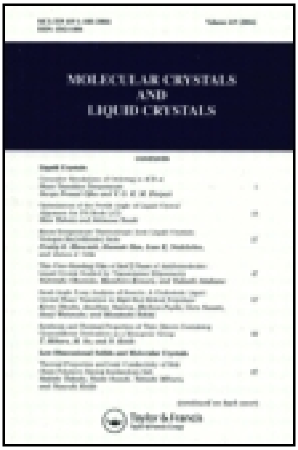

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# Biodegradable Copolymers of 3-Hydroxybutyrate-co-3-Hydroxyhexanoate (Nodax$^{TM}$), Including Recent Improvements in their Mechanical Properties

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# Biodegradable Copolymers of 3-Hydroxybutyrate-co-3-Hydroxyhexanoate (Nodax$^{\mathrm{TM}}$), Including Recent Improvements in their Mechanical Properties

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*A general review is first provided on the properties of this important member of the class of polyhydroxyalkanoate copolymers now being actively investigated as environmentally friendly materials. This soon to be commercialized material is already finding numerous applications and has the advantage of biodegradability, but its mechanical properties have not yet been fully optimized.*

*In recent work, pre-orientation of uncrosslinked and crosslinked Nodax films was found to improve their moduli, tensile strengths, and yield stresses, as well as increasing (or at least maintaining) their toughness. These improvements presumably resulted from increases in crystallinity with orientation, a conclusion supported by increases in the intensity of X-ray diffraction patterns of the pre-oriented samples relative to those of the unoriented ones. Pre-orientation techniques could therefore be very useful in processing such materials for industrial applications.*

*Addition of organoclay to Nodax was found to significantly improve thermal stability. These nanocomposites had structures ranging from exfoliated layers of clay at low contents to intercalated ones at higher contents. These changes in structure*

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*were investigated through X-ray diffraction peaks, with shifts in the peak toward lower values indicating intercalation and decreases in intensity of the clay peak indicating exfoliation. In the case of this reinforcing filler, the major advantage was increased moduli, but at the cost of decreased values of the elongation at break and toughness. Some of these disadvantages might be avoided by the use of other layered fillers, such as mica or graphite. Also, there are obviously other improvements possible in such layered nanocomposites, including decreases in flammability, and increases in solvent resistance and barrier properties.*

**Keywords:** cross-linked Nodax; mechanical properties; Nodax/clay nanocomposites; polyhydroxyalkanoate copolymers; poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (NodaxTM); pre-orientation; WAXS measurements

## 1. INTRODUCTION

Conventional polymers such as polyethylene and polypropylene resist degradation for many years after they're disposed. In contrast, biodegradable polymers can degrade by disposal in bioactive environments such as bacteria, fungi, and algae, or by hydrolysis in buffer solutions or sea water. Worldwide consumption of such biodegradable polymers has increased from 14 million kg in 1996 to an estimated 68 million kg in 2001 [1]. Target markets for these biodegradable polymers include packaging materials (for example, trash bags, wrappings, loose-fill foam, food containers, film wrapping, laminated paper), disposable nonwovens (engineered fabrics) and hygiene products (diaper back sheets, cotton swabs), consumer goods (fast-food tableware, containers, egg cartons, razor handles, toys), and agricultural tools (mulch films, planters) [1]. Among the challenges in commercializing biodegradable polymers are competition with commodity plastics that are inexpensive and familiar to the customer, and the lack of an infrastructure for disposals in bioactive environments.

Among the many categories of biodegradable polymers, polyhydroxyalkanoates (PHAs) have attracted much industrial attention due to their biodegradability and biocompatibility. They are produced directly from renewable resources by microbes which accumulate PHAs as carbon and energy storage materials under unbalanced growth conditions [2]. Poly(3-hydroxybutyrate) (PHB) homopolymer and copolymers of it and 3-hydroxyvalerate (PHBV) are the most familiar types of PHAs [3–5]. PHB itself exhibits an unusually high degree of crystallinity due to the stereoregularity of the perfectly isotactic chains created by the bio-catalyzed polymerization process. This high crystallinity results in a rather brittle and hard material that is not very useful for many applications, and its very high melting point (>170°C) make it difficult to use melt processing equipment [6]. It was hoped that the incorporation of a comonomer unit, 3-hydroxyvalerate (3HV), could decrease the excessively high $T_m$ and control the levels of crystallinity. Unfortunately, the desired effect of 3HV incorporation to control $T_m$ and the degree of crystallinity was unexpectedly limited because of isodimorphism (where HV units were easily included in the crystal lattice of the 3-hydroxybutyrate (HB) units and vice versa). This limited the desired disruption of the crystallinity from the comonomeric units [4,6].

