

IDENTIFYING THE FIBER/MATRIX INTERPHASE OF UNIDIRECTIONAL COMPOSITES (GLASS FIBER/EPOXY) WITH GRADIENT IN CROSSLINK DENSITY BY MEANS OF DYNAMIC MECHANICAL THERMAL ANALYSIS (DMTA)

XÁC ĐỊNH BỀ MẶT TIẾP XÚC PHA SỢI/NỀN CỦA COMPOSITE ĐƠN HƯỚNG (SỢI THỦY TINH/EPOXY) CÓ MẬT ĐỘ ĐÓNG RẮN THAY ĐỔI BẰNG THIẾT BỊ PHÂN TÍCH CƠ NHIỆT ĐỘNG (DMTA)

Nguyen Thanh Hoi¹, Nguyen Dinh Lam²

¹The University of Danang, College of Technology; Email: nthoi@ud.edu.vn

²The University of Danang, University of Science and Technology; Email: ndlam@dut.udn.vn

Abstract - This study was carried out on unidirectional composite samples (epoxy/glass fiber) with gradient in crosslink density within 250 μm measured from the surface contacting with air during the preparation. The $\tan \delta$ spectrum of the composite was determined by a DMA in three point bending modes (single cantilever), and so were the $\tan \delta$ spectra of the epoxy-amine resin samples, in parallel. The fiber/matrix interphase was identified by comparing the $\tan \delta$ spectra of resin and that of the composite with the Origin software. The results show that the interphase is hydrophilic and has an incomplete crosslinked network. However, its micro-structure and chemical nature are different from the matrix at the air-contacting surface that has incomplete crosslinked networks as well.

Key words - Unidirectional composite; DMTA; interphase; epoxy; viscoelastic properties.

Tóm tắt - Nghiên cứu này được thực hiện trên những mẫu composite (epoxy/sợi thủy tinh) đơn hướng và có mật độ đóng rắn thay đổi trong 250 μm tính từ bề mặt tiếp xúc với không khí trong quá trình điều chế. Phổ $\tan \delta$ của composite được xác định trên thiết bị DMA trong kiểu uốn ba điểm (single cantilever). Song song đó, những mẫu nhựa epoxy-amin cũng được xác định phổ $\tan \delta$ trong cùng điều kiện. Bề mặt tiếp xúc pha sợi/nền được xác định bằng cách so sánh phổ $\tan \delta$ của nhựa và của composite với sự giúp đỡ của phần mềm Origin. Kết quả thu được cũng cho thấy rằng bề mặt tiếp xúc pha tạo thành có tính ưa nước và đóng rắn không hoàn toàn. Tuy nhiên, cấu trúc vi mô và bản chất hoá học của nó khác với lớp vật liệu nền trên bề mặt tiếp xúc với không khí cũng đóng rắn không hoàn toàn.

Từ khóa - Composite đơn hướng; DMTA; bề mặt tiếp xúc pha; epoxy; tính chất đàn nhớt.

1. Introduction

Today the composite materials are present in all the fields of advanced technologies such as shipbuilding [1], automotive and aerospace [2]. Numerous research on the aging of composite materials due to temperature, humidity and UV pointed out that the fiber/matrix interface is the place being easily degraded [3]. Schutte et al. [4] showed that humidity was the main factor for this interface degradation. Thomason [5] also demonstrated the influence of the nature of the interface on the changing of mechanical properties. According to this author, the polyepoxy composite/glass fiber interface degradation was about 10% after aging. Furthermore, P. Bonniau [6] found that a significant decrease in the shear modulus characterizing the degradation of the chemical bonding at the fiber/matrix interface.

Several techniques are used to highlight the fiber/matrix interface such as Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and/or spectroscopic analyzes (FTIR, ToF-SIMS, AES and XPS). However, these analysis techniques are quite limited in analyzing composite samples and just can work on the thin thickness near the sample surface [7]. In order to overcome this, the analysis techniques, such as differential scanning calorimeter (DSC), dynamic mechanical thermal analysis (DMTA) as well as atomic force microscopy (AFM), are the ones used most to monitor circuit flexibility of the macromolecules on the interface. However, the studies using these techniques

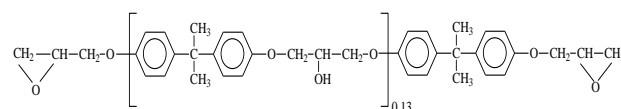
were carried out on a system which was completely cross-linked network. Therefore, using these techniques for composite with gradient in crosslink density may encounter certain obstacles.

