Evaluation of Interphase Properties in Fiber Reinforced Polymer Composite Using Contact Resonance Force Microscopy

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Abstract

The performance of natural fiber reinforced polymer composites as a structural material mainly depends on the quality of stress transfer in the interphase between fiber and polymer in the composite. Till now, researchers have not been able to measure the exact thickness and the mechanical properties of interphase in NFRPC. The purpose of this project was to characterize the interphase thickness and measure the mechanical properties of the interphase for first time using contact resonance force microscopy in cellulose fiber-reinforced polypropylene composites. The influence of different treatments on interphase was analyzed by quantitative mapping of mechanical properties using CR-FM, AFM phase imaging, and nanoindentation. According to the obtained images, the widths of the interphase modified with maleic anhydride polypropylene were estimated to be around 40-190 nm. The modulus values obtained by nanoindentation for fiber and PP matrix were around 13 GPa and 5 GPa respectively. There was a gradient of modulus across the interphase region which ranged between 6 to 11 GPa. The results from this research have demonstrated a new technique to evaluate the nanoscale mechanical properties within the interphase. Information about interphase obtained from this technique is very useful for optimum design of final FRPC products.

Keywords: Natural fiber-reinforced composites, interphase, elastic modulus, nanoscale properties

INTRODUCTION

Natural fiber reinforced polymer composites (NFRPC) represent one of the fastest growing industries today. Natural fibers have various advantages like low cost, low density, high toughness, acceptable specific strength, ease of separation and biodegradability, compared to conventional reinforcing fibers like glass and carbon fibers. NFRPC are more recyclable compared with glass or carbon fiber-reinforced ones (Karnani et al. 1997, Mohanty et al. 2000, Terenzi et al. 2007). Growing environmental awareness has also increased the use of natural fibers as reinforcing agents which are more compatible with the environment with respect to disposability (George et al. 2001, Mohanty et al. 2001). The combination of all these results has prompted a number of industrial sectors, especially the automotive industry, to consider natural fibers as substitute to glass fibers in various products. Today, the most growth in NFRPC market is in building products especially, decking.

The region between the reinforcing fiber and bulk polymer, termed as interphase, plays an important role in the performance of fiber-reinforced polymer composites. The interphase structure and properties is of the utmost importance for the transfer of load between the fiber and matrix which in turn affects the overall mechanical properties of the composites.

Interphase is a transition region between fiber and matrix and which possesses physical, chemical and chemical properties that are different from those of either bulk fiber or matrix (Cipari et al. 2006, Downing et al. 2000, Gao et al. 2001, Hodzic et al. 1999, Kumar et al. 2004, Lee et al. 2007). The nature of interphase varies from one composite system to another. An appropriately engineered interphase can significantly improve the strength and toughness of composites (Kim and Mai 1993). Therefore, a better understanding of interphase will be helpful to evaluate the overall properties of fiber-reinforced composites and for optimum design of final FRPC products (Graham et al. 2000, VanLandingham et al. 2001).

The major limitation in the field of interphase research is the lack of test methods that accurately measure interphase thickness in nanometer scale. Some of the methods which allow us to directly measure thick interphases are nanoindentation and nanoscratching. One of the major disadvantages of these methods is that weak or narrow interphases cannot be evaluated. These methods are inherently destructive methods creating hundreds to thousands of nanometers wide indents on the sample creating zone of plastic deformation (Lee et al. 2007). Nature of interphase less than1 µm thick is rarely reported in literature using these techniques. Very few studies have been performed on the interphase of natural fiber-reinforced polymer composites.

The purpose of this study was to characterize the interphase thickness and measure the mechanical properties of the interphase in cellulose fiber-reinforced polypropylene composites for first time using contact resonance force microscopy (CR-FM) (Hurley et al. 2003, Hurley et al. 2007). The CR-FM technique has significant advantage compared to nanoindentation and nanoscratching. It uses extreme low loads and small tip diameter which enables in situ elastic property information with nanoscale spatial resolution. Non-contact AFM phase imaging is also used in this study to compare the results obtained from the AFAM.