Alternative PHA copolymers therefore had to be designed to overcome this problem. Specifically, the isodimorphism was avoided by copolymerization of HB with longer hydroxyalkanoic acids which can't fit into each others' crystalline lattice [7–11]. In particular, copolymers consisting of HB and 3-hydroxyhexanoate have mechanical properties even better than those of PHBV, making them comparable with conventional plastics, such as isotactic polypropylene and polyethylene [6]. This poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) material is now part of the Nodax$^{TM}$ family. It provides a unique combination of properties such as full anaerobic degradability, moisture resistance, barrier properties, shelf stability under distribution and home storage conditions, processability on conventional equipment, dyeability, etc. Its planned applications include the manufacture of storage bags, shopping bags, slip covers for automobiles and furniture, and chemical and mechanical protective coatings for food bags [12]. It also has the advantage of biodegradability, but its strength and some other mechanical properties have not yet been fully optimized.

The present review focuses on some recent improvements in mechanical properties of Nodax through the use of chain orientation induced by pre-stretching, and by the addition of clay, mica, or talc as reinforcing fillers.

## 2. PRE-ORIENTATION TECHNIQUE AND MECHANICAL PROPERTIES IMPROVEMENTS

Anisotropic polymeric materials find a wide range of applications in many branches of industry, primarily because of their attractive mechanical properties. There have been many methods used to obtain the required segmental orientation of the polymer chains, such as flow-induced orientation, putting polymers into a liquid-crystalline media, and imposed strains (which seems to be the most promising technique for obtaining the desired anisotropies, [13,14]. The degree of orientation can be easily controlled by this latter technique, and it should be possible to drive the system into a highly oriented material having excellent high-performance properties, since the modified products should retain indefinitely much of their orientational order. Of particular interest is a novel orientation technique proposed by Erman and coworkers [15,16] for the preparation of high-strength, high-modulus films and fibers originally from lyotropic main-chain liquid-crystalline polymers, but subsequently also from more flexible chains. The technique involves cross linking the polymer, swelling it with a solvent, stretching it in the swollen state, and then drying it in the stretched state. In contrast to conventional orientation techniques, their procedure gave controlled degrees of orientation among the anisotropic domains containing the liquid-crystalline chains and such orderings persisted after the mechanical force that induced them was removed [17–19]. This produced highly oriented films with much improved mechanical properties, i.e., "high-performance materials" [17–19]. The results obtained on cellulose derivatives [17,20–22], polyisocyanates [18,23,24] and gelatin [25,26] confirmed the usefulness of this orientation technique. In this regard, the present study is part of a series of investigations that stresses the use of pre-orientation technique in general [15,16]. Due to some experimental difficulties, however, it has not yet been possible to obtain cross-linked materials suitable for the required swelling and drying under strain. For this reason, the alternative procedures described below were employed.

## 2.1. Pre-Orientation of Uncrosslinked Nodax Films

The Nodax sample used in this study was provided by the Procter & Gamble Company, West Chester, Ohio. Detailed of samples preparation and characterization can be found elsewhere [6]. The samples investigated were random copolymers, generally consisting of 87–89 mol% 3-hydroxybutyrate, and 11–13 mol% 3-hydroxyhexanoate (based on NMR analyses). They also had number-average molecular weights $M_n$ of 500,000–600,000 g $mol^{-1}$ and polydispersity indices $M_w/M_n$ of 1.9–2.1 (based on polystyrene standards). DSC measurements showed a glass transition temperature $T_g$ around $-0.21$°C, followed by a small endotherm peak at 59.6°C, and a more pronounced peak around 106.3°C [6,27,28]. The peak at 106.3°C was considered to be the melting peak for Nodax [6]. The incorporation of medium chain length 3HA units effectively lowers the crystallinity and $T_m$ in a manner similar to the effect of $\alpha$-olefins in linear low-density polyethylene. $T_m$ was lowered well below the thermal decomposition temperature of PHAs to make this material much easier to process. Therefore, adding such 3HA units provides the ductility, toughness, and flexibility required for many practical applications [6].

