Applications of the NanoRack™ Sample Stretching Stage to a Commercial Impact Copolymer

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A commercial impact copolymer (ICP), a multicomponent material typically used in automotive and appliance applications where a balance of stiffness and toughness is needed, was studied with the NanoRack™ Sample Stretching Stage accessory on the MFP-3D™ Atomic Force Microscope to investigate material deformation and interface adhesion as a function of tensile stress. Effects of deformation were observed within both the polypropylene and ethylene-propylene components, as well as at the interface between the two materials. There are no other direct measurement methods available to determine interfacial adhesive strength of polymer blends, and so AFM investigations of micro-domain deformation such as the one described here could be used ultimately to provide a direct determination of interfacial adhesion in complex polymer containing materials such as ICP. Studies of this kind improve our understanding of material structure-property relationships, ultimately enabling manufacture of better quality products.

Application to Impact Copolymer (ICP)

The commercial impact copolymer used for this study is composed of a polypropylene (PP) matrix with micron-sized domains of ethylene-propylene (EP) rubber domains produced in a serial polymerization reactor. Dogbone-shaped samples were molded of the impact copolymer measuring at ~20mm (middle straight part of dogbone) by ~4mm in width by 0.2mm thickness. A portion of the straight part of the dogbone was cryo-faced at -120˚C with a cryomicrotome to ensure a smooth sample and to remove the thin polymer surface layer that forms during the compression molding process (also referred to as a 'polymer skin'), leaving a small and smooth surface area in the middle of the dogbone that was suitable for imaging. The sample was mounted into a NanoRack Sample Stretching Stage with smooth grips. The NanoRack is a high-strain, high-travel manual stretching stage that provides two-axis stress control of tensile loaded samples and also allows control of the sample image region under different loads. Automatic load cell calibration provides integrated force measurements with MFP-3D images or other measurements and returns both stress and strain data.

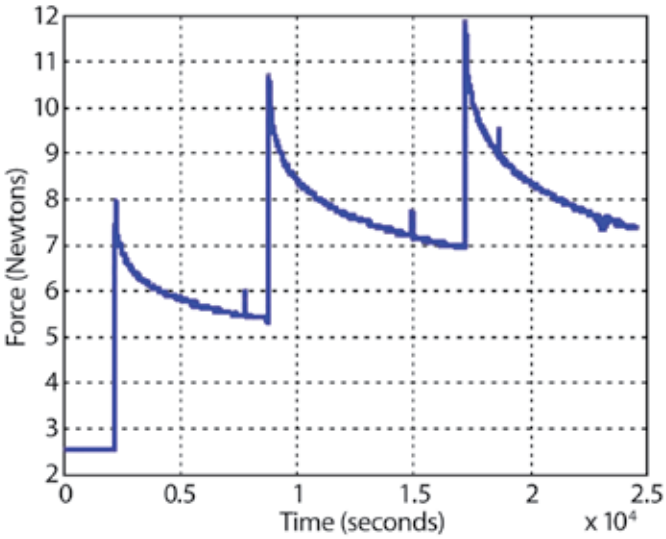

Figure 1: Stress (Newtons) vs. time (seconds) curve of ICP as it is being stretched on the NanoRack.

Figure 1 shows real-time stress vs. time curves of the ICP as the sample is being pulled in the NanoRack. The baseline force is measured at 2.55N and is a function of this particular strain gauge. Note that the force spikes immediately upon pulling and is followed by a lengthy relaxation process that is strongly

