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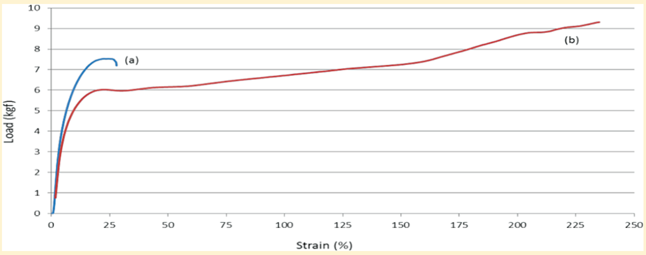
Single-Component Polymer Composites

A. Gurarslan and A. E. Tonelli*

Fiber & Polymer Science Program, North Carolina State University, Campus Box 8301, Raleigh, North Carolina 27695-8301, United States



ABSTRACT: Noncovalently bonded crystalline inclusion compounds (ICs) have been formed by threading host cyclic starches, cyclodextrins (CDs), onto guest nylon-6 (N-6) chains. N-6 was coalesced from N-6-α-CD-IC crystals by appropriate removal of the host α-CD. When added at low concentrations, the coalesced N-6 serves as an effective self-nucleating agent for the bulk crystallization of N-6 from the melt. Film sandwiches consisting of two layers of as-received, and one layer each of as-received and self-nucleated N-6 were produced by melt pressing. DSC and tensile tests were conducted on these films. As-received and self-nucleated films have their own characteristic crystallization behaviors, and the film sandwich composed of one layer each of as-received and self-nucleated N-6 show a combination of the component melt-crystallization DSC peaks, indicating that both films maintain their characteristic structures and properties even after melt-processing them into a sandwich composite. This result clearly shows that we have a composite and not a single phase material and is supported by SEM images of the composite sandwich cross section. Furthermore, when compared to the film sandwich made with two layers of as-received N-6 film, the composite as-received/self-nucleated film sandwich shows superior mechanical properties.

INTRODUCTION

Polymer composite materials, generally formed by embedding and orienting fibers (polymer, glass, carbon, etc.) in a thermoplastic matrix polymer, usually fail at the weak fiber/matrix interface, resulting from their chemical incompatibility. The ideal solution to the interface problem in such composites would be to use reinforcing fibers and embedding matrix made from the same polymer, which would eliminate the incompatibility issue. However, because fiber and matrix would generally soften at the same temperature,[1−6] it is difficult to see how such a composite could be fabricated.

Previous attempts[1−4] were made using polyethylenes (PE), where gel-spun ultra high-MW PE fibers (T_m = 150 °C) and high-density PE matrix (T_m = 130 °C) were employed. However, the mechanical properties of the UHMWPE/HDPE composites were not found to be superior to two-component composites made with UHMWPE fibers and chemically dissimilar matrix polymers.

In addition, single-component composites might potentially be fabricated using reinforcement fibers made from stereocomplexed polymers, such as poly(L- and D-lactic acids) (PLLA and PDLA),[5] or isotactic (i) and syndiotactic (s) poly(methyl methacrylates) (PMMA),[6] which have T_ms above either of their pure stereoisomeric crystalline polymers or the T_gs of their stereoirregular amorphous polymers. However, while stereocomplexed PLLA/PDLA fibers can be melt spun,[7] i- and s-PMMAs cannot, but instead have recently been electrospun from solution.[6] Furthermore, these stereocomplexed fibers are not likely to be fully compatible with matrices made with their stereoirregular amorphous or stereoregular semicrystalline counterparts.

Each of these approaches relies on the higher melting temperatures of highly oriented and crystalline gel-spun UHMW PE or stereocomplexed PLLA/PDLA or i-PMMA/s-PMMA fibers in comparison to the melting or softening temperatures of their chemically identical or closely similar matrix polymers. As such, their composites must be formed at temperatures above the softening temperatures of the matrix and below the melting temperatures of the reinforcing fibers. The resulting interfaces between them, though potentially chemically compatible, are likely not very highly interpenetrating and strong because the reinforcing fibers remain solid and their constituent polymer chains immobile as the matrix polymer is melt-processed into them.