MATERIALS AND METHODS

Materials

Lyocell fiber with around 10 µm diameter and 30 mm length were used. Isotactic polypropylene (PP) with melt flow index of 35 was provided by ExxonMobil (Irving, TX). Maleated polypropylene (MAPP) (Epolene G-3003) was used for chemical modification and provided by Eastman Chemicals (Kingsport, TN).

Preparation of the specimens

PP and MAPP (% wt based on PP weight) were mixed in dry solid states using MINILAB extruder (Thermo Fischer Scientific, Karlsruhe, Germany).The temperature, rotation time, and processing time, were 180 C, 100 rpm and 10 min respectively. The amounts of MAPP that were used were 0 % and 10 %.The obtained products were compression molded into films approximately 0.25 mm thick. Lyocell fibers were unidirectionally placed on top of the PP-MAPP films. The films were then stacked and compression molded at 200 C for 10 min in order to obtain unidirectional lyocell fiber-reinforced composites.

Experimental methods

CR-FM technique

The samples were imaged using contact resonance force microscopy (Hurley et al. 2007). The instrument used is the one shown schematically in Figure 1. The sample to be investigated is placed on a piezoelectric transducer mounted on the AFM transition stage. The transducer is excited with a continuous sine wave voltage by a function generator and the amplitude of the cantilever deflection is observed by the AFM. Photodiode signal at the excitation frequency are obtained and a spectrum of the cantilever response versus frequency is obtained (Hurley et al. 2007).

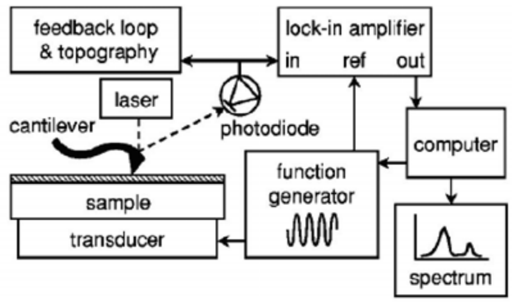

Fig 1. Schematic representation of AFAM apparatus (Hurley et al. 2003)

The principles described above for quantitative CR-FM measurements at a single sample position can also be used to acquire modulus maps. In this process, custom electronics are used to obtain images the contact resonance frequency at each image pixel. Using the frequency images, the contact stiffness is obtained, which is converted to maps of elastic modulus using nanoindentation reference values for the matrix and fiber modulus.

Obtaining phase image using non-contact tapping mode AFM

Phase Imaging is an extension of Atomic Force Microscopy (AFM) that provides nanometer-scale information about surface structure. By obtaining the phase lag of the cantilever oscillation during the non-contact mode scan, phase imaging goes beyond simple topographical mapping to detect variations in composition, adhesion, friction, viscoelasticity, and other properties. The phase lag is very sensitive to variations in material properties (Downing et al. 2000, Kim et al. 2004).

RESULTS AND DISCUSSION

CR-FM modulus mapping of lyocell/PP composites

The sample containing lyocell fibers in PP/10 wt% MAPP was imaged with CR-FM. From the experimental resonant frequencies obtained, contact stiffness images were obtained which were converted to maps of elastic modulus using nanoindentation reference values for the matrix and fiber modulus. The modulus values obtained by nanoindentation for fiber and PP matix were around 13 GPa and 5 GPa respectively. The estimated experimental spatial resolution was 10 to 15 nm.

Commercial equipment and materials are identified only in order to adequately specify certain procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