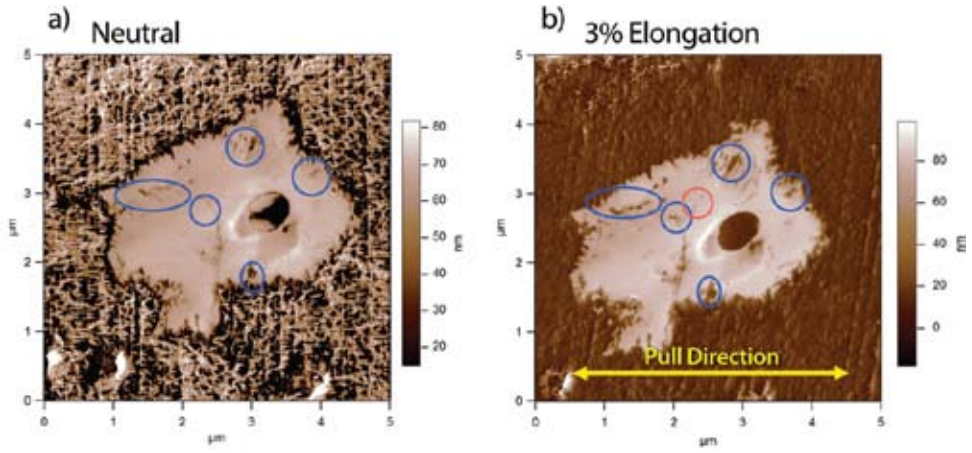

Figure 2: Amplitude mode 2 images of identical EP domain within ICP material at (a) neutral position on NanoRack and (b) 3% elongation on NanoRack.

material dependent. Even after a small initial 0.6% elongation (corresponding to pulling approximately 0.1mm on a 20mm dogbone), this ICP sample required 2-3 hours to relax after which AFM imaging could be conducted without significant drift. Stiffer samples require more relaxation time while more elastic samples may require little or no time to equilibrate after a stretch.

As the impact copolymer stretches, the individual components (PP and EP rubber) deform accordingly in response to the tensile stress. In this note, we examine the behavior within the EP rubber, within the PP, and at the PP/EP interface as the material stretches. Effects of deformation within the EP rubber are shown in the AFM images in Figure 2 where amplitude mode 2 images (from Bimodal Dual AC™ mode) are shown of the same EP rubber domain in (a) neutral position prior to any stretching and (b) after a 3% elongation stretch where the stretching direction is indicated by the yellow arrow. A 3% elongation is below the yield strain of PP. As marked by blue circles, rips within the EP rubber domain that were present in the neutral position (a) have grown both in length and width in (b) as a function of the stretching. In addition, there are areas of new growth of rips within the EP domain as shown by the region encircled in red.

The effects of tensile stress on the PP/EP interface is shown in Figure 3. The ICP material before any pulling occurs is shown in Figure 3a. After 1.1% elongation and 3.5 hours of relaxation, the image in Figure 3b shows the "stretch marks" between the EP rubber and PP at the interface. The development of stretch marks may be due to the mismatch in Poisson ratios between EP and PP materials; EP is incompressible with a 0.5 Poisson ratio, whereas PP has a Poisson ratio about 0.3 - 0.35 before yielding. If the EP domain is stretched mainly along the equatorial line as in the experiment conducted here, then stretch marks would develop mainly at top and bottom of the EP rubber domain as observed in the AFM image in Figures 3b,c. As shown in Figure 3, these marks are asymmetric about the EP rubber domain and appear to be most prominent at the bottom of the domain, though stretch marks are also observed on the top portion of the domain.

