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Measuring of fiber/matrix adhesion in thermoplastic polymer composites: A preliminary study

Bálint MORLIN[1, 2 a], Tibor CZIGÁNY[1, 2 b]

[1] Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Muegyetem rkp. 3, Budapest 1111, Hungary

[2] MTA–BME Research Group for Composite Science and Technology, Muegyetem rkp. 3, Budapest 1111, Hungary

[a]morlin@pt.bme.hu (corresponding author), [b]czigany@eik.bme.hu

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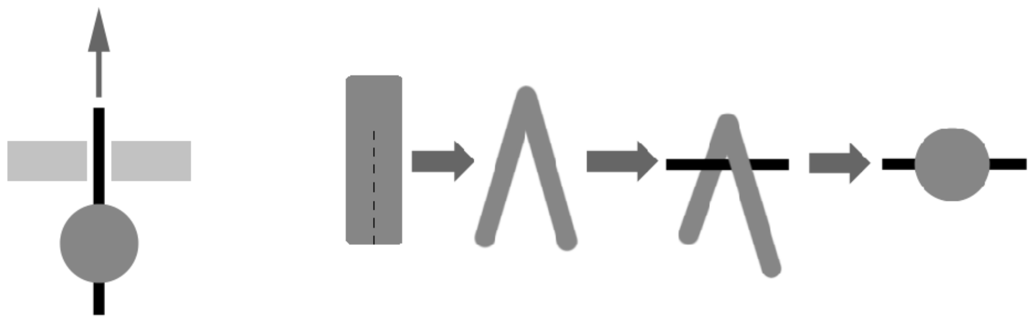
Abstract. The possibilities of the application of microbond test and cylinder tests for determining the interfacial shear strength at the fiber-matrix interface in thermoplastic matrix polymer composites were investigated. Possibilities of test specimen preparation were also investigated. Finally the applicability of the method to make high precision measurement of interfacial shear strength was evaluated.

Introduction

Fiber reinforced polymer composites can be found nowadays everywhere in practically all niches of life. This exceptionally important role is due to their controllable anisotropy, high strength and low density. The reason for these properties lays in the high strength of the fibers and toughness of the matrix, as well as the excellent adhesion between them, ensuring proper cooperation between the phases. In order to qualify and design composite structures the knowledge of adhesion relations is of primary importance, especially in short fiber reinforced (e.g. injection molded) systems. The application of the so-called microbond (or microdroplet) test is very good for this purpose (Fig. 1.a). Several tests were performed to qualify reinforced thermoplastic materials and to develop the most suitable sample preparation method [1-7]. When preparing the test specimens the first step is the application of the matrix onto the reinforcing fiber, for which several possibilities are available: for example fibers are made of the thermoplastic and a knot is placed onto the fiber, or a slit piece of polymer film is placed onto the fiber (see Fig. 1.b). In the next step the matrix is melted in order to form the interfacial interaction and the droplet. In course of the test specimen preparation it is of decisive importance that the matrix solidifies symmetrically, possibly in nearly perfect spherical shape with homogeneous material properties. The next step is the microscopic investigation of the test samples in order to eliminate specimens unfitting for tests because of shape deformity or size probblems and to determine size parameters necessary for evaluation (fiber diameter, embedded length etc.).



a) b)

Fig 1. Scheme of the microbond test (a), and sample preparation according to the literature [7] (b)

The droplet size is very important with respect to the test results. The lower limit of the diameter (D) is the size which can be still practically applied onto the fiber, but it influences the stress state in the droplet, therefore the resulting shear strength value. Much more important, direct role is played by the embedded length (L). The maximum value of this parameter is determined by the tensile strength of the fiber. It should be lower than the critical failure length as if it not true, the fiber will break and the test will be unsuccessful. The goal is the achievement of the technically possible shortest length. For testing the prepared reinforcing fiber is first clamped into the test equipment, the blades used to remove the droplet are adjusted according to the size of the droplet so that they just touch the surface of the droplet, then the test is performed usually by pulling out the fiber. As a last step the data obtained are processed by one of the many available mathematical models [8]. The disadvantage of the results obtained is that their scattering, i.e. the uncertainty of the test is high – due to the relatively ill-defined droplet shape and to the widely varying geometrical parameters.