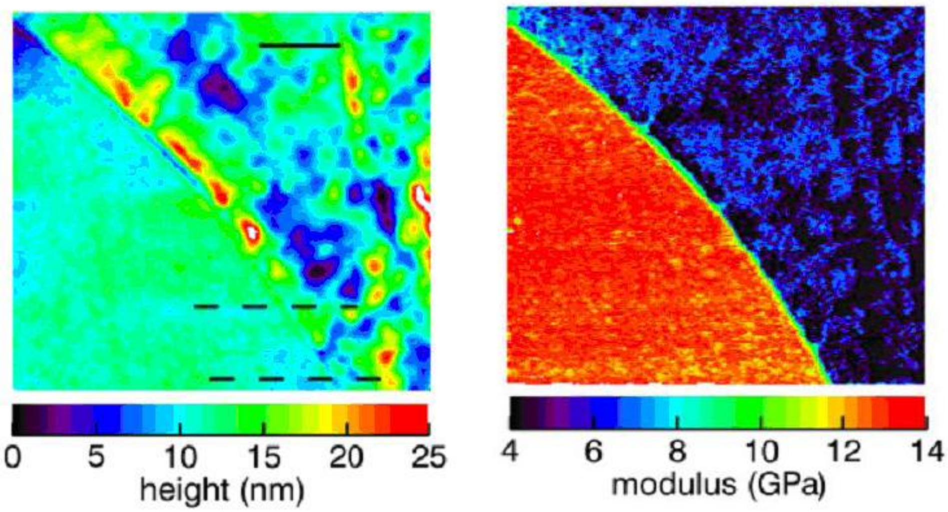

Fig 2. Topography and indentation modulus images for lyocell fiber (lower) and PP matrix (upper) in PP/10% MAPP composite. The solid line in the topography image is 500 nm wide.

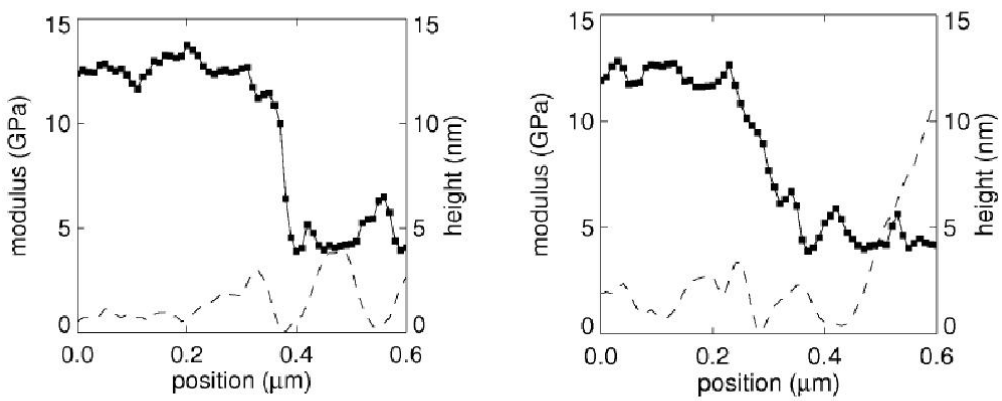

Fig 3. Variation of modulus (solid line) and topography (dashed line) across interphase region between the fiber and PP matrix. Left: upper dashed line in the topography image of Fig 2. Right: lower dashed line in Fig 2.

Different scans were analyzed from modulus map to estimate the width of interphase (fiber-matrix transition). The average width of the transition was found to be 70 ± 30 nm. There was a gradient of modulus across the interphase region which ranged between 6 to 11 GPa. Since this technique uses extreme low loads and small tip diameter and the deformation produced by the tip on the sample is elastic, the technique is devoid of any plastic deformation and is able to characterize interphase less than 100 nm.

AFM phase images of lyocell/PP composites

Phase images were obtained using non-contact mode for samples containing lyocell fibers in PP/10 wt% MAPP. Line scans were conducted on regions with minimum topographical difference to estimate the width of the interphase (fiber-matrix transition). According to the line profiles obtained from the images, the widths of the interphase modified with 10 % MAPP ranged between 80-150 nm. The values are similar to the results obtained from CR-FM measurements. From the line profile, it is quite evident that there is transition in phase change from the fiber (right) to polymer (left). Lee et al. (2007) evaluated the interphase properties in a cellulose fiber-reinforced polypropylene composite by nanoindentation and finite element analysis and based on the results, it was assumed that the interphase is less than 1 µm. The nature of interphase will always vary with different composite system.