A second approach for producing single-component polymer composites is the hot-compaction method,[8] which was employed to form single-component PE, PP, PET, PMMA, N-6,6, and N-6 composites.[9] In this technique the initial material is either uniaxially aligned fibers or woven fabric. Under appropriate applied temperatures, pressures, and processing times, partial melting occurs on the fiber surfaces and acts as a glue to bind the remaining unmelted regions. In other words, melted regions form the matrix and unmelted regions form the reinforcing units. Good reinforcements must possess properties that are superior to those of the matrix, but in hot-compaction composites the reinforcements are partially melted fibers with reduced performance. Improving the properties of the reinforcing units will be necessary to improve the properties of composites made by hot compaction.

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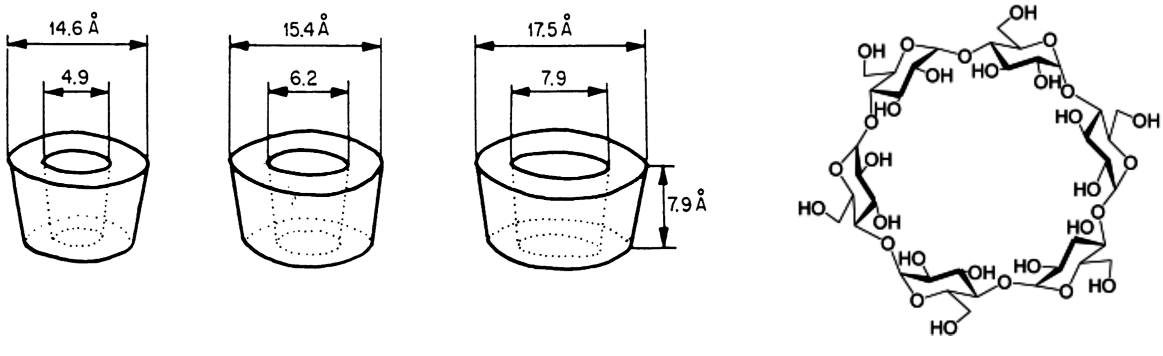

α-CD **β-CD** **γ-CD** **α-CD**

Figure 1. Cyclodextrin structures and dimensions.

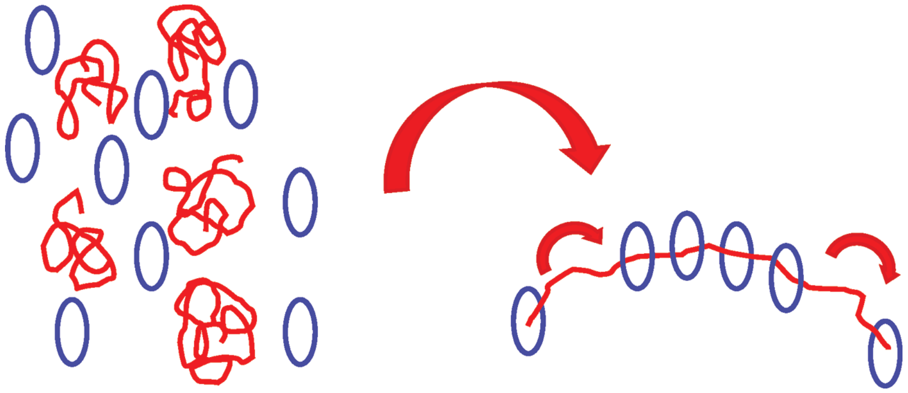

Figure 2. Schematic illustration of host CDs threading over guest polymers to form ICs.

Another potential solution would be to make the reinforcing component from the same polymer as the matrix, but with the constituent polymer chains in the reinforcing component organized in a way that provides superior mechanical properties and prevents their diffusion into the matrix polymers during their melt-processing into a single-component composite. Such a reorganization of polymer chains may be achievable by coalescing guest polymers from their crystalline inclusion compounds (ICs) formed with the host cyclic starches, cyclodextrins (CDs).

