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Blister appearance in thermoplastic composites

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Abstract—Blisters were observed in thermoplastic composite materials after a thermal shock during the manufacturing process of electronic parts. The aim of this paper is to describe the blister appearance and its mechanism. First, an experimental study is presented about the environmental conditions and the evolution of blister appearance on the specimen, then the mechanism of their formation and propagation in the material is suggested, and finally an attempt is made to explain the origin of the phenomenon. Experiments show that the water content of the material, the time and the temperature of the thermal shock play an important role. Observations made by SEM show the blister progression in the core of the material. A crack is initiated and then propagates on the interface fiber–matrix. After a crack reaches a sufficient length, the internal stress field opens it and a blister appears.

Keywords: Thermoplastic matrix; thermal shock; absorption; blister; composites.

1. Introduction

The use of thermoplastic composites offers several advantages compared to that of the thermoset matrix materials. Some examples of their useful properties are: high impact resistance and damage tolerance, low price and, not the least important, they are recyclable materials [1, 2]. Recently industrial interests have been focused on them. New impregnation techniques have been developed allowing production of materials of quality for the high-tech industry [3, 4]. Computer makers use them for the production of electronic components.

During the manufacturing of thermoplastic composites one can observe a rare but not unknown phenomenon, the blister appearance. Although blister tests are used to determine the adhesion properties of polymers [5, 6], the spontaneous appearance of blisters is to be avoided. In the case of the studied material, blisters occurred on the surface of short fiber reinforced PA46 composite during the manufacturing

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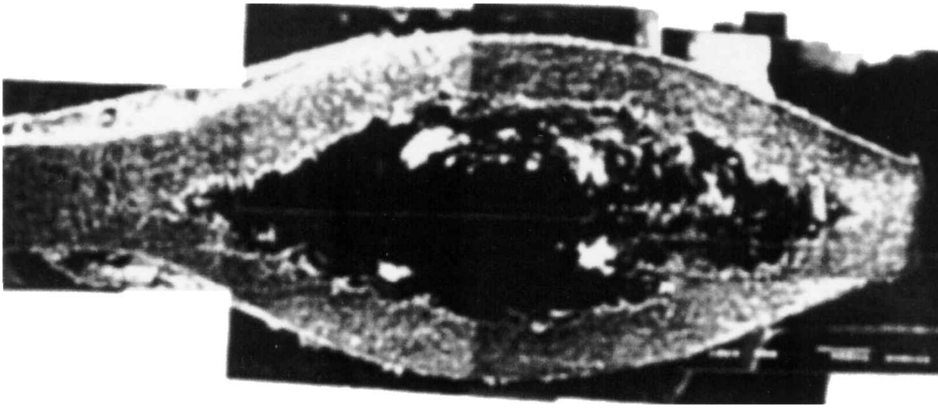

Figure 1. Blister occurred in a thermoplastic composite material.

process of electronics parts, like integrated circuit supports in South-Eastern Asian countries. In that part of the world, the relative humidity of the air is very high, and the material used can absorb water molecules from its environment while it is stored and handled. One of the most damaging effects of the water absorption [7–12] is that the water molecules destroy the fiber–matrix interface and the properties of the material decrease in the long term [13, 14]. When the electronic circuit panels are soldered with the base sheet, they are heated up to about 250°C for a short time. At that moment, blisters occur on their surface. Ceramic [15–18] and polymer [19, 20] matrix fiber reinforced composites were studied to understand the fracture propagation [21] and damage due to the thermal shock. In the case of PA46 and PA66 materials, the thermal shock temperature was close to that of the melting point, so only experiments with relatively short thermal shocks time could be performed.