The aim of this study is to identify of the fiber/matrix interface of unidirectional composite with gradient in crosslink density by means of dynamic mechanical thermal analysis (DMTA) with the support of the Origin software. This topic characterizes the relaxation phenomena that reflect the mobility of chain segments of the polymer matrix. The experimental results show that the micro-structure and chemical characteristics at the interface, as compared to epoxy/amine resin, are different from the matrix.

2. Materials and testing methods

2.1. Materials

The prepolymer was a diglycidyl ether of bisphenol A (DGEBA), $n=0.13$ and the hardener was a Diethylene Triamine (DETA). Both compounds were provided by Sigma-Aldrich and their chemical formulas are showed in Figure 1.



Diglycidyl ether of bisphenol A (DGEBA)



Diethylene Triamin (DETA)

Figure 1. Chemical formulas of prepolymer and hardener.

The reinforcements of E-glass fibers used in this study were provided by Owens Corning Reinforcements (OCV™ Reinforcements) as roving. The optimized size was chosen for its compatibility with epoxy resins.

The compound of DGEBA/DETA was mixed with the mole ratio of $\frac{n_{DETA}}{n_{DGEBA}} = \frac{2}{5}$ and equally distributed in mold with and without glass fibers to create unidirectional composite and resin plates with the size of 200x200x2mm³. The curing cycle was optimized to reach a maximum conversion rate (2 hrs at 60 °C followed by 2 hrs at 120 °C and 2 hrs at 140°C). The mass ratio of reinforced glass fibers was 28,4% (±0,7).

2.2. Testing methods

➤ A differential scanning calorimeter (DSC-Q100) from TA Instrument was used to monitor the degree of curing of composite sample following the glass transition temperatures evolutions by the different surface layer analysis. The samples weighed about 6-8mg were heated with gradient temperature of 20°C/min from 30°C up to 200°C. The glass transition was measured on the second cycle to eliminate relaxation effects.

➤ The glass fibers distribution in sample thickness was observed by SEM (ZEISS, Supra 40VP Class). The sample was cut perpendicularly to glass fiber by diamond saw blade, and then ground on the discs with different roughness levels and finally with diamond pastes sized 1µm.

➤ The fiber/matrix interface was determined by DTMA 2980 from TA instruments with the bending mode of single cantilever (Figure 2). The composite samples sized 40x10x2mm³ were cut perpendicularly to the fiber axis by diamond saw blade as shown in Figure 2.

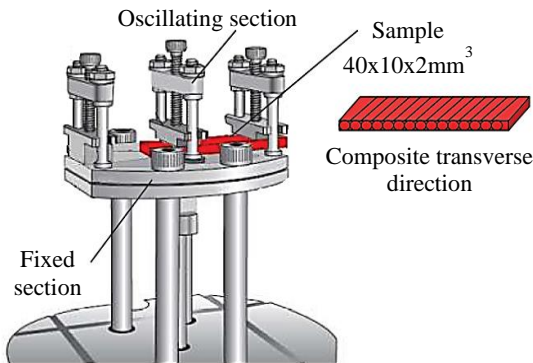


Figure 2. Schematic illustration of the sample assembly in DTMA 2980.

The measurement tasks were executed on the temperature range of 30°C - 180°C for a fixed frequency at 1Hz. To avoid thermal gradient in the sample, the heating rate was chosen as 20°C/min. On the other hand, to keep the viscoelastic in the linear region, the vibration amplitude was determined at 7 µm with a frequency scan of 1Hz in the room temperature

3. Results and discussion

3.1. The fiber reinforcement distribution and the degree of curing according to the thickness of the sample

As shown in SEM image in Figure 3, the distribution density of glass fiber with composite plate thickness is not uniform.

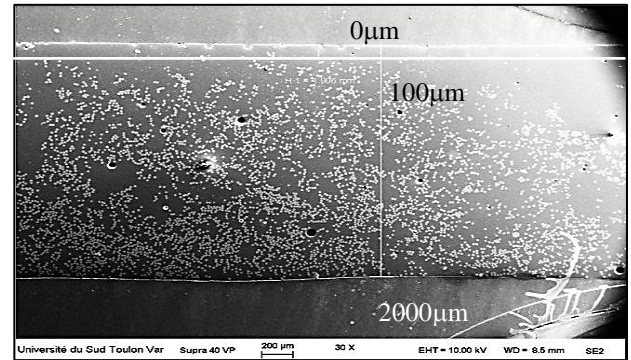


Figure 3. Figure SEM (x30) the cross section of the composite

At the composite plate surface exposed to air the glass fiber distribution density is low, 100µm-thickness from the surface. On the other hand, at the surface contacting with mold the glass fiber density is high. These results indicate that the micro-structures at the surface contacting with air (0-100µm) of the composite and resin are similar. Furthermore, DSC analysis shows that, for the composite plate thickness, the Tg values of the composite and resin are also the same. This result, again, confirms the similarity in the micro-structure that contact with air for composite and resin. The Tg value as a function of the plate thickness is shown in Figure 4 with the temperature error bar of 2°C.