CDs are water-soluble, cyclic, oligomeric saccharides formed during the enzymatic degradation of starch and generally contain 6 (α-CD), 7 (β-CD), or 8 (γ-CD) α-1,4-linked glucose units (see Figure 1). They are widely known to act as hosts for a large variety of guest molecules, including polymers,[10,11] forming noncovalently bonded inclusion compounds (ICs), as illustrated in Figures 2 and 3. Polymer chains included in CD-ICs are necessarily both highly extended and isolated from neighboring chains because they are threaded through and confined in the narrow CD channel cavities (see Figures 1−3). As suggested in Figure 3, if the host CDs in polymer-CD-ICs are carefully removed, permitting the guest polymer chains to coalesce into a bulk solid sample, then it can be reasonably expected that the arrangement of chains, i.e., their conformations and packing, might be significantly different from that normally produced from their randomly coiling and entangled solutions or melts. This expectation has indeed been confirmed numerous times in our laboratory.[11]

Processing with CDs in this manner can serve to nanostructure polymers, leading to new properties and a greater understanding of their behaviors. Particularly critical in the present context is the observation[11,12] that the thermal and temporal stabilities of the organization of coalesced neat homopolymers, well-mixed homopolymer blends, and block copolymers, are substantial, thereby suggesting retention of their as-coalesced structures and morphologies under normal thermal processing conditions. The thermal stability of polymers coalesced from their CD-ICs has recently been suggested[12] to be the result of the long times necessary to establish a fully entangled melt between the many chains influenced by a single coalesced polymer chain, after it has randomly coiled.

As a consequence, here we suggest the formation of single-component fiber/polymer composites, where the reinforcement is provided by melt-spun fibers nucleated with small amounts of chemically identical polymers coalesced from their CD-ICs. In the melt, polymer chains from these self-nucleated fibers should not rapidly diffuse into the matrix and upon cooling will crystallize before the matrix and should retain their distinct structural/morphological/positional integrity. Because both the reinforcement fibers and the matrix melt during processing, their interfaces are expected to be at least somewhat interpenetrating, as well as chemically compatible, and, as such, they may provide superior reinforcement.

To assess the potential success of our approach, we measure our results against whether or not the single-component polymer composites described here show distinct behaviors for the matrix and the reinforcement and improved mechanical properties over the matrix alone.

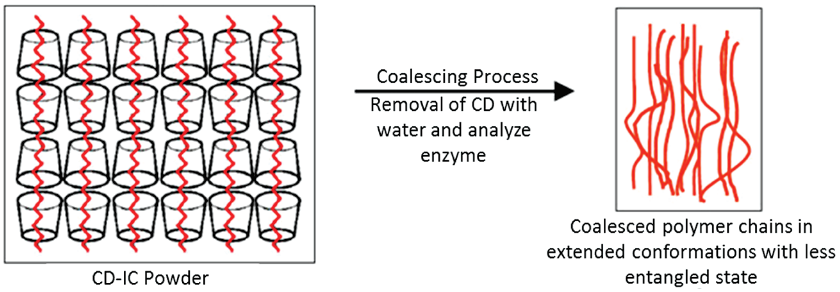

Figure 3. Illustration of the process of coalescing polymer chains from their crystalline CD-ICs to form a bulk coalesced polymer sample. Please note that, though the guest polymer chains in each crystal of the CD-IC powder are expected to be coalesced as indicated, we do not mean to imply that this results in overall macroscopic orientation of all extended unentangled chains. Rather, we believe the macroscopic organization to be something like a collection of small "nematic-like" regions randomly arranged without a preferred orientation of their directors.

EXPERIMENTAL SECTION

Materials. Nylon-6 (N-6) having a molecular weight of 60 000 was obtained from BASF (Ultramid B4001). All solvents were obtained from Sigma-Aldrich, α-cyclodextrin was obtained from Cerestar, and a nonstick film made of Teflon PTFE was obtained from McMaster-Carr.

Methods. Formation of stoichiometric 1:1 N-6-α-CD-IC followed our previous work,[13,14] where here we increased the scale of preparation. 2 g of N-6 was dissolved in 60 mL of 90% formic acid at room temperature, and 240 mL of 99% acetic acid was added to the solution. 17.08 g of α-CD was dissolved in 84 mL of 99% dimethyl sulfoxide. The dissolved α-CD was then added to the N-6 solution. Their combined solution was stirred and heated on a hot plate at 50 °C for 2 h, then cooled to room temperature, and continuously stirred for another 6 h. The precipitate was vacuum filtered after rinsing with formic acid and deionized water and finally dried in a vacuum oven for 24 h.

The coalescence process to remove the host cyclodextrin channels from 1:1 N-6-α-CD-IC was accomplished by stirring the IC in excess deionized water for 2 h. In this process coalescence occurs faster if the particle size of precipitated IC is small.