Films were prepared by press molding the polymer into Teflon-coated aluminum molds at 130°C. Pre-orientation of a film was performed by heating the sample at 130°C for about 10 min, annealing it for 5 min and then uniaxially stretching it to the desired length. Stretched samples were then air-cooled to room temperature in the stretched state. The resulting percent pre-stretch ratio was defined as $100(L-L_0)/L_0$, where L was the final length of the sample, and $L_0$ its initial length (30 mm) [27,28].

Unusually high draw ratios were achieved for these Nodax films. This could be due to several reasons. The morphology of the initial undrawn material presumably had a folded-chain lamellar structure, with the coherence between individual lamellar crystals being provided by trapped entanglements [29]. At the high draw ratios attained, the drawing process should involve the unfolding of the chains in the direction of completely extended chains. The high draw ratios could also have been due to the annealing of the samples before their being stretched. The annealing could have given a higher level of cohesion between the lamellar crystals through trapped entanglements.

Stress-strain curves obtained for the films at a strain rate of 40 mm/min (Figs. 1a,b) [27,28] showed some of the characteristics typical of semi-crystalline polymers [30,31]. Polymers with low degrees of crystallinity show no necking or a yield maximum. These polymers may consist of small crystallites randomly distributed in a matrix of disordered chains that are in liquid-like conformations and subject to few constraints. When a stress is applied to such a system, the disordered regions are preferentially deformed in a recoverable manner by motions past the crystallites that are not discernibly affected [32,33]. In polymers with higher degrees of crystallinity, which could be the case of our unoriented Nodax samples, lamellar crystallites can form and the thickness of the disordered region between crystallites can decrease.

Some relevant results are given in Figures 1a,b. The initial modulus is being influenced by the crystalline regions acting in parallel with some of the disordered regions. This results in an increase of the initial modulus as the crystallinity/ordering of the lamellae develops [32,33]. At this stage, the crystallites are constrained to deform cooperatively over a complete cross-section. Thus, one observes the beginnings of neck formation (as was visually observed during these measurements). The limited flexibility of the surrounding disordered chains gave a certain diffuseness of the neck. A yield peak on the stress-strain curves was evident, but it was relatively broad. This observation is particularly clear in the case of the unoriented Nodax film, as shown

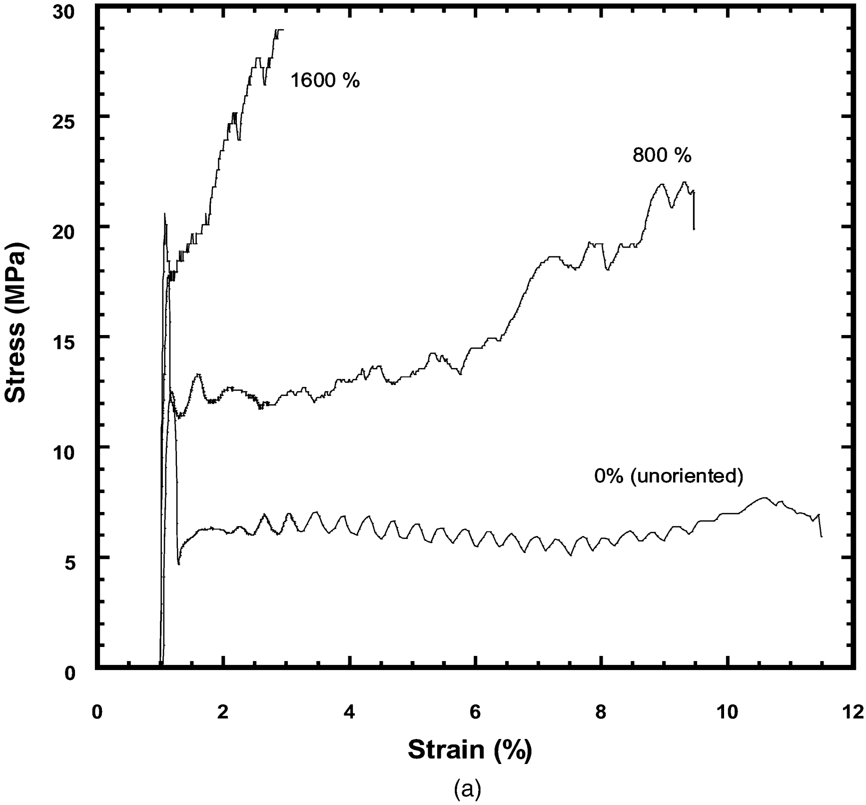


**FIGURE 1** (a) Effect of pre-orientation on the stress-strain curves of uncross-linked Nodax films (entire curve); (b) Effect of pre-orientation on the stress-strain curves of the uncross-linked films (expanded part of curve given in Figure 1a).