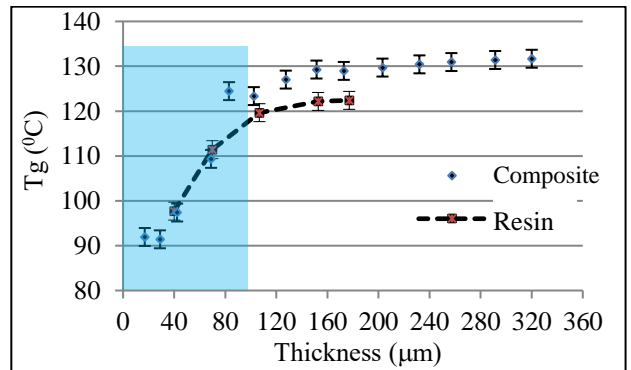


Figure 4. Evolution of the Tg as a function of the composite and resin plate thickness

As can be seen, from the surface to the 150µm depth, the Tg value increases in both composite and resin. This result indicates that the crosslink network is not uniform, and that near the surface the composite is cross-linked incompletely, which can be attributed to amines evaporation on the surface during synthesis process, leading to the shortage of amines (excess of epoxy) [8]. On the other hand, when comparing the changes in glass transition temperature of the composite plate and resin plate, we can see a deviation of about +7°C in the composite thickness of 150µm. In addition, the Tg value of the surface layer in contact with the mold is measured as 134°C (± 2°C) in both composite and resin.

It demonstrates that the presence of glass fiber does not affect the Tg values. Therefore, the increase of Tg of about 7°C on the film thickness of 150µm can be explained by

the presence of the glass fiber that prevents the diffusion of amines on the surface, leading to an increase in the hardened density of this layer.

3.2. Determining the fiber/matrix interface of the composite

The results from the dynamic mechanical thermal analysis of resin and composite show that the tan delta spectra of the composite begin at 50°C with the temperature peak T_{α} at 129°C (Figure 5a). In comparison with resin whose tan delta spectra begin at 70°C, T_{α} of the composite is 7°C less than that of resin (Figure 5b).

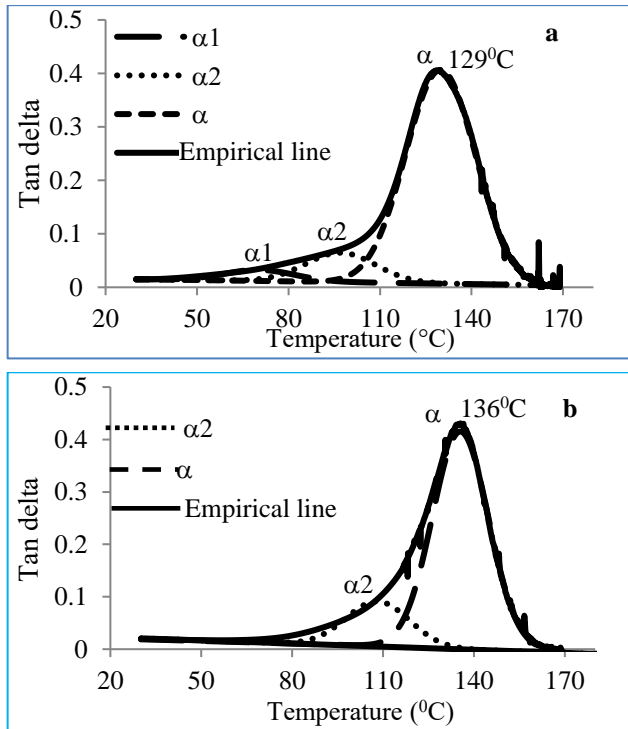


Figure 5. Tan delta spectra of composite (a) and resin (b) before and after pic separation by Origin software.

By modeling these spectra with Gaussian distribution thanks to Origin software, the tan delta spectra of the composite are proper to be separated into three pics of α , α_1 , α_2 (Figure 5a) while those of resin are separated into two pics of α and α_2 (Figure 5b).