In our earlier works [9, 10] cylinder test developed form the microbond test has been introduced (Fig. 2.), which is devoid of the aforementioned disadvantages, the advantages and disadvantages of this method have been so far tested by thermoset matrices.

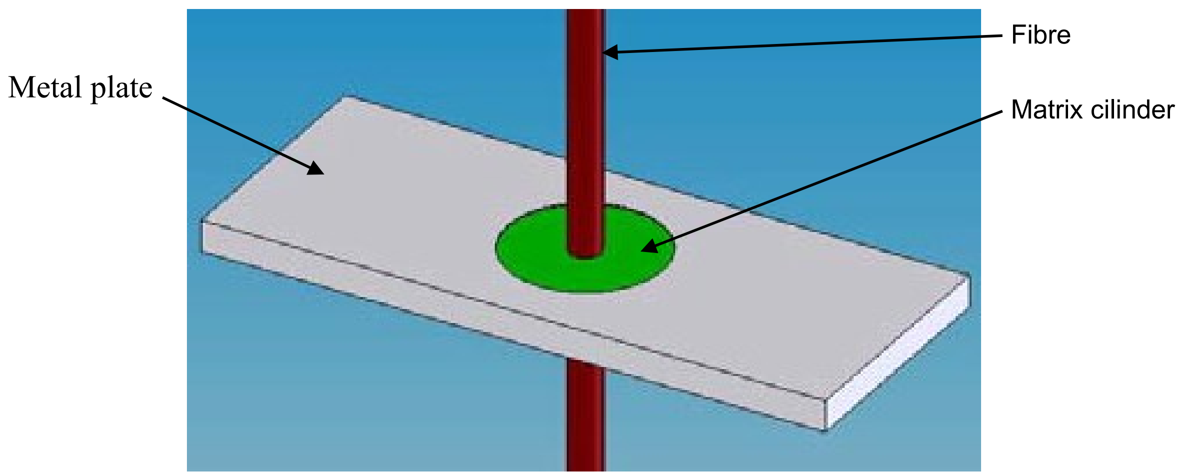


Fig. 2. Test sample of the cylinder test

The essence of this method is the single fiber embedded centrally in a borehole prepared in a metal sheet, which provides favorable conditions for load transfer between the fiber and the matrix. When preparing the test specimen the sheet is fixed by fork shape part of a special instrument which ensures simultaneously the proper centeredness and concentric position. When performing the test the sheet is fixed and the fiber can be pulled out by a tensile tester, based on the geometrical size and the recorded force the interfacial shear strength can be reliably calculated using the simplest methods used so far (Eq. 1):

$$\tau = \frac{F}{\pi * d_f * L}. \qquad (1)$$

where τ is the interfacial shear strength, F is the pull-out force, d_f is the fiber diameter, L is the embedded length. The advantage of the method is the high precision which can be explained by the concentric and uniaxial positioning of the fiber and the matrix cylinder, i.e. by the simple, circularly symmetric stress state, and by the elimination of the effect of variable size of the test specimens. Repeatability also improves and the dependence on operator and sample preparation skills decreases. All this greatly improves the reliability of the tests. A droplet (cylinder) placement method was designed and built for this purpose.
The goal of this article is to apply the method proven for thermosets also for thermoplastic matrices, in comparison to the traditional microbond test.

Materials and Methods

The matrix used is Copolyester GN071, Natural PET-G of Eastar (processing temperature 249-271°C). The reinforcing fiber is RT310 0001 100 glass fiber of Saint-Gobain.

Preparation of thermoplastic specimens

Microbond test: The fiber to be tested was always glued onto a paper test window. According to our experience the methods described in the literature are not expedient, e.g. certain parts of the thin polymer films become easily burnt while at other places the material does not even melt, therefore the shape and material properties of the droplets will not be uniform, which precludes exact measurements. Preparing knots from matrix material fibers yields good results but it requires high concentration on the part of the operator and there are several possibilities of error [7]. We used the following method for microbond tests: matrix was applied from a matrix melted on a heated plate. From the melted pellets a fiber was formed on the tip of a needle, and before it was frozen the matrix fiber was bent over the reinforcing fiber placed into the test window. The amount of the applied resin could be regulated by the thickness of the matrix fiber. One can prepare even very small droplets this way, sometimes so small that they could not be clamped during the droplet removal. After some practice it can be achieved that the thermoplastic fiber does not cool down exceedingly and adheres to the reinforcing fiber and there is no need for further attachment procedure. Fig. 3 shows the process of droplet application used by us.