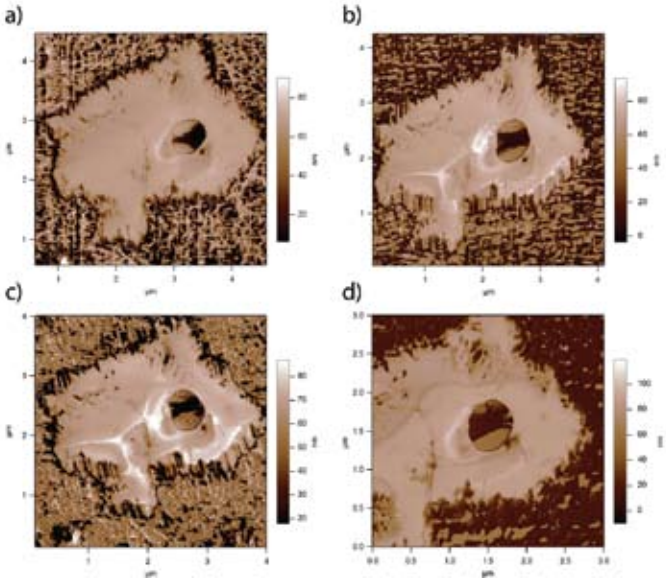

Figure 3: Amplitude mode 2 images of identical EP domain within ICP material tracked as a function of different sequential stresses exerted by the NanoRack. Sample in neutral position shown in (a). Experiment start time was marked at time of initial pull of 1.1% in length of total dogbone length. Image of ICP at 1.1% elongation length shown in (b) 3.5 hours after start of experiment. ICP image at 1.7% elongation length shown in (c) 7 hours after start of experiment. Image of ICP at 1.7% elongation length after sample in (c) equilibrated overnight for a total of 26 hours after start of experiment shown in (d).

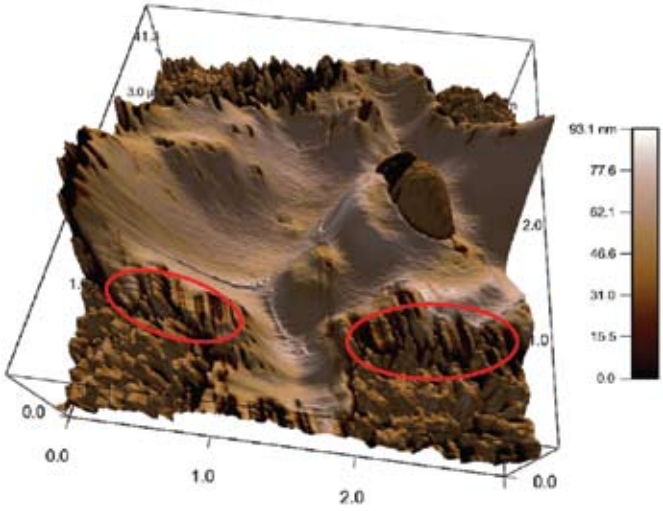

Figure 4: 2nd mode amplitude overlaid onto 3-D topography of ICP material rendered from Figure 3b. Interface showing stretching of the EP domain as it adheres to the PP is circled in red.

These stretch marks remain throughout the pulling experiment on the first day as evidenced in the AFM image of the same domain at 1.7% elongation and 7 hours after initial pull (Figure 3b,c). The sample was allowed to sit overnight at 1.7% elongation and the next morning revealed a disappearance of the stretch marks as shown in the AFM image of Figure 3d, suggesting the yielding of the PP matrix overnight. An overlay of amplitude mode 2 on top of the underlying topography of Figure 3b is shown in Figure 4, showing topographic deformation within the EP domain but the absence of a gap between the two components, indicating reasonable adhesion between the two components.

Finally, the effect of the stress within the PP matrix at 2% elongation is shown in Figure 5. Both topography (a) and phase (b) images of a large-area (15µm) scan size show a number of areas where cracks have formed at the EP-PP interface and propagated into the PP matrix; some of the cracks are highlighted in blue/orange circles. The developments of cracks or shear bands and micro-voids may come from stress amplification in the ICP material due to the presence of EP rubber domains. Note that this sample, whose images are in Figure 5, was pulled on a different day than the one shown in Figure 3. In the latter, the stress exerted on the sample did not reveal micro-voids or cracks within the PP – at least in the narrow region that was being imaged in Figure 3, where a single EP domain was being followed. Maximum stress amplification by a spherical EP rubber domain is inversely proportional to the square root of the crack tip radius and occurs at the poles of the EP rubber domain. All these cracks and shear bands in Figure 3 appear to originate at the polar locations of the EP rubber domains, probably at sharp corners of the rubber domain with extremely small crack tip radii (and therefore