For resin (Figure 5b), pic α and pic α_2 are representative of the relaxation of completely crosslinked resin and the relaxation of incompletely crosslinked resin, respectively, on the surface contacting with air. In terms of composite (Figure 5a), another pic appears possibly because of the relaxation of the interface. Theoretically, there is no generation of a new pic by an ideal interface (completely crosslinked) [9, 10]. As a result, an incompletely crosslinked interface is not generated because of the size of the glass fiber on the surface.

In order to determine exactly which pic of the composite, α_1 or α_2 , characterizes the relaxation of the matrix on the surface contacting with air or the fiber-matrix interface, the composite sample with the size of 40x10x2

mm³ was cut along into two pieces (40x10x1 mm³ each). Accordingly, one sample is in contact with air (less fiber) and the other is in contact with the mold. The tan delta spectra of the samples before and after pic separation by Origin software are displayed in Figure 6.

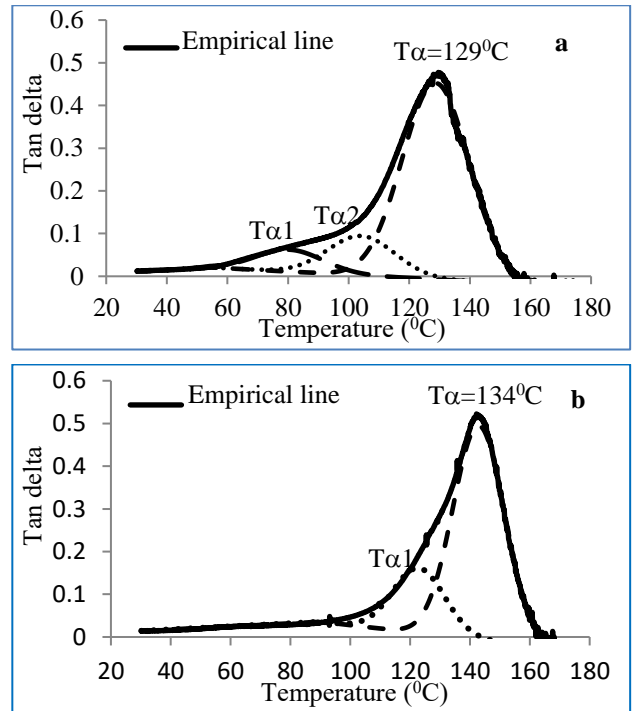


Figure 6. Tan delta spectra of the samples in contact with air (a) and with the mold (b) before and after pic separation by Origin software.

Regarding the sample in contact with the mold, the tan delta spectrum is separated into 2 pics (Figure 6b). The pic with $T_{\alpha} = 143^{\circ}\text{C}$ logically refers to the completely crosslinked matrix and the other, with less height and lower temperature ($T_{\alpha 1}$), refers to the fiber/matrix interface.

The tan delta spectrum of the sample in contact with air, meanwhile, is separated into 3 pics (Figure 6a). The pic with temperature $T_{\alpha} = 129^{\circ}\text{C}$ is correspondent with the more crosslinked matrix whose the crosslink density is incomplete (lower than that of the matrix layer on the surface contacting with the mold). As for the pic with temperature $T_{\alpha 2}$, when compared with the case of resin (Figure 5b), the pic α_2 of resin and composite begins at 80°C. Moreover, the temperature difference between the peak T_{α} and $T_{\alpha 2}$ is about 30°C, which corresponds to the maximum difference between the glass transition temperature T_g measured on the surface layer and that in the center of the resin sample (Figure 4). These helps confirm the second pic with the peak temperature $T_{\alpha 2}$ corresponds to the matrix (resin), which is incompletely crosslinked network, on the surface contacting with air, and the pic with the lowest peak temperature $T_{\alpha 1}$ to the fiber/matrix interface. As opposed to the sample in contact with the mold, pic α_1 of the sample contacting with air is lower in height due to the less fiber ratio in this sample,

which has been shown in the SEM analysis. On the other hand, the crosslink density of the fiber/matrix interface on the sample contacting with the mold is larger than that on the sample contacting with air and on the matrix layer of the air-contacting surface of the resin sample. This is shown by the fact that the temperature, where pic α_1 of the sample contacting with the mold begins to appear (100°C), is larger than that of the sample contacting with air (60°C) and also larger than the temperature where pic α_2 appears (80°C).

3.3. The hydrophilicity of the fiber/matrix interface

The DTMA result also allows us to identify plasticizers phenomenon through moisture in the air absorbed into the sample during the preparing process. The Tan delta spectra of the composite samples before and after drying until reaching the constant mass at 70°C is shown in Figure 7.