N-6 films containing 2 wt % coalesced N-6 (c-N-6) as a nucleant were produced by dissolution of N-6 in 90% formic acid at room temperature, suspension of the nucleant upon addition with stirring, and removal of the formic acid by evaporation. Four kinds of films were obtained by placing the appropriate materials on a constraining, nonstick Teflon sheet. 1 g each of as-received N-6 (asr-N-6) pellets and self-nucleated N-6 (nuc-N-6) were melt-pressed at 240 °C with an applied pressure of 1.75 MPa for 6 min to produce asr- and nuc-N-6 films, respectively. Also, 1 g of asr-N-6 film was melt-pressed at 240 °C onto 1 g of either asr-N-6 film (reference) or 1 g of nuc-N-6 film (single polymer composite) under a pressure of 2.62 MPa for 1 min to create two film layer "sandwiches".

Infrared spectral studies were conducted with a Nicolet 510P FTIR spectrometer in the range 4000−400 cm^{-1}, with a resolution of 4 cm^{-1}. Powdered α-CD, asr-N-6, N-6-α-CD-IC, and c-N-6 samples were pressed into KBr pellets for the FTIR absorption measurements.

Differential scanning calorimetric (DSC) thermal scans were performed with a Perkin-Elmer Diamond DSC-7 instrument. The measurements were run in the range 25−250 °C at a heating and cooling rate of 10 °C/min. Nitrogen was used as the purge gas.

Tensile tests were conducted according to ASTM D-882-97 using a MTS Q-Test/5, CRE type tester. The test specimens were prepared by cutting 0.25−0.29 mm thick films into 6 mm wide and 90 mm long dog bone shapes using a template. Tensile tests were performed using a 250 lb load cell, and the gauge length was 50 mm. The cross-head speed was 500 mm/min for the film sandwiches with two layers of asr-N-6 films and 50 mm/min for the other films. Modulus, peak load, and % elongation at break data were acquired at the end of each test from the load−elongation curve, and each value of the mechanical properties reported was an average of at least five test specimens.

Scanning electron microscope (SEM) images were recorded on the N-6 film sandwiches using a FEI Phenom. The film sandwiches were placed onto specimen mounts with double-sided conductive carbon tape and coated with gold/palladium to reduce charging. A Quorum Technologies SC7620 mini sputter coater was employed for 45 s.

RESULTS AND DISCUSSION

It has been demonstrated that coalesced polymers, when added in small amounts, effectively nucleate the melt-crystallization of the same bulk polymers.[13−15] More importantly, the finer scale morphology produced during the melt-crystallization of polymers containing their coalesced polymers as nucleants has been observed to translate into significant improvements in their mechanical properties.[14,15] As a consequence, polymer layers self-nucleated with the same coalesced polymer may provide superior reinforcement in composites made with the same matrix polymer for two reasons: (1) compatibility of the self-nucleated polymer with the matrix and (2) mechanical properties superior to those of un-nucleated polymer.

In order to produce self-nucleating agents, stoichiometric N-6-α-CD-IC's were produced and N-6 coalesced from them by appropriate removal of host α-CD. This procedure can be confirmed by FTIR. Figure 4 shows the characteristic peaks for α CD (a) and N-6 (c). The 1:1 N6-α-CD-IC (b) possesses both N-6 and α-CD peaks, while after removing the host α-CD, only c-N-6 polymer chains remain, as seen in (d). Should c-N-6 contain small amounts of remnant α-CD, they should have little if any effect on nuc-N-6 because only 2 wt % c-N-6 is used to nucleate asr-N-6 and produce nuc-N-6.

Note the improved resolution of the c-N-6 spectrum, which may be a consequence of the previously suggested improved order in the noncrystalline regions of the sample (see Figure 3), where the chains are not as nearly randomly coiling or interpenetrating as those in the noncrystalline regions of asr-N-6.[16] The generally broad IR bands observed in polymer samples are undoubtedly due to the large variety of polymer conformations and chain packing environments surrounding each vibrating molecular bond or group. Because of the improved order in the noncrystalline regions of the c-N-6, vibrating molecular bonds and groups are subjected to smaller variations in their local conformational and packing environments.