in Figure 1b (which is simply a magnification of part of the entire curve given in Fig. 1a). For pre-stretched samples with the highest levels of crystallinity, the intermolecular region containing the disordered structures is relatively small. In this case, the isotropic regions cannot be deformed independently of the crystallites. Consequently, the deformation will be conserved on microscopic bases across a complete cross-section. The resulting modulus could thus be described by a model in which the crystalline and noncrystalline regions are deformed in parallel (making the modulus an approximate linear function of the crystallinity). This was reflected by the existence of sharp yield points in the stress-strain curves and a well-defined neck during the measurements. These features were particularly significant for samples that had been pre-stretched 800–1600%, as

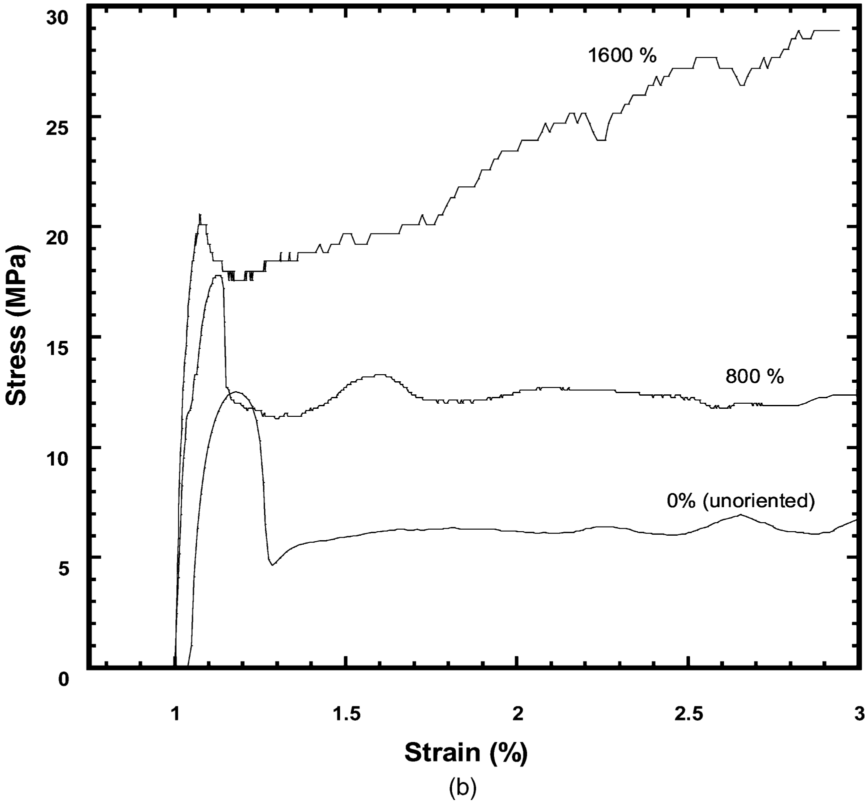


**FIGURE 1** Continued.

shown in Figures 1a,b. Elongation at break decreased very much for the pre-stretched samples. Entanglements could be responsible for such decreases, specially with the relatively high molecular weight of the polymer used in this study. Numerous entanglements could severely reduce the deformability of the noncrystalline sequences between lamellae [32]. They will then serve as weak points of the total system. Rupture might then occur among these sequences before the full elongation benefits of the melting-recrystallization process could be realized [32].

As expected, increases in the pre-orientation increased the modulus and the toughness (as defined by the area under the stress-strain curves given in Fig. 1a). This was particularly significant for samples that had been pre-stretched 200–1000%, as is shown in Figure 2 [27,28]. Beyond 1000% pre-extension, toughness decreased while the

