

## The Interphase in Natural Fiber Composites - Transcrystallinity Effects on Thermomechanical Properties

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The use of thermoplastic reinforced with lignocellulosic fibers has been increasing steadily in the past few years. Compatibilizers have been used to improve the stress transfer between the matrix and fibers. This paper deals with the use of dynamic mechanical analysis along with optical polarized microscopy to get a better understanding of the interphase in kenaf fiber-polypropylene composites.

Kenaf fibers are extracted from the bast of the plant *Hibiscus cannabinus* and filament lengths longer than 1 m is common. These filaments consist of discrete individual fibers, generally 2 mm to 6 mm long, which are, themselves, composites of predominantly cellulose, lignin and hemicelluloses. Filament and individual fiber properties can vary depending on the source, age, separating techniques, and history of the fiber. Details on the mechanical properties of kenaf composites can be found elsewhere (1,2).

A new "solventless" technique was used to prepare samples to observe the transcrystalline zone. In prior work, to observe transcrystallinity in coupled systems, model systems were used where the coupling agent, a maleated polypropylene (MAPP), was first reacted to the fiber using a solvent (3). The fibers are then placed between films of the polymer before proceeding with the hot stage microscopy. In this work, we have used a new "solventless" technique to obtain thin films of fibers in polymer to be placed in a polarizing microscope with a hot stage. The fibers, PP and the MAPP (if used) were first blended in a thermokinetic mixer. The granulated blend was then diluted to about 1 % by adding pure PP. Samples were injection molded at higher than typical pressures. This higher pressure resulted in "flashing" in the molded specimen. The fibers in the "flashed" film

were well dispersed so individual fibers could be clearly observed. We did try using a 20 % "flashed" layer, but it was not possible to observe individual fibers. Both coupled and uncoupled blends were prepared. Since the MAPP reacts with the fibers during the compounding process, the fibers dispersed in the diluted "flashed" samples already have the reacted surface layer. Samples were heated to 220 °C to, remove the polymer morphological history, and crystallization was conducted under isothermal conditions at 130 °C. As soon as the transcrystalline zones were formed, the samples were quenched and photographed. The transcrystalline zone is formed for both coupled and uncoupled kenaf fiber-PP composites. It was observed that the crystallization rate appeared higher for the coupled system, although the quantitative rates of crystallization were not studied. The zone nucleated at several points on the fiber surface, and then grew radially outwards. Neighboring crystals impinged on each other to limit the range of lateral growth.

Dynamic mechanical analysis suggests that the transcrystalline zones contain a significant amount of defects. The  $T_{\alpha}$  relaxation in semi-crystalline polymers is due to the presence of amorphous chains in the crystalline phase (defects) a.k.a. "rigid" amorphous molecules (4,5,6). A very interesting empirical relationship was observed! The peak amplitudes or intensities of the 20, 30, 40 and 50 and 60 % fiber blend, (all weight percent) were proportional to their respective *fiber volume fractions* ( $V_f$ ) estimated from specific gravity data (figure 1, table 1). The  $\alpha$  peak amplitude or intensity is the  $E''$  increase from the onset of the  $\alpha$  transition to the peak of the transition. The similarity in the ratios of the intensities to the  $V_f$  is remarkable. This proportionality should also hold between the intensities and the fiber surface area. It is thus possible that the defects in the crystals that cause the  $T_{\alpha}$  transition for kenaf-polypropylene composites are predominantly near the fiber-matrix interface and exist in the transcrystalline zone.

The behavior of the interphase is dominated by the characteristics of the crystals. In the case of the uncoupled system, defects are formed in crystals due to restricted molecular mobility in the vicinity of a solid surface. In case of the coupled system, two independent crystalline phases (if the MAPP and PP phase separate) or a single co-crystalline phase is possible. Work by Duvall, et al. (7,8) suggests that low anhydride content maleated polypropylenes co-crystallize with PP. In our case, no indication of a separate crystalline phase was observed with the addition of MAPP, thus indicating co-crystallization. In addition to the restricted mobility provided by the fiber surface, the presence of MAPP in

the crystalline phase resulted in higher  $\alpha$  intensities for the coupled composites.

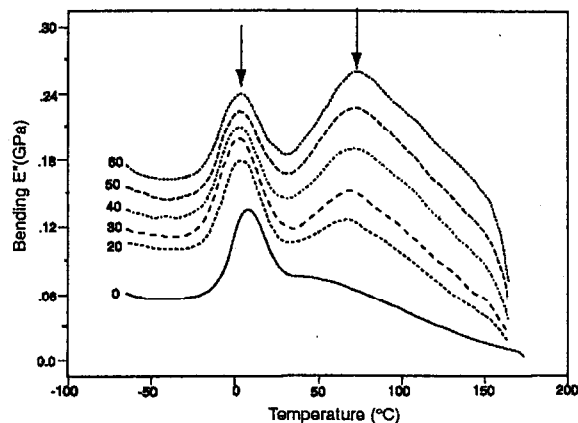


Figure 1: Variation of Loss Modulus versus temperature. (The numbers to the left of the curve indicate percent of kenaf by weight. All kenaf composites were coupled.)

TABLE 1: Intensity of the  $\alpha$  relaxation for the coupled kenaf composites.

fiber weight fraction (%)	estimated fiber volume fraction- $V_f$ (%)	Intensity (MPa)	Intensity/ $V_f$
60	47.79	76.52	1.60
50	37.89	60.87	1.61
40	28.92	45.22	1.56
30	20.73	33.91	1.64
20	13.24	20.87	1.58

## CONCLUSIONS

A new "solventless" technique to prepare samples to observe the transcrystalline zone indicated that the zone is formed for both coupled and uncoupled kenaf fiber-PP composites. Dynamic mechanical analysis suggests that the transcrystalline zones contain a significant amount of defects. The intensities of the  $\alpha$  relaxation ( $E''$  spectra) of the coupled composites were proportional to the fiber volume fractions. This may be due to the presence of MAPP in the transcrystalline zone and also to the presence of the solid fiber surface which limits the packing efficiency of the crystals. Details can be seen in the paper (9).

The MW and amount of grafted MA are important characteristics of the coupling agent. Longer molecular chains and lower anhydride content could result in crystals with fewer defects. The presence of highly

grafted molecules leads to poor crystal packing efficiencies. A minimum amount of MA is necessary to obtain good stress transfer and this is due to a strengthening of the fiber surface-transcrystalline zone interface. Longer molecules help in strong physical cross-links between transcrystalline zones and adjacent spherulites or adjacent transcrystalline regions, and also between the fiber surface and the transcrystalline zone.

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