Coalesced N-6 at 2 wt % was used as a nucleating agent during the melt-crystallization of asr-N-6. These self-nucleated

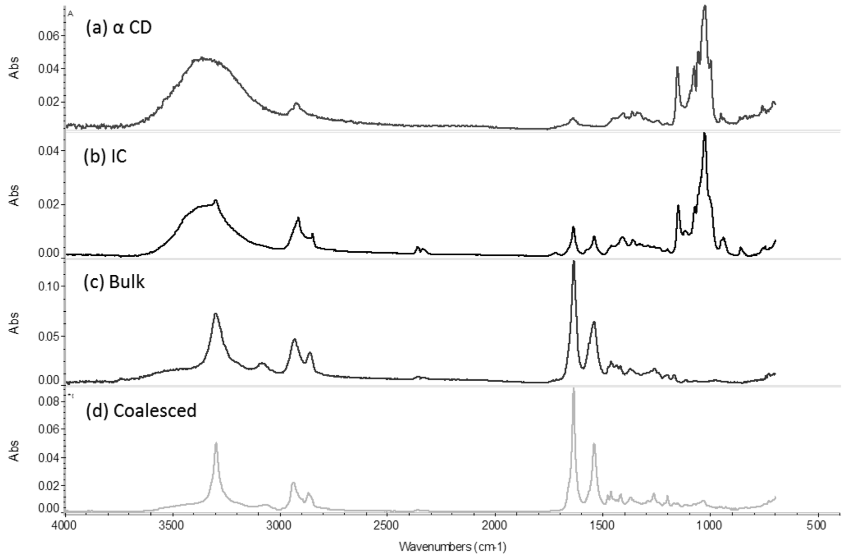

Figure 4. FTIR spectra for (a) α-CD, (c) 60 000 g/mol asr-N-6, their (b) 1:1 stoichiometric IC, and (d) c-N-6.

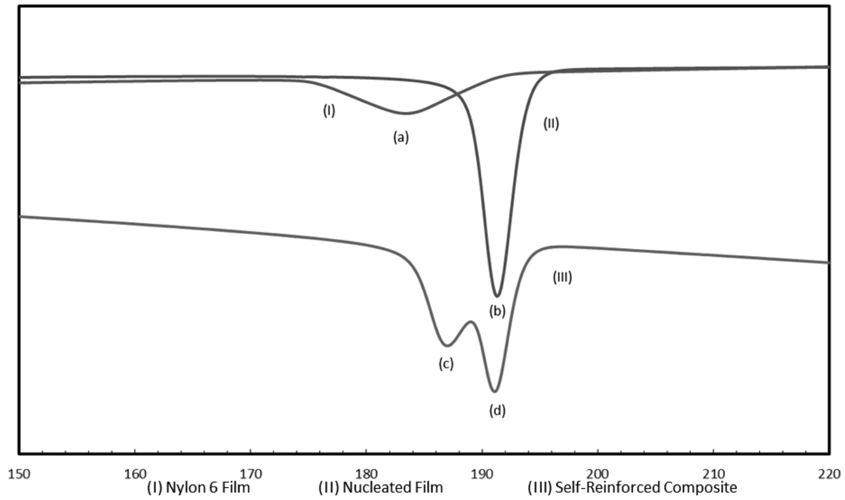

Figure 5. DSC cooling scans from the melts of (I) asr-N-6, (II) nuc-N-6, and (III) asr-N-6/nuc-N-6 sandwich films. Peaks (a), (b), (c), and (d) correspond to T_cs of 183.5, 191.5, 186, and 191.1 °C, respectively.

(nuc-N-6) films were melt-pressed onto asr-N-6 films, and asr-N-6/nuc-N-6 sandwich films were obtained. DSC results of asr-, nuc-, and the asr-N-6/nuc-N-6 sandwich are presented in Figure 5. Each sample spent a total of ~10 min in the melt during melt-pressing and DSC observations. It is evident that, upon cooling from the melt, the two-layer asr-N-6/nuc-N-6 sandwich film shows two crystallization exotherms that are characteristic of each layer. These observations prove that the asr-N-6 film and the film (nuc-N-6) made from asr-N-6 nucleated with c-N-6 do not become homogeneously mixed during melt-processing.

As a control experiment to ensure the central role played by the host α-CD in restructuring N-6, asr-N-6 was dissolved in formic acid and stirred for 8 h, filtered and washed with deionized water, dried in a vacuum oven, and pressed into a film. DSC observation of this control asr-N-6 film showed a broad melt-crystallization peak at 184.5 °C, which is close to that observed for the untreated melt-pressed asr-N-6 film in Figure 5.