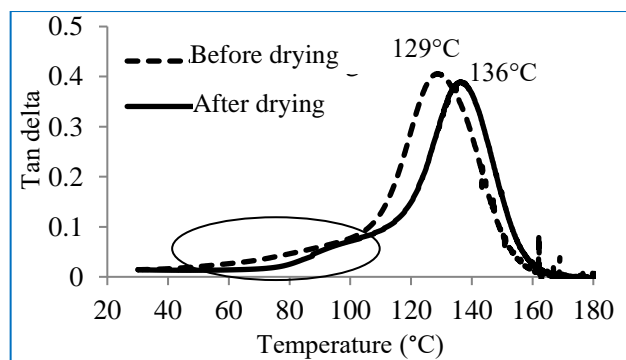


Figure 7. Tan delta spectrum of composite before and after drying (DMTA: 1Hz, 7 μ m, 2°C/min)

Plasticizer phenomenon can be clearly seen when the peak temperature (characterizing the matrix crosslinked network completely) increases by 7°C after drying while the peak heights are nearly constant. This can be explained by the desorption of water molecules absorbed in the sample during the preparation. Indeed, during the preparation, the water molecules in the ambient are absorbed into the sample, causing the networking plasticizer phenomenon [11]. The removal of the water molecules in the drying process allows to reset the chemical bonds between the macromolecules, leading to reduced flexibility of the molecular and increasing the peak temperature. The influence of the drying process is also clearly expressed at the temperature where the pic starts to appear. That the temperature where pic α_1 emerges increases to approximately 20°C suggests the interface absorbs more water than the matrix which is completely crosslinked networks or, in other words, the hydrophilicity of the interface is greater than that of the matrix.

The DTMA measurement is also carried out on the resin sample with the same above operating parameters. The obtained tan delta spectra are shown in Figure 8.

From the graph, we find that the peak temperature increases slightly (by 2°C) while the temperature where pic appears is seemingly leveled off before and after the drying

process. This means that the resin layer which is incompletely crosslinked on the surface exposed to air absorbs less water than the resin layer crosslinked completely.

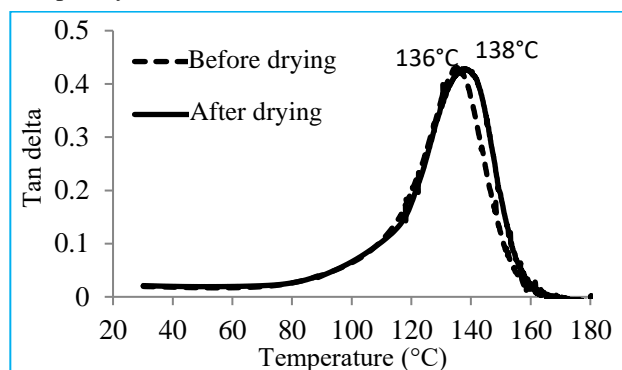


Figure 8. Tan delta spectra of resin before and after drying (DMTA: 1Hz, 7 μ m, 2°C/min)

The DTMA results of the composite and resin samples show that the fiber/matrix interface is incompletely crosslinked and it has greater hydrophilicity than the material layer on the surface exposed to air. Therefore, the microstructure and chemical nature of the two layers are completely different. Indeed, the study of Grave [12] on the effect of stoichiometric proportions r (amine/epoxy) to the water absorption in the DGEBA/TETA system reveals that the kinetics of water absorption and the amount of absorbed water at equilibrium increase according to the amount of amine residues, while the residual epoxy does not cause much impact. Moreover, the study of Astruc [13] on the system DGEBA/Polyamido amine indicates that the concentration of hydrophilic groups in the research system increases when the stoichiometric proportions increases. All of these suggest that the interface in DGEBA/DETA system has an excess of amine. This phenomenon can be explained by the high affinity of amine with glass fiber as well as with the layer sizing on the fiber surface [14] that leads to high concentration causing excess amine.

4. Conclusion

This study allows us to identify the fiber/matrix interface which exists around the glass fibers in unidirectional composite with gradient in crosslink density on the thickness of the samples. This article is accomplished by the measurement of dynamic mechanical thermal analysis (DTMA) with Origin software.

By comparing the obtained results from the implementation of the resin samples, this study also points out that the created interface is incompletely crosslinked network and has greater hydrophilic properties than both resin and the matrix with completely crosslinked network. Although the surface of the sample exposed to air is also incompletely crosslinked network, its hydrophilic property is smallest. The difference implies the microstructure and chemical nature of the interface (with excess amine) are different from those of the material layer on the surface exposed to air (with excess epoxy).

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