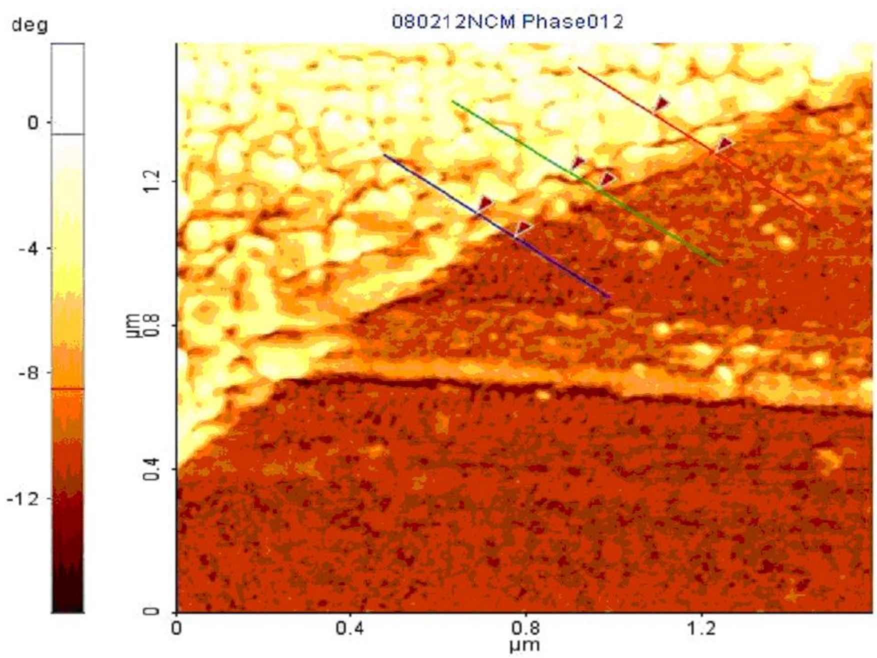

Fig 4. Phase image of PP/10% MAPP composite

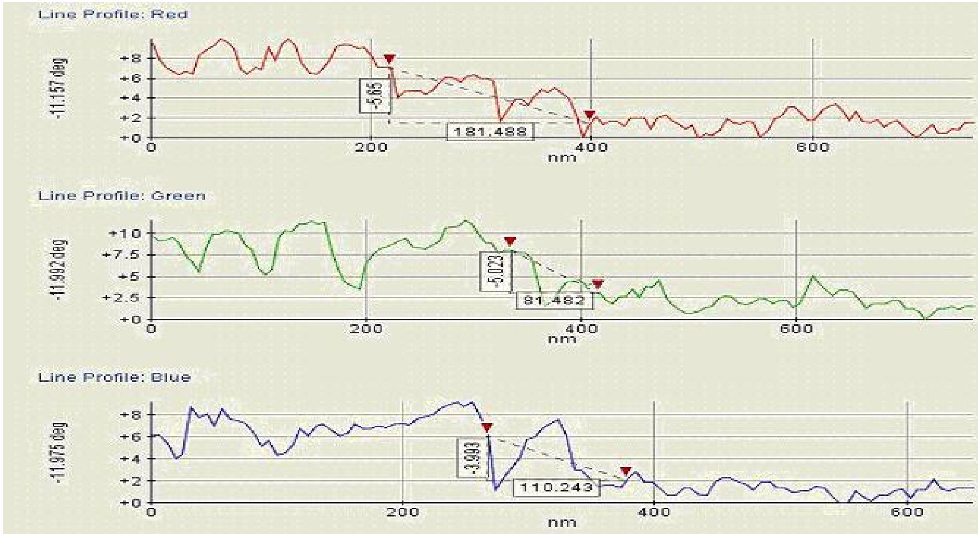

Fig 5. Line profile of the phase image for PP/10% MAPP composite

CONCLUSION

This study has revealed that CR-FM techniques can be helpful in accurately measuring the interphase thickness on the nanometer scale. The results from this study have also demonstrated the use of CR-FM as an important technique to evaluate the nanoscale mechanical properties within the interphase. According to the obtained images using CR-FM and phase imaging, the widths of the interphase modified with 10 wt% MAPP were estimated to be between 40- 190 nm. There was a gradient of modulus across the interphase region which ranged between 6 to 11 GPa.

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