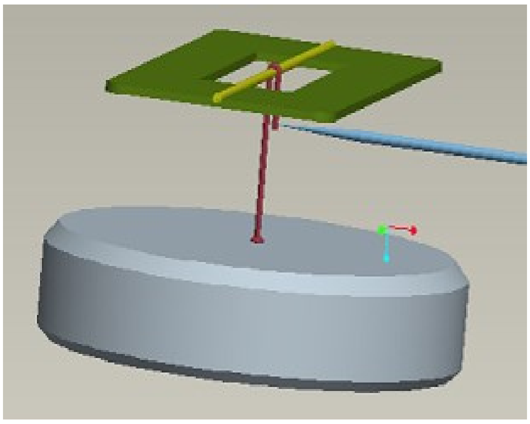
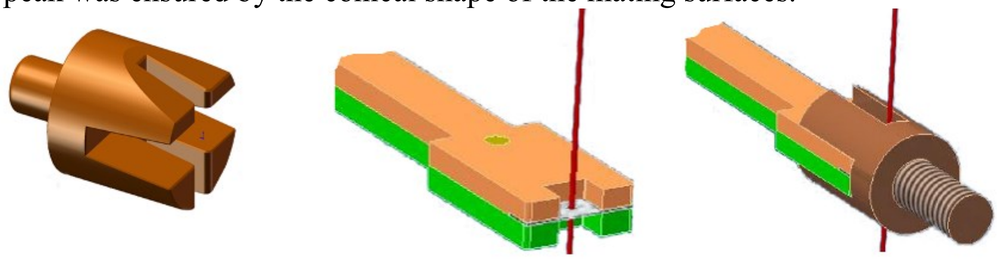


Fig 3. The method used by us for droplet application

Cylinder test: In the cylinder test the thermoplastic material should fill in the narrow gap between the reinforcing fiber and the adjacent wall of the concentric borehole. For this a fairly low melt

viscosity is needed. In order to achieve this, a proper temperature should be reached as soon as possible in a small area to avoid heat losses. Another important requirement is the exact maintenance of the set temperature to avoid the degradation of the material at excessive temperatures.
Taking into account these requirements a soldering iron of SOLDER01 type with controllable temperature was modified and used. The head of the solder iron is exchangeable (with screw) and a properly shaped copper heating element was placed here (Fig. 4/a). When applying the droplet the fork holding the sheet with the borehole fits well the wall of the heating element because of their conical shape, therefore the heat transfer is good. The fiber is placed in the central vertical groove. In order to prepare the test specimens a version of the forks fitting the shape of the heating element was also necessary. This consisted of two copper sheets, the sheet with the borehole was fixed by a screw pressing the two halves together (Fig. 4/b and c). The proper fitting between the fork and the solder iron peak was ensured by the conical shape of the mating surfaces.



a) b) c)

Fig. 4. The heating element (a) used to prepare the test samples in the thermoplastic cylinder test, the corresponding fork (b) and its application (c)

The preparation of the test specimens is only a little bit modified as compared to those of thermoset samples: the sheet with the borehole was fixed in the fork, then the reinforcing fiber in inserted and centered. The heating element was screwed onto the controllable soldering iron and the necessary temperature was set (according to the controller of the soldering iron between 350 and 400 °C, depending on the material). Thereafter a proper amount of the matrix to be applied is placed near the fiber onto the sheet and finally (while taking care of the fiber) the soldering iron is pressed to the fork. After a proper time (usually 20-30 seconds) the matrix melts and fills the borehole. Of course the temperature of the sheet (due to the limitations of heat transport) is much lower than that of the soldering iron and was enough only for the melting of the matrix. For this reason and because of the short dwelling time the degradation of the polymer is improbable. Then the soldering iron is removed and the ready specimen is removed from the droplet application equipment similarly as before. This method yields acceptable results in the case of certain low viscosity matrices (as e.g. CBT).