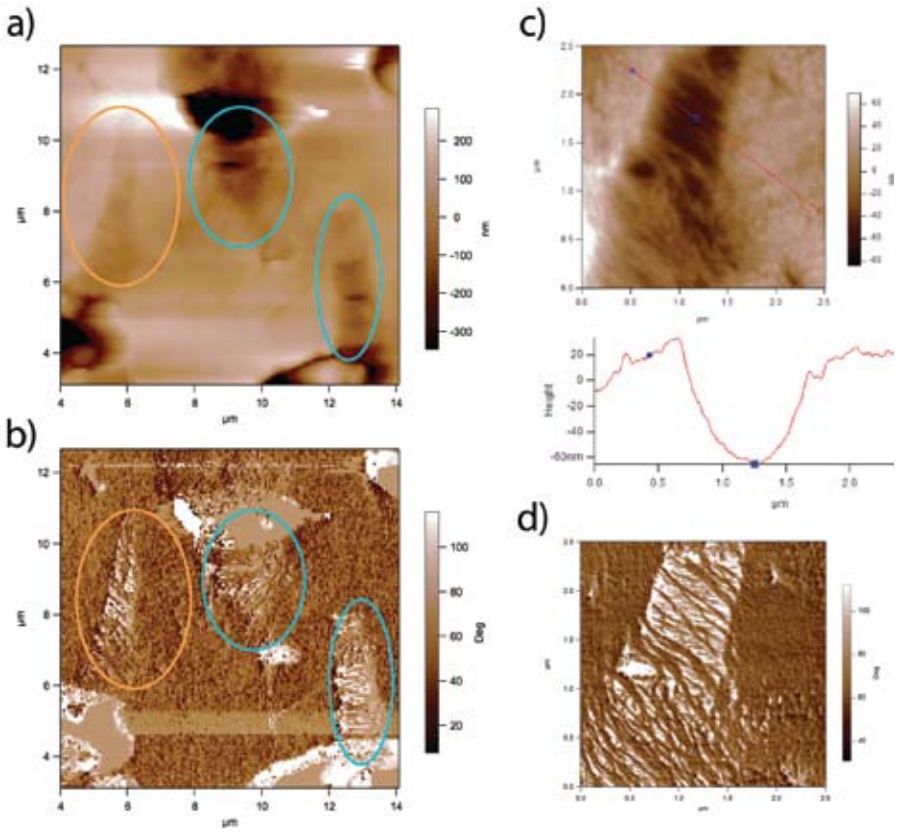

Figure 5: Corresponding topography (a) and phase (b) images of 15µm x 15µm area of PP matrix within ICP material at 2% elongation. Regions of large crack formation are highlighted in orange and blue circles. Zoom in on crack highlighted in orange circle in (a) is shown in corresponding topography (c) and phase (d) images. Line scan in (c) along red line measures width and depth of crack.

maximum stress amplification resulting in a stress singularity at that point). The appearance of these shear bands and micro-voids suggests that the local stresses well exceed the yield stress despite the 2% global deformation.

As shown in Figure 5, the larger (highlighted) cracks propagate several microns. However, there are also several cracks with significantly smaller dimensions of a couple hundred nm in length and tens of nm in width. Zooming in on the crack circled in orange (in Figure 5b) reveals tiny PP fibrils stretching across the entire width of the track, as shown in the corresponding topography (c) and phase (d) images, at about 45 degree to the stretching direction suggesting that the cracking is induced by shear deformation. This particular crack is measured to be ~80nm in depth and ~600nm in width.

Summary

Morphology and interface adhesion of an impact copolymer (ICP) were studied using atomic force microscopy with a NanoRack tensile stage. Effects of deformation were observed within both PP and EP components as well as at the interface between the two materials. A continued stretching of the ICP could lead to delamination of EP from PP matrix. The strain required to separate the EP domains from the PP matrix could be used as a measure of the interfacial adhesion between EP and PP. Most importantly, the corresponding local interfacial stretching extent or void length between EP and PP upon delamination, which can be measured directly by AFM, can be used to calculate the interfacial strength between EP and PP. Presently, there are no direct measurement methods available to determine interfacial adhesive strength of nano- and microscale domains within polymer blends, especially blends generated in-situ in polymerization reactors. This AFM examination of micro-domain deformation through the usage of the NanoRack described qualitatively here could be used for direct determination of interfacial adhesion in complex polymer-containing materials such as blends and composites.

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