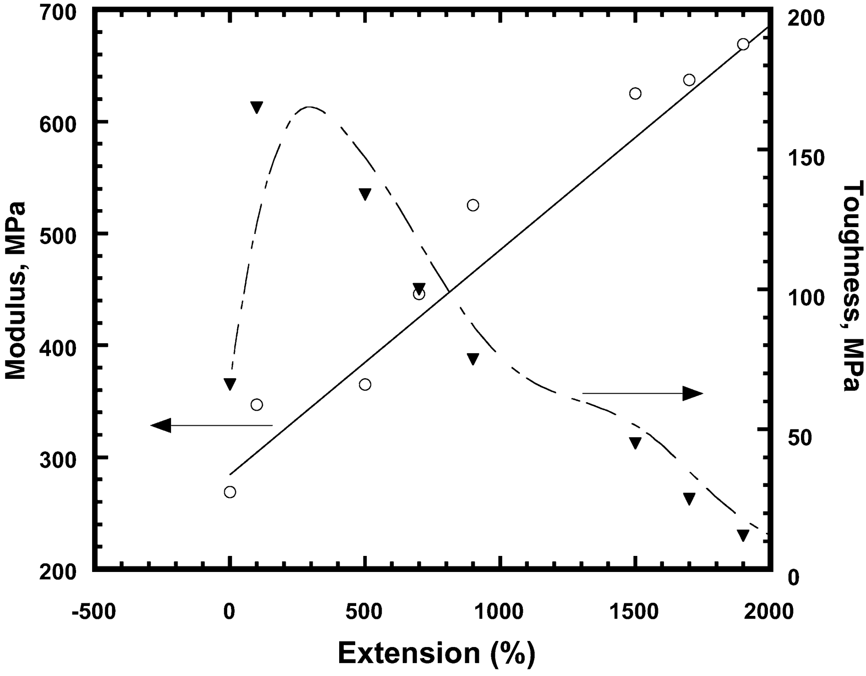


**FIGURE 2** Effect of pre-orientation on the tensile modulus and the toughness of uncross-linked films.

modulus continued to increase. For all values of the pre-extension, a plateau developed after the yield point that was similar to that observed for the unoriented sample. This indicates a higher level of ordering from the higher stretch ratios [19]. An increase in the modulus with pre-orientation is presumably due to increases in crystallinity, as was reported for random ethylene copolymers [33]. Of considerable interest is the continuous increase in the modulus with increasing levels of crystallinity (as would be predicted from increasing the orientation level). It indicates that both the crystalline and non-crystalline regions are major contributors to the initial deformation mechanism and the value of the initial modulus [33].

Also, an increase in the pre-stretching of the films resulted in an increase in the yield stress and the tensile strength (the stress at break) as shown in Figure 3 [27,28]. This result is in agreement with results previously reported for polyethylenes and polyamides. In these studies, there was a linear increase of the yield stress at room temperature with increase in density and thus with degree of crystallinity [32–37].

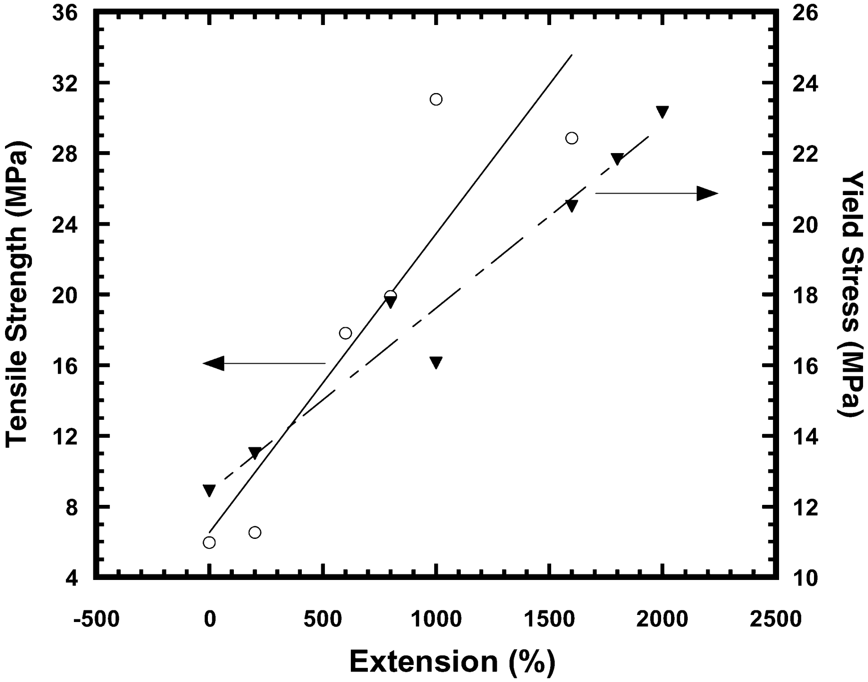


**FIGURE 3** Effect of pre-orientation on the tensile strength and yield stress of uncross-linked films.

Examination of the X-ray diffraction patterns of the unoriented and oriented films showed a significant increase in peak intensity due to pre-orientation. Typical results are given in Figure 4 [27,28]. The peak at $2\theta = 13.4^\circ$ increases with increase in the extent of pre-orientation, confirming the expected increase in crystallinity. This supports the fact that chain orientation is a strong function of the draw ratio [32]. In the case of the peak at $2\theta = 17^\circ$, samples that had been pre-stretched 800% had almost the same area as that of the unoriented samples. Some of the chains could have become oriented to a considerable extent in the draw direction while other chains were still oriented perpendicular to the film surface [27,28]. Also, this could indicate that some lamellar crystalline morphology of the copolymer is still retained even after drawing to 800% [29,38,39]. These results explain the increases in the modulus, and the stress and elongation at break, with increase in the pre-stretching ratio.

