Macromolecular Symposia
www.ms-journal.de

BMI-Based Coupling Agent to Improve Adhesion in Self-Healing Composites

*Stefania Dello Iacono, Eugenio Amendola, and Alfonso Martone**

Recently, the availability of thermo-reversible epoxies is interesting for research and industry due to its implication in the implementation of the next generation of advanced materials. However, fiber-reinforced composites made with self-healing epoxies have lower performances than commercial products. Therefore, the availability of a suitable treatment to improve the adhesion between fiber and matrix will compensate the lack of performances experienced in thermo-reversible composites. Here, a route for decorating dry commercial preform with bismaleimide (BMI) is presented in order to promote the adhesion between matrix and reinforcement. The grafting of BMI on the glass support is measured by means of contact angle. The interfacial strength between fiber and resin is measured by micro-droplet pull-out test. The BMI-based coupling agent leads to a 92% increase in interfacial strength for a self-healing system.

1. Introduction

The interphase plays a key role in determining the mechanical interfacial properties, supporting the transfer of stress between the matrix and the reinforcement and attenuating the mismatch of the mechanical properties between the matrix and the reinforcing fibers. Marked differences in mechanical properties lead to stress concentrations, with the consequent micro-cracks formation and propagation up to failure.[1,2] Preventing or repairing interphase damage could be a new strategy for the design of high-performance composites. In recent years, many research groups have focused on the development of new self-healing neat resin, and on their multiple recovery mechanism.[3–5] However, FRP composites based on intrinsic self-healing epoxy can only recover the damages related to the cohesive failure of hosting matrix[6]: the delamination between matrix and reinforcement would not benefit from the reversible reaction to restore the pristine condition, due to the lack of reversible functional groups grafted onto the fibers. A comprehensive approach would combine intrinsic healing of the hosting matrix with the reversible Diels–Alder reaction to the interface between suitable functionalized reinforcements and thermoset matrix,[7–9] to promote a mixed-mode recovery strategy for cohesive failures within the hosting matrix and adhesive at the interfaces between polymer and reinforcement.[10] In this paper a coupling based on Diels–Alder chemistry, carrying reversible bonds compliant to a self-healing epoxy, previously synthetized by the author, has been developed and experimentally characterized. With the aim of introducing at the interface the same pendant D–A dienophile present in the matrix, in this paper, the glass fiber was first activated with an aminosilane and then reacted with bismaleimide (BMI) through Michael's addition reaction. The sizing proved to be effective for self-healing epoxy systems.

S. D. Iacono, E. Amendola, A. Martone
National Research Council
Institute for Polymers
Composites and Biomaterials
P.le Enrico Fermi 1, 80055 Portici (NA), Italy
E-mail: alfonso.martone@cnr.it

DOI: 10.1002/masy.201900107

2. Results and Discussion

The study of surface energy by measuring the contact angle is one of the most used methods to evaluate the wettability of solid fibers and propensity to bind with the matrix. Nonetheless, contact angles on fibers cannot directly be measured due to geometrical constraints. In the case of glass reinforcement, surface interactions can be evaluated using a plane model geometry. Owens and Wendt[12] hypothesized that the total surface tension could be expressed as the sum of two surface tension components, each of which is derived from a specific type of interaction: the dispersive surface tension component γ^d, and the polar one γ^p, related to hydrogen and dipole–dipole bonding. Assuming that the solid surface tension is constant for a solid surface, the value of the experimental contact angle, in combination with Young's equation, determines the solid surface tensions. The plain glass surface and its amino-functionalized and BMI-decorated analogues are compared in **Table 1**, where the contact angles of water and diiodomethane are reported, as well as the polar, dispersive, and total surface tensions. The results confirm the modification of the surface after the aminosilane and the following BMI treatments: both surface treatments induce a similar reduction in total surface tension, with an increase in the wettability.

Therefore, the further BMI treatment is effective in modifying the nature of chemical interactions with the cross-linking resin, favoring reversible interactions through the Diels–Alder reaction.

2.1. Characterization of Interfacial Debonding and Fiber Pull Out

The micro-droplet pull-out test consists in dabbing a small amount of liquid resin on to the fiber surface. After the resin

 © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1. Water and diiodomethane contact angles and surface energy parameters.