Table 1. Tensile Test Results for asr-N-6/asr-N-6 and asr-N-6/nuc-N-6 Sandwich Films

film sandwich	Young's modulus [MPa]	% strain at break
2 as-r N-6 layers	758	250
as-r/nucN-6 layers	861	19.6

In a previous study,[14] we showed that self-nucleated single layer nuc-N-6 films have higher moduli and lower elongations at break than asr-N-6 films, and even asr- N-6 films annealed to achieve the same amount of crystallinity as the nuc-N-6 film. For this reason we decided to use the nuc-N-6 films as reinforcing components in the N-6 composites. Table 1 shows that the asr-N-6/nucl N-6 film sandwich has an increased Young's modulus (+14%) and reduced elongation at break (−92%) compared with the asr-N-6/asr -N-6 sandwich films. We also previously showed that c-N-6 crystallizes predominantly in the α-polymorph, while asr-N-6 shows a significant amount of the

γ-polymorph as well.[17] Though not presented here, powder X-ray diffraction of nuc-N-6 is closely similar to asr-N-6, so the improved strength of nuc-N-6 is not caused by a different crystal structure, but rather by a finer scale more homogeneous semicrystalline morphology, as demonstrated in ref 14.

From sample to sample, the yield stresses of the composite and control film sandwiches were comparable, with average yield stresses of 42.3 and 41.1 MPa, respectively. Load at break values of asr-N-6/asr-N-6 film sandwiches are higher because they fail as a ductile material with necking. It is well-known that necking creates a new microstructure, which requires a much higher load to break the material than to cause yielding/necking. On the other hand, asr-N-6/nuc-N-6 film sandwiches are brittle and break without necking at loads very similar to those at which they yield.

SEM images of the cross-section of asr-N-6/asr-N-6 and asr-N-6/nuc-N-6 film sandwiches are presented in Figure 6. While the interface between the asr-N-6/asr-N-6 layers is not apparent, it is for the asr-N-6/nuc-N-6 film sandwich. Consistent with our DSC results, the asr-N-6 film and the film made from asr-N-6 nucleated with c-N-6 do not become completely and homogeneously mixed during melt processing. Figure 6 also indicates excellent compaction of the two layers.

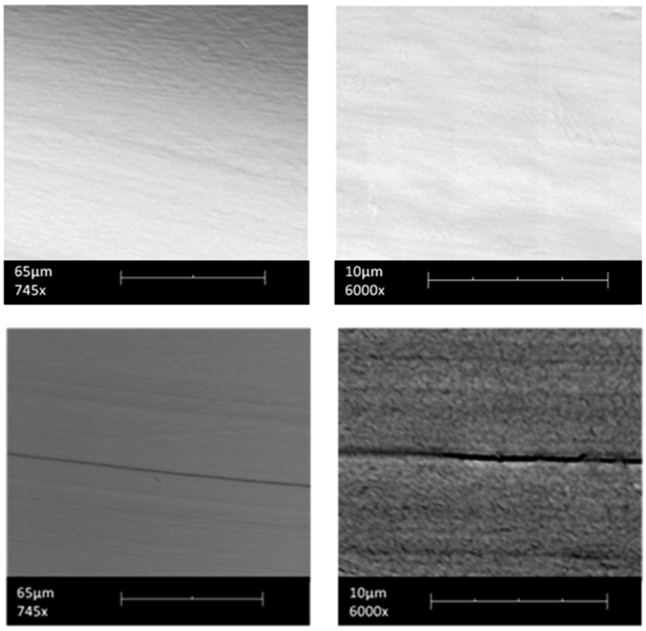

Figure 6. SEM images of the cross section of as-pressed asr-N-6/asr-N-6 (upper) and asr-N-6/nuc-N-6 (lower) film sandwiches.

During tensile testing of the film sandwiches, the applied load creates shear stress between the two layers. If the adhesion forces between the layers are weaker than the resulting shear stress, then delamination occurs and can be observed in the tensile load−extension curves. We did not observe any delamination in asr-N-6/nuc-N-6 sandwich films during our tensile tests, indicating interfacial adhesion stronger than the shear stress between film layers (see Figure 7). Moreover, the asr-N-6/nuc-N-6 film sandwiches break with low elongation values similar to single layer nucleated films.[14] From this observation we can infer that interfacial forces also prevent the elongation of the inherently more extensible as-received layer. This strong interface is the result of both component films melting during their pressing into a sandwich. Apparently spending ~10 min above their melting temperature provides sufficient time for the mobile N-6 chains in both film layers to partially interpenetrate each other, but not enough time to diffuse entirely through each layer.

