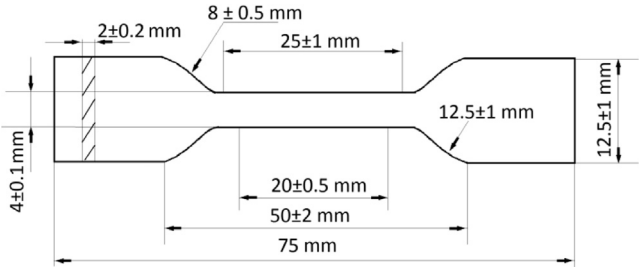

Fig. 3. Illustration of adhesive tensile bar specimen.

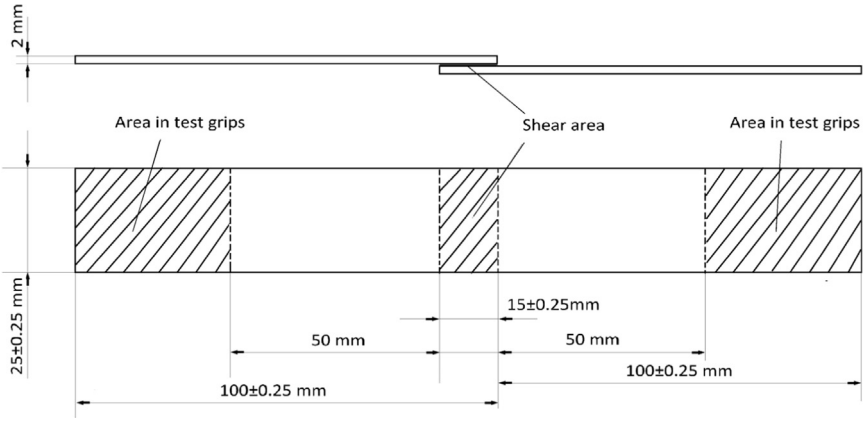

Fig. 2. Dimensions of single-lap-joint specimen.