Owens–Wendt method	Water [degree]	Diiodomethane [degree]	Superficial free energy [mJ m^{-2}]		
			γ_S^p	γ_S^d	γ
Plain glass	49.16	52.70	28.68	22.00	50.68
NH_2-functionalized glass	72.50	57.00	12.18	22.85	35.03
BMI grafted glass	88.66	45.20	2.23	32.01	34.24

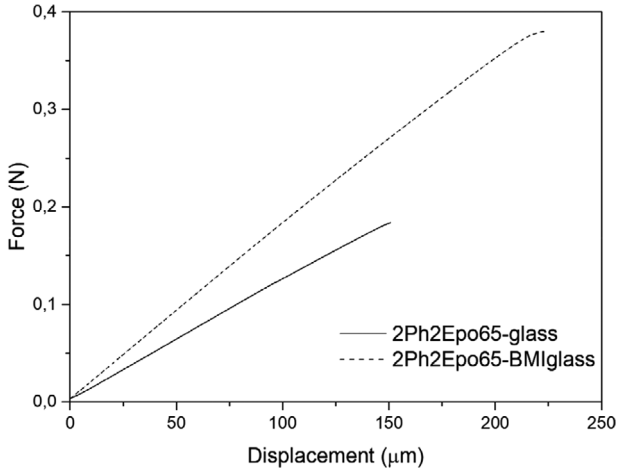

Figure 1. IFSS of 2Ph2Epo65 on glass fiber.

droplets are cured, they form concentric elliptical micro-droplets around the fiber. The fiber specimen is suspended at a load cell of a mechanical testing machine. The shearing force at the interface is transferred to the fiber through the fiber–matrix interfacial bond and is recorded by the load cell. The interfacial shear strength (IFSS) between glass fiber and epoxy matrix can be calculated according to Equation (1).

$$\tau_i = \frac{F}{(\pi DL)} \quad (1)$$

where F is the maximum fiber axial force recorded at the onset of micro-droplet debonding, D is the fiber diameter, L is the embedded fiber length, and πDL is the embedded area.

The appropriate size range of the micro-drops was selected in order to avoid fiber breakage due to excessive load transfer: the embedding length is limited to the range 100–150 μm. Tests were carried out on self-healing epoxy, namely 2Ph2Epo65, dropped on pristine fiber and fiber with BMI coupling agent. **Figure 1** reproduces the load versus displacement curves. The resin deposited onto bare fibers exhibited a weak strength (38.6 MPa); the developed coupling agent led to strengthening the interface and therefore the overall stiffness of the system (74.4 MPa).

The debonding that occurred during the test at the interface between fiber and matrix was investigated by optical microscopy (**Figure 2**) in bright field and polarized light, before (2a, 2a′) and after (2b, 2b′) the test. Polarized light microscopy shows residual stresses related to the polymerization stages (Figure 2a′), while the image taken after the test shows the complete release of shear stresses and the loss of chemical bonding (Figure 2b′).

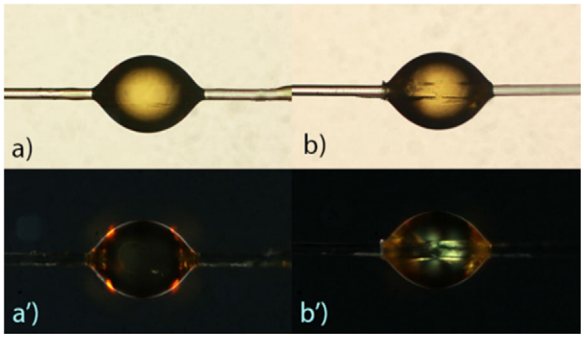

Figure 2. Resin drops onto fiber (20× magnification), in bright and polarized light, respectively, before (a,a′) and after the mechanical test (b,b′).

3. Conclusion

Thermo-reversible polymers developed in recent years have achieved good damage recovery efficiency; however, a more comprehensive approach is required for fiber-reinforced composites. In this context, the development of a smart interface would be capable of recovering delaminations and debonding by exploiting Diels–Alder bonds present in the resin bulk and at fiber interface. Here, a methodology has been implemented for the functionalization of commercial dry preform. The micro-droplet pull-out test performed on 2Ph2Epo65 self-healing resin revealed a 92% increase in IFSS. Additional tests will be carried out to verify the healing capability at the interface.