CONCLUSIONS

In this study, we made single-component polymer composites with mechanical properties that are superior to those of the as-received matrix polymer. Our approach relies on producing reinforcement material made from polymers processed with CDs. When coalesced from their CD-ICs and used as nucleants for melt-crystallization of the same bulk polymer, the CD-processed (coalesced) polymers are reorganized, with structures morphologies and properties distinct from samples produced from their neat randomly coiling and entangled melts. Furthermore, and critical to our approach, is the observation that they remain distinctly reorganized even after annealing above their T_gs and T_ms for long periods of time.[12] For this reason a layer nucleated with the same coalesced polymer remains structurally, morphologically, and positionally distinct from the as-received layer when melt-processed into a composite.

Unlike UHMWPE/HDPE composites,[1−4] that relied on the elevated T_m of gel-spun UHMWPE fibers, both the CD-processed/self-nuleated layer and the as-received layer melt during the formation of their single-component composites.

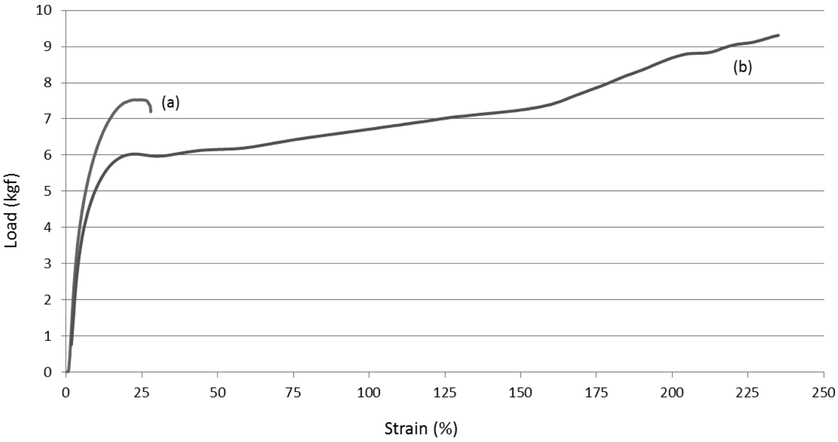

Figure 7. Strain responses of asr-N-6/nuc-N-6 (a) and asr-N-6/asr-N-6 (b) sandwich films to applied loads.

In other words, due to the slow melt diffusion of polymer chains[12] between the nuc-N-6 and asr-N-6 films, they are able to retain their distinct structural and positional integrities, while producing necessarily compatible and stronger interfaces. Unlike the UHMWPE/HDPE[1−4] composites or those suggested by using fibers formed with higher melting stereocomplexed polymers,[5,6] both the CD-processed (nuc-N-6) and asr-N-6 layers melt during composite processing, providing an opportunity for polymer chains near the film surface to at least partially penetrate into or be penetrated by chains from the contacting adjacent film. Stronger interfaces are obtained because at least some limited interpenetration of nucleated and as-received polymer chains occur during their processing into a single-component composite. In addition, unlike the hot-compaction method,[8,9] the self-nucleated (nuc-N-6) layer provides a reinforcement component stronger than the asr-N-6 matrix layer.

Future Work. These "proof-of-concept" experiments are sufficient to suggest that our proposed approach for constructing single-component composites with CD-processed and restructured reinforcement films and chemically identical matrix polymers can produce mechanically superior composites. This despite the fact that no attempt has been made to align chains and crystals in the reinforcing self-nucleated films. Consequently, we anticipate further and more detailed processing and characterization of these one-component composites, particularly for reinforcement fibers made from self-nucleated polymers. This would include drawing of both the nucleated reinforcing fibers and subsequently formed composites to improve the orientation of polymer chains and reinforcing fibers, respectively; annealing the composites, during drawing, between the melt-crystallization temperatures of the reinforcing fibers and the matrix; further mechanical testing (impact, flexural, and peel strengths); and measurement of small molecule diffusion through the composite film sandwiches.

AUTHOR INFORMATION

Corresponding Author

*E-mail: alan_tonelli@ncsu.edu.

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