Thermoplastic polymer matrices usually exhibit too high viscosity to fill the borehole from the surface of the sheet without external pressure. If a polymer pellet is placed onto a heated plate and is melted, then the sheet with the borehole is pressed onto it, the melt usually fills completely the borehole. Afterwards on one side of the sheet the excess matrix is removed down to the surface of the sheet and the matrix cylinder is drilled with a borer of 0.15 mm diameter. The position of the borehole can be checked by microscopy. Thereafter the sheet is fixed into the fork and placed into the droplet application equipment and so the reinforcing fiber can be inserted into the borehole of the matrix. Finally the sheet is heated up by the solder iron, under the effect of heat the drilled matrix cylinder melts and fills in the borehole of the sheet, but this time it contains the inserted reinforcing fiber. The drilled volume is replaced by the material remaining on the surface of the sheet, no material shortage was observed (Fig. 5.). Finally the side ensuring the excess material is planed to the sheet surface before the droplet removal, so the reinforcing fiber is surrounded only the matrix cylinder with a thickness identical to that of the metal sheet.

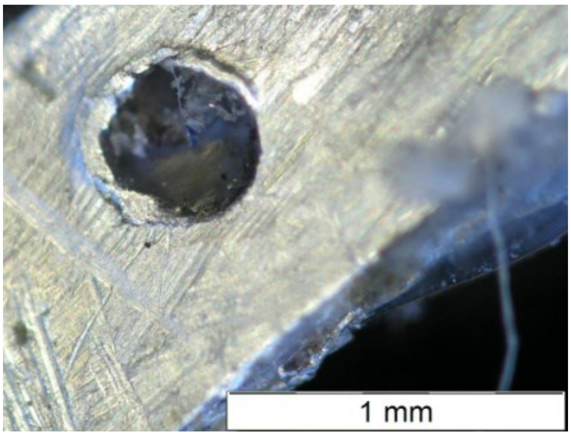


Fig. 5. Micrograph of the test specimen used in the cylinder test

Results and Discussion

The test results are shown in Table 1. The relative scattering calculated as a ratio of the scattering of the measured values and the shear stresses is much lower than in the case of the paper-window method, i.e. the reliability of the test improved considerably also for thermoplastic materials, due to the uniform size and shape used in the cylinder test. Earlier, in the case of thermoset matrices the cylinder test yielded 7-14% relative scattering [11], which can be explained by the simpler test specimen preparation. It is conspicuous, however, that about 50% lower shear stresses were obtained using this method, as compared to the microbond test. This is probably due to the large temperature difference and to the consequent heat expansion. The matrix initially fills out the borehole but it is conceivable that during the second heating-cooling cycle microcracks appear in the matrix, which may lead to a reduced adhesion. According to our microscopic observations these are microscopic in size or do not even reach the surface of the material (see Fig. 5.). The slight worsening of the relative scattering with respect to those of thermosets may also be explained by the aforementioned cracks.

Method	d_{fiber} [μm]	D [μm]	L [μm]	τ [MPa]	Relative scattering
Microbond test	13.19±1.41	61,3±13,7	93.89±16,88	24.92±7.38	29.65%
Cylinder test	12.94±0,87	400	200	12.43±2.37	19.03%

Table 1. Results obtained on glass fiber - PETG material pair

Based on our results, therefore, a further development of cylinder method seems necessary to determine exactly the fiber/matrix interfacial properties in thermoplastic matrix systems. This may prove to be useful taking into account the special technological characteristics of processing (e.g. high pressures and fast cooling during injection molding, etc.) as the molecular structure evolving in the matrix around the fiber influences considerably the interfacial shear strength.

Conclusions

Methods of using the cylinder test and the microbond test and the methods of sample preparation were investigated for determining the interfacial shear strength of the fiber/matrix interface in composites with thermoplastic matrices. We proposed a new method for preparing test samples for the microbond test and performed experiments to apply the cylinder test to high viscosity, thermoplastic materials. We concluded that it is possible to prepare cylindrical test specimens amenable to testing even form these materials. Their usefulness is, however, limited to deter mine the interfacial hear strength with high precision as, in spite of the more advantageous stress sate the measured shear strength values are smaller than those measured in the traditional microbond test, presumably due to the microcracks developing because of the thermal expansion of the test specimen.

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