4. Experimental Section

Materials: The reagents and solvents 3-aminopropyltriethoxysilane (APTES), ethanol, and 1,1-methylenedi-4,1phenylene-BMI, furfuryl glycidyl ether, chloroform, *O*,*O*-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeff 500), 4,4'-diaminodiphenylmethane, and acetonitrile were purchased from Sigma-Aldrich and was used without further purification; diglycidyl ether of bisphenol-A (DGEBA) was provided by Elantas. The self-healing epoxy 2Ph2Epo65, was prepared according to the procedure previously developed by the authors.[4,11]

Coupling Agent Synthesis and Deposition Route: In order to promote reversible bonding at the interface between polymer and substrate, a two-step route was carried out to graft BMI onto the surface. The amino functionalization was performed through an immersion in a solution of 1% w/w APTES in ethanol and water (25:75 by weight ratio)[9] at boiling temperature for 2 h and that allowed the introduction of the primary amino group. The further BMI grafting was carried out by an immersion of substrates in *N*,*N*-dimethylformamide solution with 5% w/w of BMI at 80 °C for 2 h led to Michael addition of BMI onto surfaces.

© 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Experimental Characterization: The contact angle was measured by sessile-drop technique using Dataphysics OCA-20: water and di-iodomethane drops (1 μL) were dispensed at rate of 0.5 μL s^{-1}. The glass fibers, extracted from commercial dry preform for composite, supplied by GURIT, were prepared following the same protocol described for flat glass substrates. Resin droplets were dispensed on individual glass fibers and cure at 90 °C for 24 h before testing. Optical microscopy was carried out, before and after the mechanical test, by means of optical microscope Olympus BX 51. The images were captured with a 20× magnification in bright field and polarized light. Micro-droplets single fiber pull-out tests were carried out using a TA instrument thermo-mechanical analyzer TMA 2940 at rt, applying a linear force increase of 0.1 N min^{-1}.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

Diels–Alder, interphase, self-healing

[1] B. Aïssa, D. Therriault, E. Haddad, W. Jamroz, *Adv. Mater. Sci. Eng.* **2012**, *2012*.
[2] G.-P. M. Fierro, F. Pinto, S. Dello Iacono, A. Martone, E. Amendola, M. Meo, *Smart Mater. Struct.* **2017**, *26*, 115015.
[3] Y.-L. Liu, T.-W. Chuo, *Polym. Chem.* **2013**, *4*, 2194.
[4] S. Dello Iacono, A. Martone, A. Pastore, G. Filippone, D. Acierno, M. Zarrelli, M. Giordano, E. Amendola, *Polym. Eng. Sci.* **2017**, *57*, 674.
[5] A. Gandini, *Prog. Polym. Sci.* **2013**, *38*, 1.
[6] J. S. Park, T. Darlington, A. F. Starr, K. Takahashi, J. Riendeau, H. T. Hahn, *Compos. Sci. Technol.* **2010**, *70*, 2154.
[7] B. Gacal, H. Durmaz, M. A. Tasdelen, G. Hizal, U. Tunca, Y. Yagci, A. L. Demirel, *Macromolecules* **2006**, *39*, 5330.
[8] A. S. D. Wang, *Compos. Mater. Ser.* **1989**, *5*, 69.
[9] A. M. Peterson, R. E. Jensen, G. R. Palmese, *Compos. Sci. Technol.* **2011**, *71*, 586.
[10] A. Martone, S. Dello Iacono, S. Xiao, F. Xu, E. Amendola, *AIP Conf. Proc.* **2018**, *1981*, 020046.
[11] E. Amendola, S. Dello Iacono, A. Pastore, M. Curcio, M. Giordano, A. Iadonisi, S. Dello Iacono, A. Pastore, M. Curcio, A. Iadonisi, *J. Mater. Sci. Chem. Eng.* **2015**, *03*, 162.
[12] D. K. Owens, R. C. Wendt, *J. Appl. Polym. Sci.* **1969**, *13*, 1741.

© 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim