The Influence of Oxidative-Thermal Degradation of Polypropylene on Measured Interface Strength of Glass Fibre-Polypropylene

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Abstract

It was previously found that thermal-oxidative degradation of the polypropylene could significantly affect the measured interfacial strength of glass fibre reinforced polypropylene (GF-PP) micro-composite. In this work, different approaches have been employed to justify this influence. Hot-stage microscopy was used to establish a degradation profile of PP microdroplets that had different initial dimensions and results revealed that the reduction in droplet dimensions was affected by not only its initial droplet size and but also the presence of the fibre in the droplet. The Young's moduli of PP microdroplets with different heat treatments were examined by using nanoindentation technique and the results showed that there was significant stiffness deterioration in degraded samples and the severity is also related to the droplet size for a given heat treatment. Comparison of adhesion for GF-PP was also made between degraded and non-degraded samples. It shows that non-degraded samples give much higher values for interface strength of GF-PP than degraded ones

1. Introduction

The interfacial properties of glass fibre reinforced polypropylene (GF-PP) have been studied for decades [1][2], due to the crucial role that the interface tends to play in the control of overall composite properties. A great deal of interest has been drawn into research and development activities that focus on enhancement of the adhesion [1-4] and investigation of interfacial morphology [5], due to the inherently poor chemical interactions between these two constituents and the ability of PP to crystallise. In contrast, effect of thermal degradation of PP on the interface has received much less attention, probably because degradation of PP has no longer seemed to be a major concern in commercial composite manufacturing after the addition of a package of stabilisers. Notwithstanding this, the sound academic documentation desires adequate work done for some less studied aspects. In fact, stabilised PP still readily suffers from thermal-oxidative degradation at elevated temperature. This degradation may not give rise to severe consequence for bulk material under the usual processing conditions, since a very limited amount of air has access to the melt during the extrusion or moulding of PP [6]. However, it may not be the case when it comes to small composite samples that are usually fabricated in the presence of sufficient air and require just a little amount of PP, for instance, a pellet or PP fibre. This seems to be the exact scenario that have been seen during the sample preparation for direct adhesion measurement by single fibre pull-out test and its variant, microbond test. Currently there seems to be no overall consensus among these techniques and different laboratories tend to develop their own methods to carry out the adhesion

measurements [7]. Large scatter in the experimental results seems to be a common issue, which has been inhibiting the development of effective data reduction [8]. These disadvantages stem from the small inspection window in common micromechanical tests. Sampling just a little amount of material could mean increasing the effectiveness of some elements that are not considered to matter when dealing with the bulk material.

A direct attempt at evaluating the effect of thermal degradation of several thermoplastic polymers on the interface strength to a steel wire can be found in [9]. In this work, large samples of LLPE, HDPE, and PP were tested and the fabrication temperature was varied from 150°C to 220°C combined with the variation in fabrication time from 5 h to 24 h. It was concluded that both prolonged heating at low temperature and short periods of time at high temperature can reduce the strength of the adhesive joints to a certain extent. The question of why the thermal-oxidative degradation of a polymer leads to a reduction in adhesive strength was then raised. Since then, there has been not much follow up.

The present paper is a continuation of the early work [10] and the purpose of this paper is to provide direct evidence of oxidative-thermal degradation of PP during the sample preparation for both microbond and pull-out test and further reveal its effect on measured interface strength of GF-PP.

2. Experimental

2.1 Material

In order to minimise the complexity, choice of the materials was limited to uncoated glass fibre and homopolymer polypropylene. They were boron free uncoated E-glass fibres (Ave. diameter = 17.5μm) from Owens Corning and commercial isotactic homopolymer polypropylene (PP47: SABIC®PP 579S with melting flow index = 47 g/10 min at 230°C).

2.2 Hot stage microscopy

A transmitted light optical microscope equipped with a Mettle FP 82 hot stage was employed to visualise the formation of PP microdroplet on the glass fibre and the dimensional change of the droplet under the heat treatment was also measured. A single glass fibre was suspended slightly above a glass slide. A PP fibre was then deposited on the surface of the glass fibre. The sample was inserted into the hot stage, where it was heated rapidly from ambient temperature up to 220°C. Time started to be registered when the temperature reached 218°C. For those droplets whose formation had fully completed within the first 1 min, a series of photographs of the droplets were then taken at time interval of 30 sec for 60 min. The fibre embedded length and diameter of the PP droplet in each picture were then measured.

2.3 Nanoindentation test

The GF-PP microbond samples with PP microdroplets that had different initial dimensions were heated separately at 220°C under air for 4 min and 6 min respectively. The mechanical properties of these droplets were then measured by an Agilent Nano Indenter G200 equipped with the continuous stiffness measurement (CSM) technique. In the conventional nanoindentation test, the measurement of contact stiffness is made just at the point of unloading, whereas the CSM technique offers a direct measure of dynamic contact stiffness at any point during the loading portion of an indentation test by imposing a small sinusoidally

varying force, which is added to the nominally increasing load, on the indenter. The force oscillation and the relevant displacement response of the indenter allow Young's modulus of the resin droplet to be continuously probed as a function of indentation depth. Details about this technique and its applications can be found in [11]. In this work, the microbond samples were first secured on a highly stiff substrate. The specimen was then placed into the indenter and the top area of each droplet was located as the testing field. The indentation test was conducted with maximum indentation depth and spacing division set to 1μm and 20 μm respectively throughout all the samples. Figure 1 shows a typical plot of the continuously measured Young's modulus of the sample against the indentation depth.
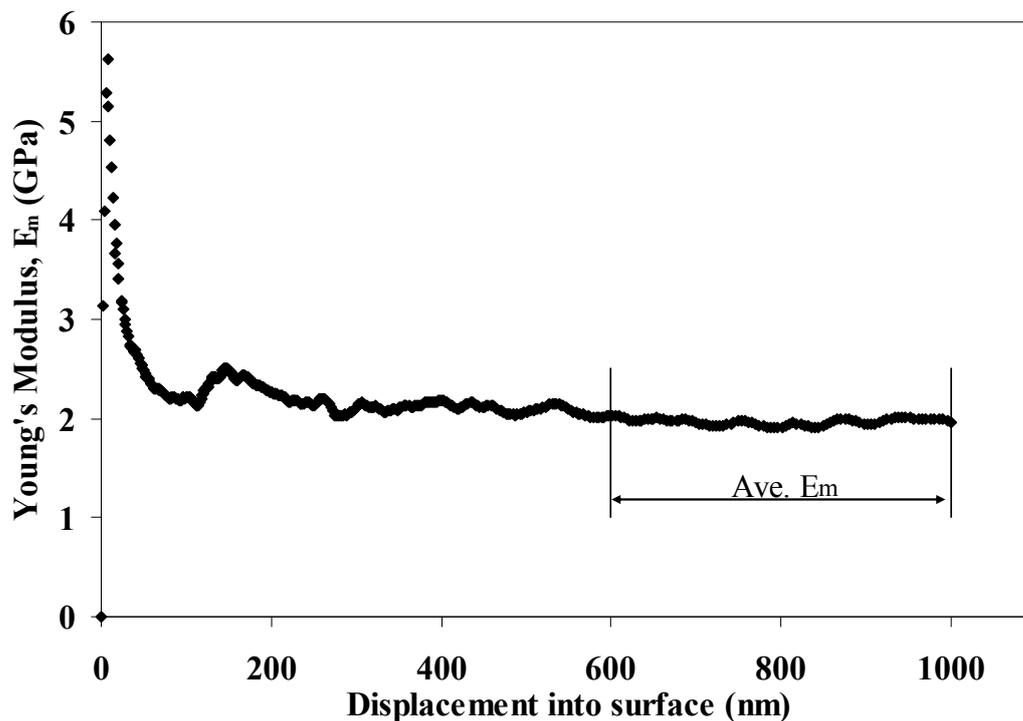
Figure 1. Young's modulus continuously measured as a function of indentation depth for one of PP mirodroplets.

Complexity could arise from curved surface of PP microdroplets and nonhomogeneity in their mechanical properties from the surface to the core. Therefore, the individual values in the defined depth range from 600 μm to 1000 μm were chosen to calculate the mean Young's modulus as shown in Figure 1. At least 9 measurements were carried out on each PP microdroplet to obtain average Young's modulus.

2.4 Single fibre composites

In this work, the interfacial shear strength (IFSS) was measured by both laboratory-developed microbond and single fibre pull-out techniques. The specific procedure to form a PP microdroplet on a glass fibre and details for the microbond test can be found in [10]. In the present work, the formation of PP microdroplets for the microbond test was carried out under the nitrogen to avoid oxidative-thermal degradation of PP. In order to have non-degraded samples for single fibre pull-out test, the method schematically illustrated in Figure 2 was adopted to make pull-out samples.
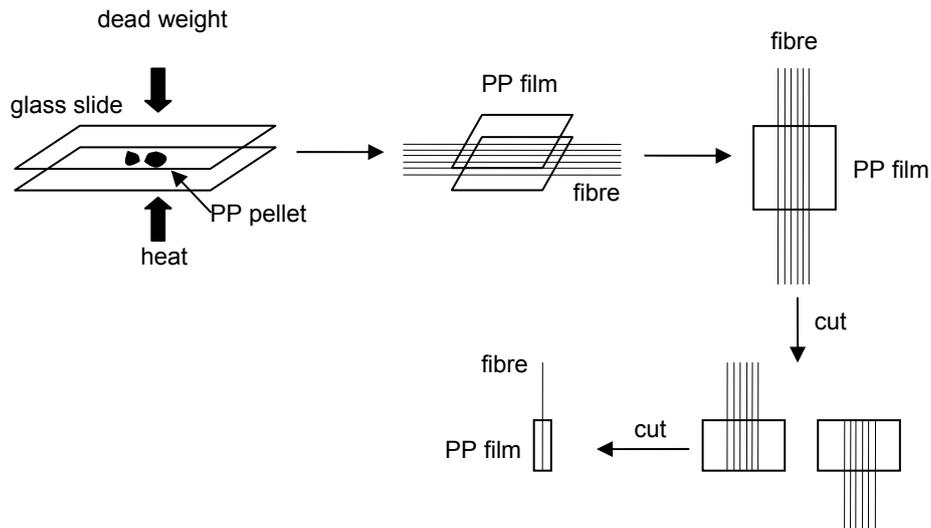
Figure 2. Procedure to make single fibre sample for modified single fibre pull-out test.

A PP47 film with thickness of about 100 μm was first made on a hot plate at 230°C by having two PP pellets sandwiched between two glass slides and pressed by preheated 5 Kg weights for 1 min. A film cutter with 2 parallel blades 13.5 mm apart was used to cut the film into a square shape. 12 fibres were then placed between two of these films parallel to each other and perpendicular to the film edges. The sample was then heated in a Mettler FP82 hot stage at 220°C for 4 min. After air cooling at ambient temperature, the sample was cut in the middle to produce 24 individual pull-out samples. Both microbond and modified pull-out test were conducted in the same experimental setup as shown in Figure 3.
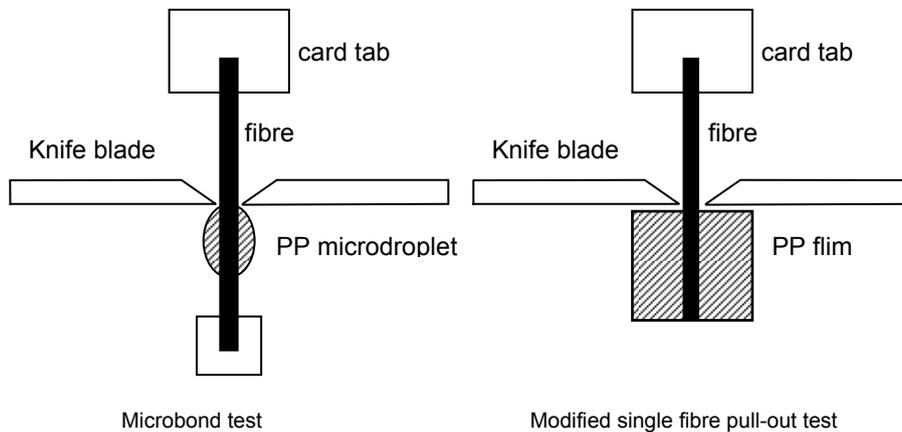
Figure 3. Schematic illustration of microbond test and modified single fibre pull-out test.

The free fibre length above the matrix and rate of fibre end displacement were set to 5 mm and 0.1 mm/min respectively. The load-displacement curve from each test was recorded to obtain the maximum force (F_{max}), which, along with the corresponding fibre diameter (D) and embedded length (L_e) was used to calculate the IFSS according to Equation (1).

$$\tau = \frac{F_{max}}{\pi D L_e} \qquad (1)$$

The tested samples were then examined under the Nikon Epiphot Inverted optical microscope to see if pure debonding process had occurred. Approximate 30 tests for each method were carried out to obtain both IFSS for each sample by Equation.1 and average IFSS for the entire data by a least-squares regression (i.e. slope of linear fitting line for the entire data).

3. Results and discussion

3.1 Oxidative Thermal Degradation of PP microdroplets

Figure 4 shows a set of black-and-white pictures of a GF-PP microbond sample heated at 220°C under the air.
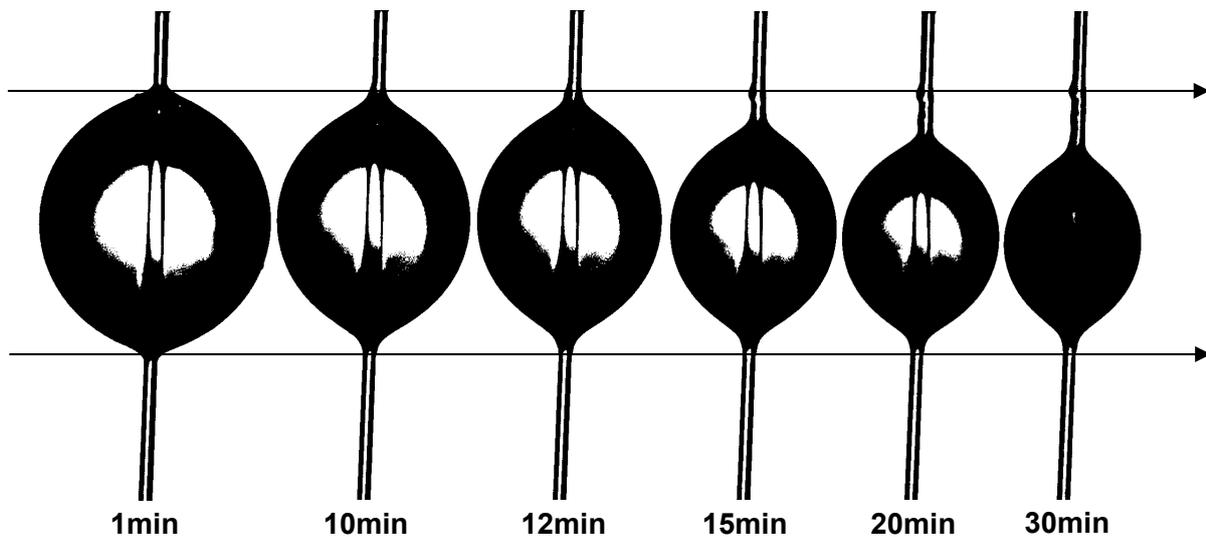
Figure 4. Photographs of the GF-PP microbond sample heated at 220°C under the air

It visually displays the dimensional reduction of the PP microdroplet on the glass fibre. It can be clearly seen that there is a considerable reduction in the volume of the PP droplet within the 30 min. Even in the first 10 min, the volume loss is significant. This strongly indicates that the PP droplet has undergone severe degradation during the heating process, because such volume reduction can only be attributed to massive evaporation of degraded products. It is well known that during oxidative thermal degradation of PP, the oxidation of PP leads to a step termed as chain scission, which involves the formation of a free radical at some point on the polymer backbone. The chain scission produces small series of oligomers with a broad range of the number of carbons in the backbone. If this process is repeated successively in a polymer, the resulting products will become small enough to evaporate without further bond cleavage [12]. Thus, oxidative thermal degradation of PP initially leads to a decrease in molecular weight and ultimately weight and volume loss. The sample at 30 min shows a complete opaque PP droplet because of the degradation. It is also noticed in Figure 4 that unlike the reduction in the diameter of the PP microdroplet, the decrease in the length of the droplet (i.e. fibre embedded length) during the heat treatment is not symmetrical relative to the centre of the droplet. It occurs to much greater extent on the upper part of the droplet than the lower portion. A small bump also emerges from the upper portion of the droplet as the droplet length decreases and remains on the fibre. The observation of other samples indicates

that asymmetrical length reduction exists in each sample but preference does not seem to be consistent. The appearance of the remainder does not seem to be necessary.

To further reveal these interesting features caused by oxidative-thermal degradation of microbond samples of GF-PP, the maximum droplet diameter and fibre embedded length of six microbond samples with different initial PP droplet sizes are plotted against the processing time in Figure 5 and 6 respectively.
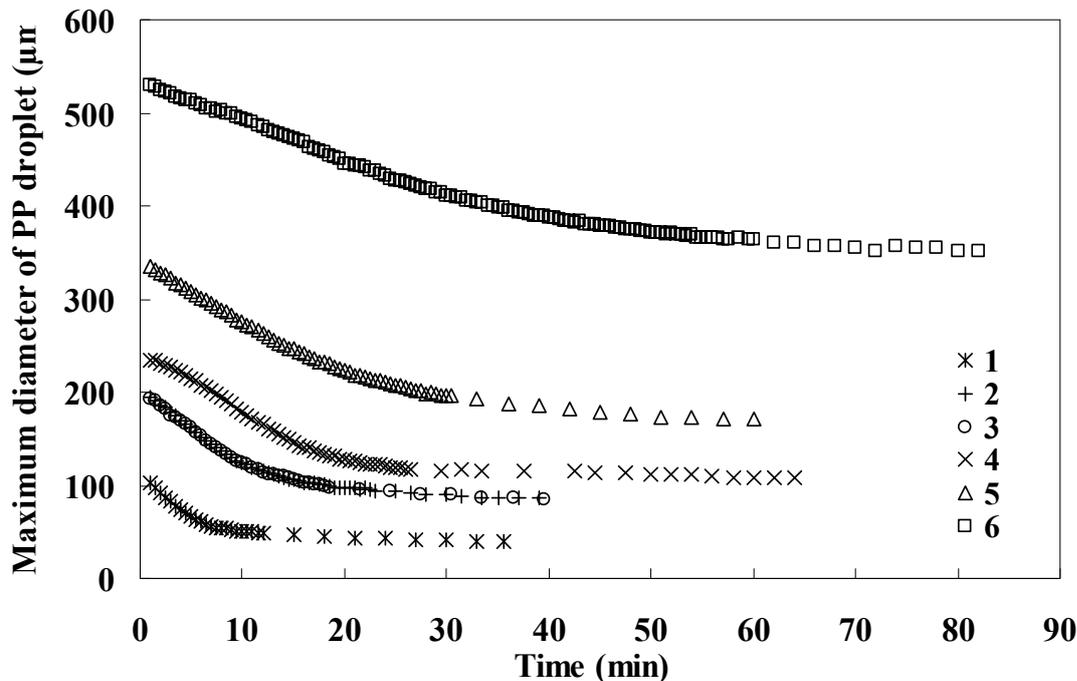
Figure 5. Reduction of the maximum diameter of PP microdroplet heated at 220°C under the air

As seen in Figure 5, the decrease in the droplet diameter begins immediately when time registration starts. Oxidation induction time (OIT) can hardly be observed in this case. In addition, the diameter reduction for all six samples appears to follow the same pattern. It linearly decreases at the similar rate and gradually levels out. In fact, the independence of reduction rate from initial diameter is a manifestation of the effect of surface area-to-volume ratio on oxidative-thermal degradation of PP microdroplets. It means that the big PP droplet has lower normalised rate of diameter loss than the small one does. Compared with big PP droplets, Small droplets possess a higher surface-to-volume ratio and offer a bigger portion of polymer molecules exposed to the hot air. As a consequence, they are more susceptible to oxidative attack at elevated temperature and undergo more severe thermal oxidation and degradation within a given time.
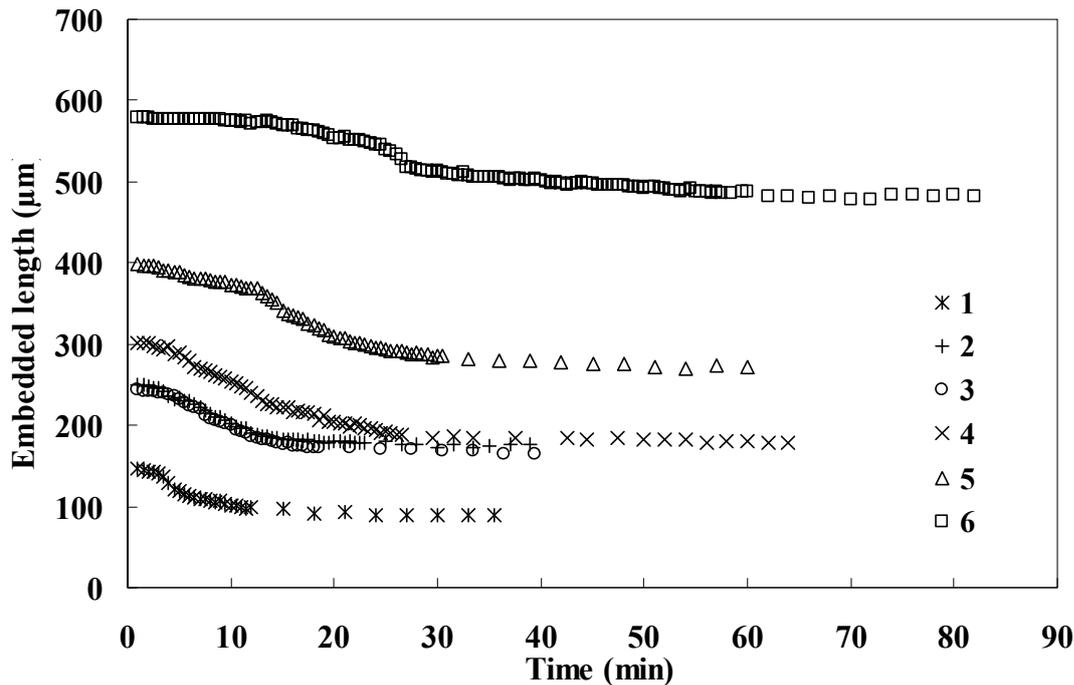
Figure 6. Reduction of fibre embedded length of GF-PP microbond sample heated at 220°C under the air

The length reduction along the fibre in Figure 6 is apparently complicated by the presence of the glass fibre. Instead of having a mono-linear rate in the reduction of droplet diameter, the degraded microbond samples tend to exhibit relative slow linear decrease of fibre embedded length before moving on to the next linear reduction rate, which is comparable with the rate of diameter loss. The sharp kinks observed in the curves of sample 1, 5, and 6 in Figure 6 are found to correspond to the emergence of the residue on the fibre as seen in Figure 4. This information implies that shear stress between the glass fibre and the molten PP droplet could be induced during the degradation of the PP droplet. The reduction in the droplet thickness transverse to the glass fibre may lead to the decrease of their contact angle. Assuming the surface tensions of the glass fibre and the PP melt and interfacial tension between them remain constant in a short period of time, PP melt would tend to restore the contact angle by pulling the melt inwards. The shear stress could be induced when viscous PP melt tends to move relatively to the static glass fibre, which could also constraint the movement of immediate PP melt by friction. When the shear stress reach to some critical level, the sudden sliding between the PP melt and the fibre surface would occur. This melt debonding is presented by the kinks in Figure 6. The induced shear stress might have negligible effect on measured IFSS but it could be one of the factors for the scatter in the data.

3.2 Mechanical properties of PP microdroplets

The results for elastic moduli of PP microdroplets prepared for 4 min and 6 min at 220°C are presented in Figure 7.
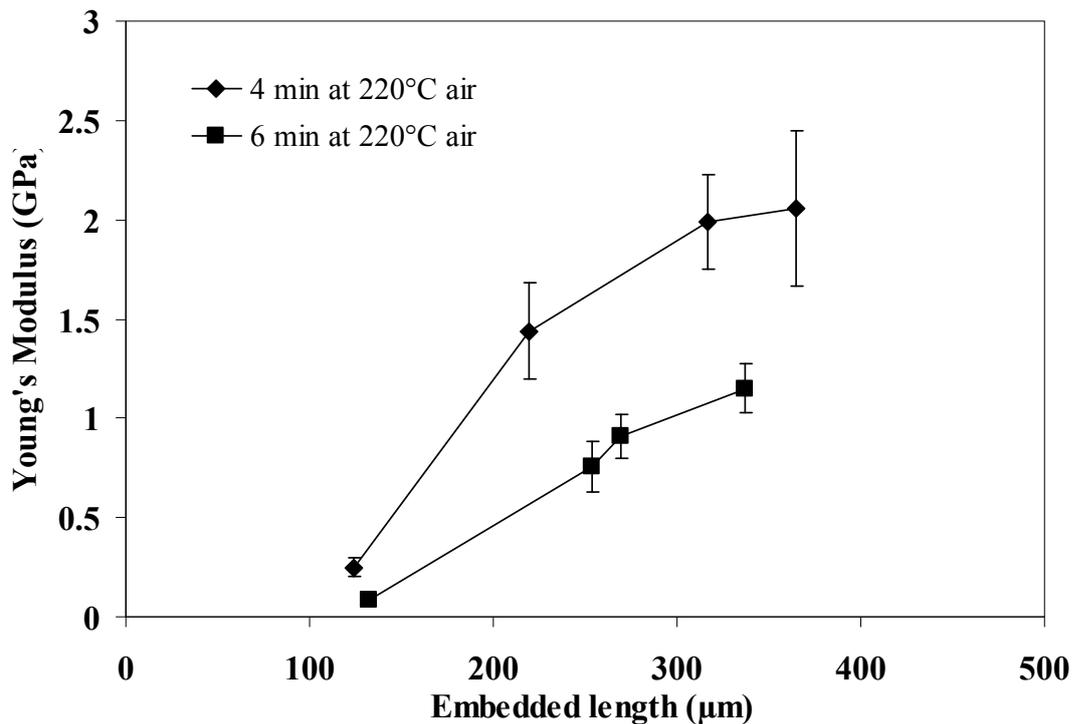
Figure 7. Young's modulus of PP microdroplets with different embedded lengths after undergoing different thermal loads.

As the correlation between the size of the PP droplet and severity of its degradation seen in the previous section, Young's modulus for a given thermal load is also strongly related to the dimensions of the droplet. For PP microdroplets that undergo a relatively mild thermal treatment (i.e. 4 min at 220°C in the air), elastic modulus increases rapidly as the droplet size is increased. When the embedded length reaches to about 300 μm, elastic modulus seems to become independent of the sample size. Comparing the two sets of data, it can also be seen that the extra heat treatment has considerably lowered the elastic moduli of the PP microdroplets. The absolute difference between the two data sets decreases when the size of the PP droplet becomes small. The modulus of semi-crystalline polymers is considered to depend on the degree of crystallinity. The regularity and long-range order along the polymer chains can be reduced by both the addition of oxygen atoms on polymer chains and chain breakage via thermal oxidation and degradation. Upon cooling, decreased chain regularity leads to the reduction in the degree of crystallinity in PP microdroplets and in turn the decrease of the stiffness.

3.3 Interface strength of GF-PP

Results for both microbond and modified single fibre pull-out tests in this work are presented together with the results from the previous work in Figure 8.
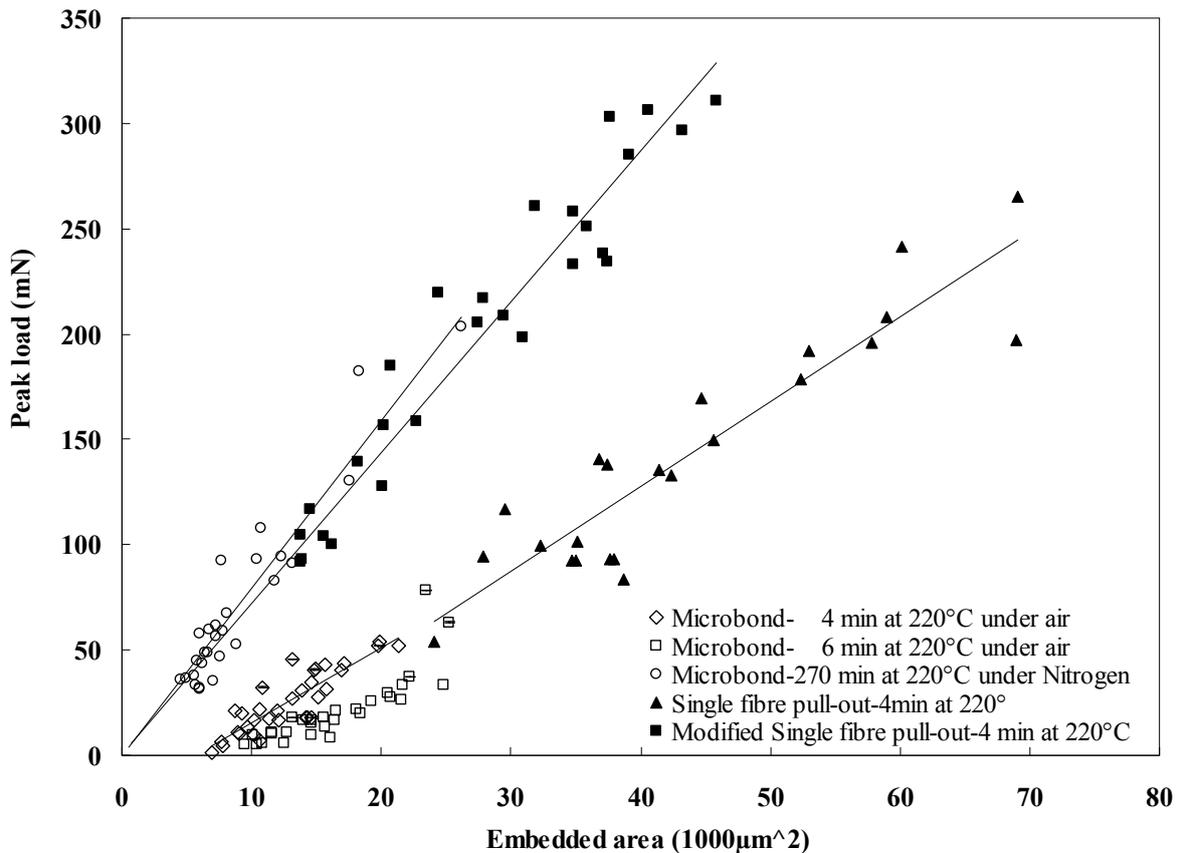
Figure 8. Comparison of effect of oxidative-thermal degradation of PP on the measured IFSS of bare GF-homopolymer PP47 using microbond and single fibre pull-out methods

Detailed discussion about the results in the early work can be referred to [10]. It can be clearly seen in Figure 8 that measured IFSS for GF-PP is significantly affected by the thermal load (i.e. temperature and time) and the atmosphere (i.e. air or nitrogen) in terms of thermal-oxidative degradation in PP matrix. Without the degradation in the PP for the microbond and pull-out test, measured average IFSS for GF-PP is over two orders of magnitude bigger than that obtained from degraded samples. 7.9 and 7.2 MPa are obtained for average IFSS measured by the microbond and modified pull-out test in this work. Excellent compatibility between two methods can be obtained in both sets of data. The fact that the linear fitting lines of the data from non-degradated samples go through the origin indicates that thermal degradation of PP was the reason for the regression lines of the previous data not passing through the origin. One may wonder whether the increase in measured IFSS for non-degradated microbond samples was caused by the extremely long processing time during the heating. This may be indirectly answered by the fact that non-degradated pull-out samples undergoing 4 min heating process gave 7.2 MPa for average IFSS, which is well comparable with the value obtained from microbond test on non-degradated samples.

4. Conclusions

The observation of microbond samples made by the hot stage microscopy clearly shows thermal degradation of PP during the heat treatment. The reduction in droplet dimensions is affected by its initial droplet size and the presence of the fibre in the droplet. The results for the Young's moduli of PP microdroplets with different heat treatments showed that there was

significant stiffness deterioration in degraded samples and the severity is also related to the droplet size for a given heat treatment. Comparison of measured average IFSS for GF-PP between degraded and non-degraded samples shows that oxidative-thermal degradation of PP can markedly reduced the adhesion of GF-PP.

Acknowledgements

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