As can be seen in Fig. 1, a blister looks like a bubble-like swelling under the surface of the composites. Closer observations show that in fact it is a big opened crack in the core of the material, which deforms both surfaces while its inside is empty. A schematic drawing of a blistered material and the structure of a cut blister are presented in Fig. 2. The shape and size of blisters vary, but the average shows an ellipse with a length of 4–6 mm, a width of 3–4 mm and a high of 0.5–1 mm, as can be seen in Fig. 3. The mechanism of the blister occurrence seems to be the same for all studied materials. However, the blister size and the environmental conditions of the blister appearance are slightly different for each of them. In this paper the behavior of different materials during the thermal shock will not be compared. Instead, this study has been focused on the mechanism of blister appearance: we shall try to describe it and find out its origins.

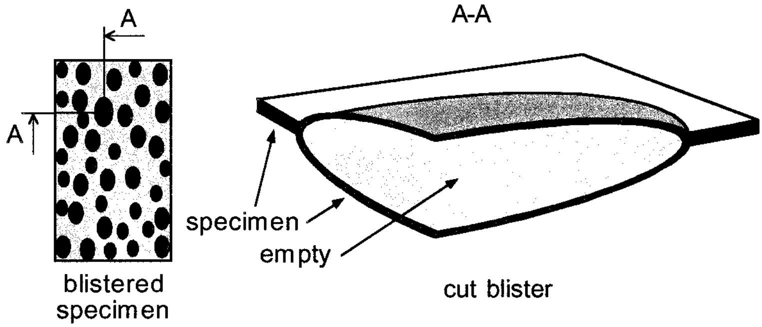

Figure 2. Schema of a blister.

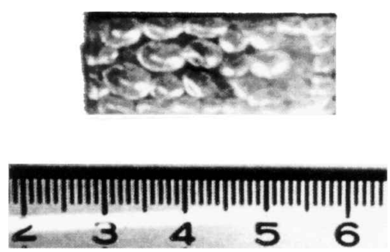

Figure 3. Size of a blister.

2. Materials

The studied materials showed very similar mechanical properties; they all are polyamides: PA46, PA66 and PPA. All of them are largely used in the electronics industry to cover IC and LSI panels. Specimens supplied by The Japan Synthetic Rubber Co. Ltd. with 0.8 mm thickness were made by injection molding, reinforcing the thermoplastic matrix by short glass fibers. The fiber length is about 20 mm; fibers are randomly oriented in the composite sheet. Rectangular specimens were cut from the sheet, with the size of $30 \times 12.7 \times 0.8$ mm. The weight fraction of fiber is about 30%.

3. Environmental conditions of blister appearance

Experimental conditions have been chosen to be close to these of the real manufacturing process. Parameters influencing the blister appearance were studied. The process shown in Fig. 4 has been used to simulate the thermal shock of an initially wet specimen. At first, samples were dried at 80°C in vacuum, then immersed into water and finally put into an oven for a short time. Two different water temperatures were investigated for the aging, 20°C and 100°C. However, materials aged in both cold and hot water showed the same behavior *vis a vis* the blisters. Apparently, only the absorbed water quantity is important, while the temperature of the water had no effect on the blister appearance. After immersion, rectangular specimens were

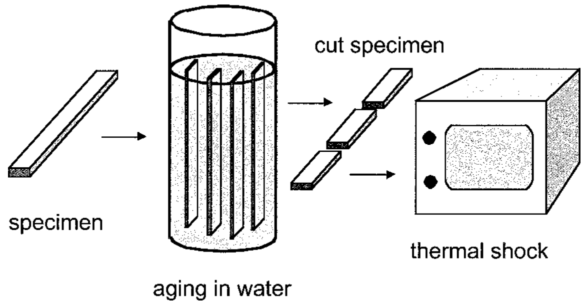

Figure 4. Experimental process simulating the thermal shock.

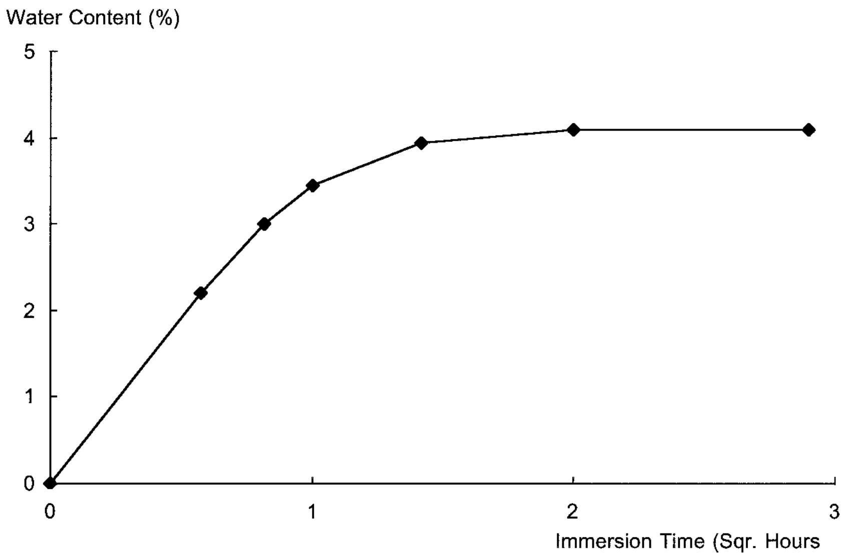

Figure 5. PA66 Absorption curve at 95°C.

cut out from the long sheets. In that way the water content level is the same at any point of the specimen. We wanted to be certain that the position of the first blister appearance will be independent of the water distribution in the material.

Absorption curves and the effects of the water content of the composite material on the blister appearance were first studied. Figure 5 shows the absorption curve of PA66. This thermoplastic material follows a Fick type absorption law.

$$\Delta \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}, \tag{1}$$

where c is the water concentration in the material, x and t are the space and time variables respectively, and Δ is the diffusion coefficient.

The saturation level is nearly 5% at 95°C. The time necessary to reach this level is about 4 hours. Thermal shock was performed on specimens having different water content level. The temperature and the time of the shock were chosen close

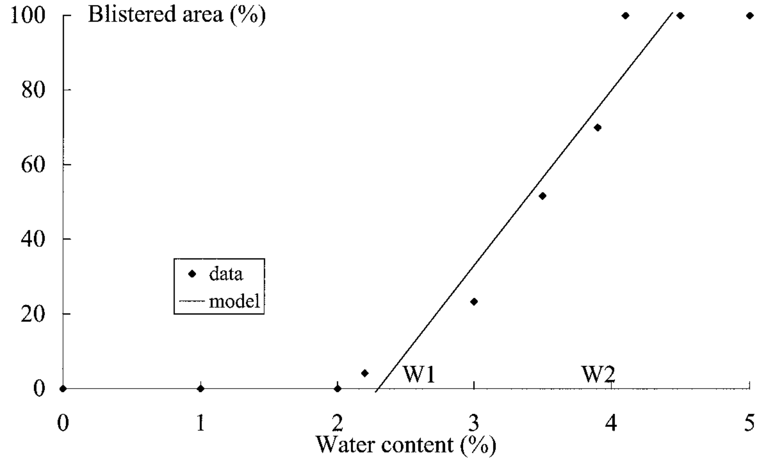

Figure 6. Blister evolution on PA66 in function of the water content level.

to these of the real process, around 240°C and 1 minute. Results of these tests are presented in Fig. 6. Blisters do not occur under 2% water content. The blistered area on the surface increases with the water content level. This function is quasi linear between the points $W1$ and $W2$, representing the appearance of the first and last blisters respectively. A simple mathematical description of the relation between the blister occurrence and the water content of the material could be proposed with the following equation:

$$\begin{cases} B_t = 0\% & \text{if } W_t < W1, \\ B_t = \text{flinear}(W_t) & \text{if } W1 < W_t < W2, \\ B_t = 100\% & \text{if } W_t > W2, \end{cases} \tag{2}$$

where W_t is the water content level at the time t, $W1$ and $W2$ are particular water content levels, and B_t is the ratio of the blistered surface at the time t.

Normalized curves are presented in the Figs 7 and 8. As may be seen in the Fig. 7, the growth of the blistered area is similar to that of the water absorption curve. Thus, the evolution of blisters can be described by the same mathematical formula, the Fick law. Blisters occur at that part of the material where the water content is over a critical level. The first blisters appear when the water content in the material is approximately half of the saturation level. Normalized values of the water content rate W_t/W_s and the blistered surface rate B_t/B_s, show linear dependence (Fig. 8). W_s is the water content level at saturation and B_s is the blistered area of the surface when no more blisters occur, i.e. the surface of the sample.

After we studied the relation between the water content level and the blistered surface, the effects of the temperature and the time of the thermal shock on the blister appearance were investigated separately. Specimens having the same saturated water content level were subjected to a thermal shock. Firstly, the oven temperature was modified while keeping the same time of thermal shock (Fig. 9), then the time of thermal shock was modified while keeping the same oven

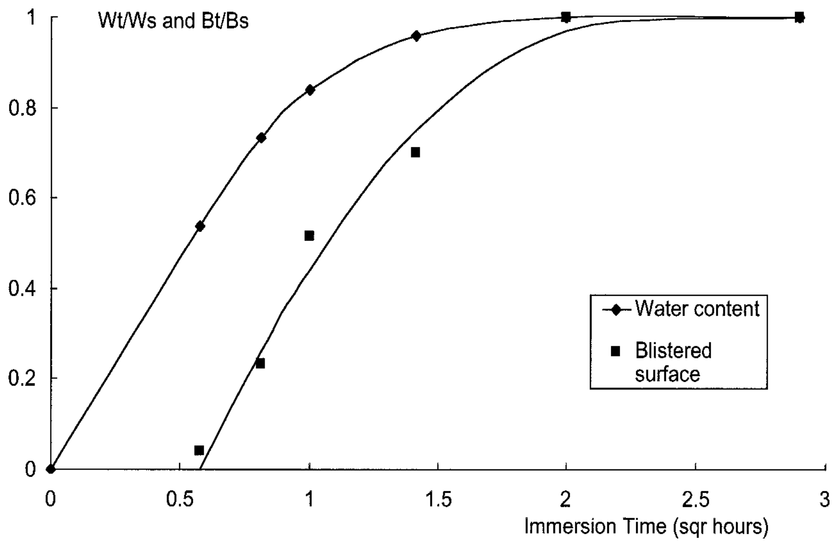

Figure 7. Normalized values; W_t/W_s and B_t/B_s in function of the immersion time.

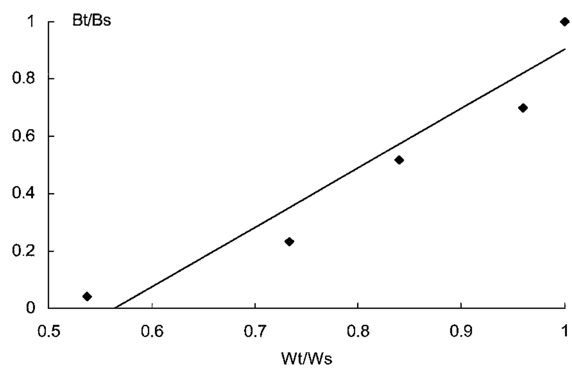

Figure 8. Normalized values; B_t/B_s in function of W_t/W_s.

temperature (Fig. 10). In that way we determined the necessary minimal value of each parameter for the blister appearance. As can be seen in Figs 6, 9 and 10, the evolution of the blistered area is similar in the three studied cases. Although there are only a few data points, the function can be considered linear between the points 1 and 2, which represent the first and last blister appearance respectively. Equations similar to the previous ones are proposed to take into account the effects of the temperature of the thermal shock:

$$\begin{cases} B_t = 0\% & \text{if } Temp < Temp1, \\ B_t = \text{flinear(Temp)} & \text{if } Temp1 < Temp < Temp2, \\ B_t = 100\% & \text{if } Temp > Temp2, \end{cases} \tag{3}$$

where *Temp* is the value of the thermal shock temperature while *Temp*1 and *Temp*2 are particular values of the thermal shock temperature.

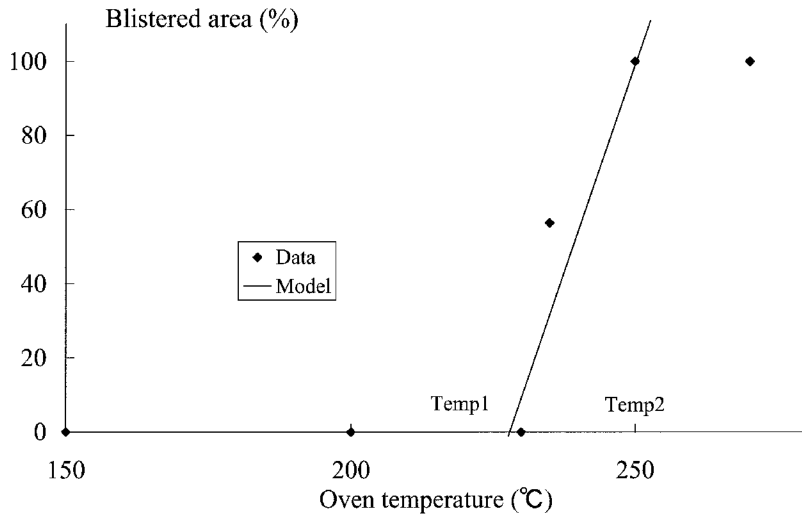

Figure 9. Blister evolution on PA66 in function of the thermal shock temperature.

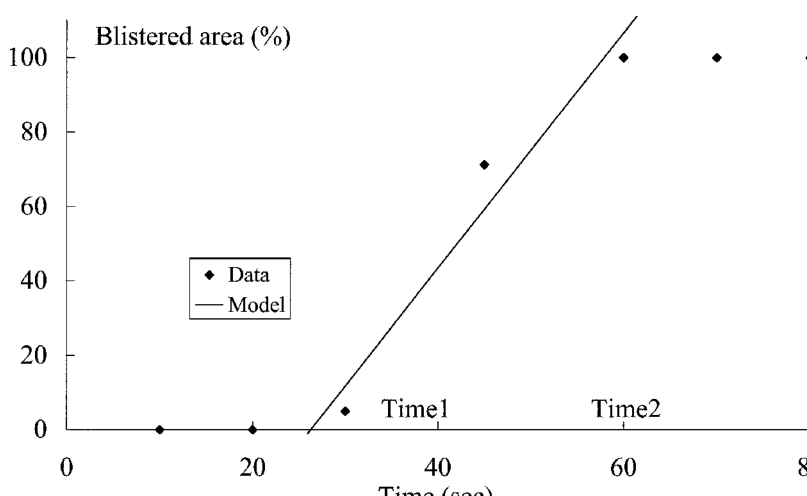

Figure 10. Blister evolution on PA66 in function of the thermal shock time.

For the effects of the time of the thermal shock:

$$\begin{cases} B_t = 0\% & \text{if } Time < Time1, \\ B_t = \text{flinear(Time)} & \text{if } Time1 < Time < Time2, \\ B_t = 100\% & \text{if } Time > Time2, \end{cases} \quad (4)$$

where *Time* is the value of the thermal shock time while *Time*1 and *Time*2 are particular values of the thermal shock time.

Now we can summarize the blister evolution as follows:

$$\begin{cases} B_t = 0\% & \text{if } Temp \text{ or } Time \text{ or } W_t < \text{Values 1}, \\ B_t = \text{flinear}(Temp, Time, W_t) & \text{if Values 1} < Temp \text{ and } Time \\ & \qquad \text{and } W_t < \text{Values 2}, \\ B_t = 100\% & \text{if all are over Values 1} \\ & \qquad \text{and } Temp \text{ or } Time \\ & \qquad \text{or } W_t > \text{Values 2}. \end{cases} \tag{5}$$

If the water content of the material, the time or the temperature of the thermal shock are under a critical value, then blisters cannot appear. If all these parameters are higher than the critical values (Values 1 in the equation), blisters appear and their evolution is a linear function of these three parameters. After reaching a second critical value (Values 2 in the equation) by one of these parameters, the whole surface is covered by blisters, and they do not occur any more. If one of the above mentioned parameters is under Value 1, blisters can not appear, even if the two other parameters are higher than Value 2.

4. Blister evolution

For all the specimens, the first blister appears always in one of the corners. More follow it near the corner; then they appear on the side and finally progress towards the center (Fig. 11). Most of them reach their average size before a new one appears. This same kind of evolution was observed for all three studied parameters. When the

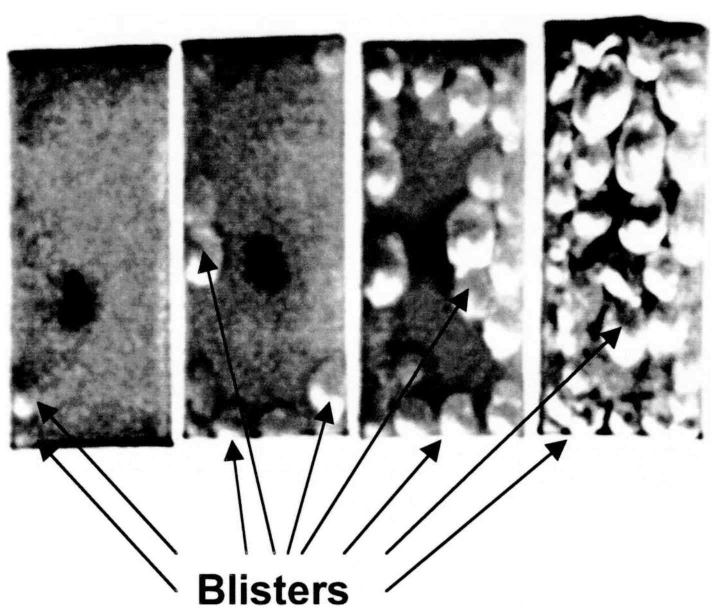

Figure 11. Blister evolution on the surface of the specimen.

water content of the material, the temperature or the time of the thermal shock are increased, the surface occupied by blisters increases in the same way, as described in the previous section.

SEM observations were made to understand the mechanism of blister occurrence. When blisters appear, first a crack initiates and then propagates in two directions along the fiber–matrix interface (Fig. 12). This kind of debonding occurs quite easily since the fibers are in the same plane, parallel to the surface of the sheet. Only the interface and the matrix properties determinate the resistance of the material.

Patch of crack grow and when their size allows, they are opened from the center of the debond area. At that moment the crack becomes a blister. The growth of the blister continues up to a specific size, then stops. In another place in the specimen, another blister will occur. The average size of blisters depends probably on the properties of the matrix and the interface. It is nearly the same for both PA46 and PA66 but about half this size for the PPA.

Actually, as suggested by the photographs, the interface strength should play an important role in the blister propagation mechanism. In the case of a strong interface, only high internal stresses can break it because of the good adherence between fibers and matrix. Blisters will not occur or only small ones. In the future, we envisage studies on materials having different surface treatment to see clearly the role of the interface. It might be the key to avoid blister occurrence during thermal shocks.

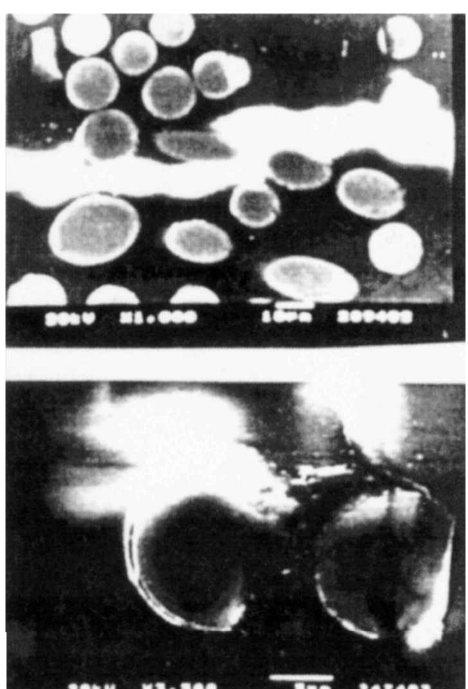

Figure 12. Cracks around a fiber and crack propagation in the material.

5. Origin of the blister occurrence

The first idea that came to mind was that the absorbed water may be transformed into steam during the thermal shock, then the pressure would cause the blister to form. Unfortunately, this theory has some weaknesses that we shall discuss in the following.

First, microscopic observations show that the absorbed water has not enough space to be in liquid phase in the composite. The water molecules can infiltrate into the composite between the polymer chains but they will probably remain in molecular phase. But let us suppose that there is some micro-crack and cavity in the material. These could contain water and in a thermal shock this would become steam and form a blister. In this case, the first blisters would occur randomly on the surface, not in the corners.

Second, as can be seen in Fig. 1, although blisters are empty, they are always closed even when situated on the limit of the specimen. If blisters were due to the steam pressure, the side would probably not be able to resist; it would yield to this pressure and be opened.

Third, blisters situated along the side, curve the straight line of the border towards the inside (Fig. 13). If there were a cavity full of steam under pressure in the material, it would curve the border towards the outside.

These facts suggest that we should look for the origin of the phenomenon in the internal stress field, resulted from the swelling and the shrinkage of the matrix. The first is due to the water absorption while the second happens in the oven. Although increases and decreases in length are very small, it can be measured on the specimens after the immersion and the thermal shock (Fig. 14). If we admit this hypothesis, then the mechanism is probably the following:

- The matrix absorbs water and swells. The interface is weakened by the stresses provoked by the swelling.
- During the thermal shock the molecular structure of the matrix is modified, and it shrinks.

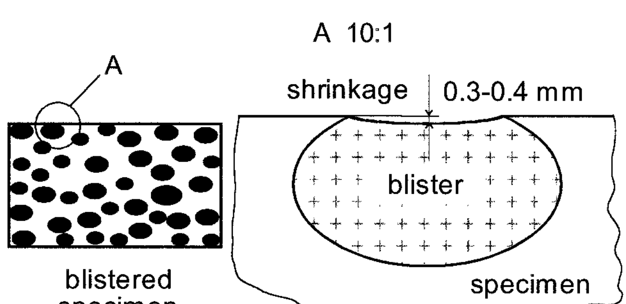

Figure 13. The border of the specimen deformed by blister.

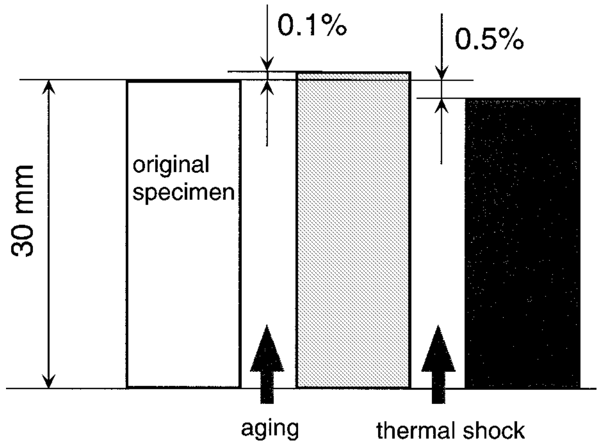

Figure 14. Swelling and shrinkage of the material.

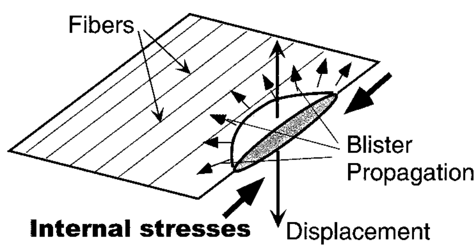

Figure 15. Origin of blister occurrence.

- The shrinkage is blocked by the glass fibers, which keep their length. After that moment, an internal stress field parallel to the fibers, trying to contract the matrix further appears in the material.
- Cracks form and propagate along the fiber–matrix interface (debonding).
- When the delaminated fiber length allows it, buckling occurs; then fibers curve under the stresses, and the crack opens. A blister appears.
- The size of the blister increases until it reaches optimum size.
- Other blisters occur at free places.

This mechanism can be seen in Fig. 15. For easy understanding, we simplified the real material by considering a unidirectional composite. The matrix suffers a shrinkage in all the three directions, but the free displacement is blocked only in one direction, the fiber's direction. Internal stresses grow, the fiber–matrix interface yields, a crack appears then progresses in the plane of the specimen.

The result of tensile tests performed on dry and aged (5.2% water content) specimens is presented in Fig. 16. Although the failure strain remained the same (7.2% at rupture), the final tensile strength and the Young's modulus were both decreased by 25%. These facts indicate an important degradation of the fiber–matrix interface. As it is widely observed, the interface of composite materials becomes weaker

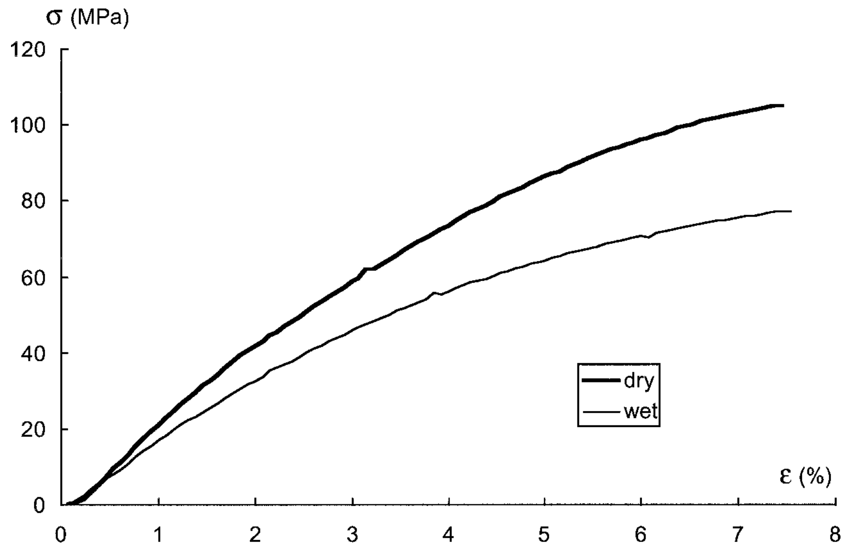

Figure 16. Tensile test results obtained from dry and wet materials.

in a wet environment. This weak interface can be broken easily by the above mentioned internal stresses. Since it is possible that the effect of the absorbed water is only to make the interface weaker, then the internal stresses induced by the thermal shock are able to cause blisters.

6. Conclusion

As we showed in the present study, blisters occur in thermoplastic composites during the manufacturing process of electronics parts. They start in the corners then progress along the side and toward the center of the specimen. Cracks form at the fiber–matrix interface and grow into a blister by being opened from their center. After reaching a maximal size, their growth is stopped.

The blistered area of the surface increases if the water content, the time or the temperature of the thermal shock is increased. However, to make blisters appear, all of these parameters should be above a minimum value.

The absorbed water weakens the interface while the swelling and shrinkage of the matrix induce an internal stress field in the composite. These stresses together with the weakness of the interface are the key factors of the blister occurrence.

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