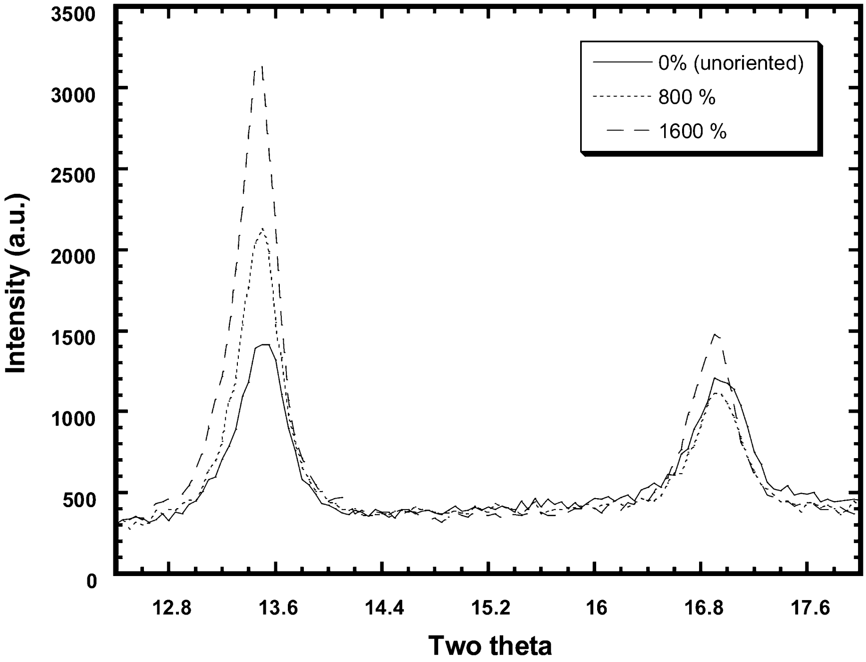


**FIGURE 4** X-ray diffraction patterns for the unoriented and oriented uncross-linked films.

## 2.2. Pre-Orientation of Crosslinked Nodax Films

There has been growing interest in polymer networks prepared from semirigid chains [18,21,40–42]. The chains of these networks typically acquire their stiffness from aromatic or other ring structures having large rotational energy barriers, and their segments tend to be self-aligning, forming liquid-crystalline mesophases in the melt or in solutions. Networks consisting of these chains usually show exceptionally high degrees of segmental orientation and an isotropic-to-nematic phase transformation under macroscopic deformation [21]. Thus, their properties are quite different from those of the idealized rubbery networks described by the classic theories of elasticity and photoelasticity [21,43,44]. Some of these considerations are also relevant to more flexible chains such as those investigated here.

Crosslinking of the Nodax films has been achieved by mixing different amounts of the initiator, dibenzoyl peroxide (DBP), in the range 0.5–10% by weight of Nodax in chloroform. Dried films were then heated in a vacuum oven under argon atmosphere at 130–140°C from

2 to 10 h [28]. Homogeneous mixing of the dibenzoyl peroxide with the Nodax is essential to achieve homogeneous cross linking or curing of the films [45,46]. The curing was carried out by using chloroform, which is a good solvent for both dibenzoyl peroxide and Nodax. Another important factor is carrying out the crosslinking reaction under an argon atmosphere, which would prevent any oxidation from atmospheric oxygen. Sol fractions of the resultant films were calculated by extracting the samples in chloroform and deswelling with the proper amounts of methanol. The sample used in this study was crosslinked using 2% dibenzoyl peroxide for a crosslinking period of 2 h, and had a sol fraction of 0.014 [28].

Samples were pre-oriented by stretching them 200–800% of their original lengths. Their stress-strain isotherms were obtained at a strain rate of 10 mm/min, with results shown in Figures 5a,b. As was reported in many studies, cross linking diminishes the drawability of

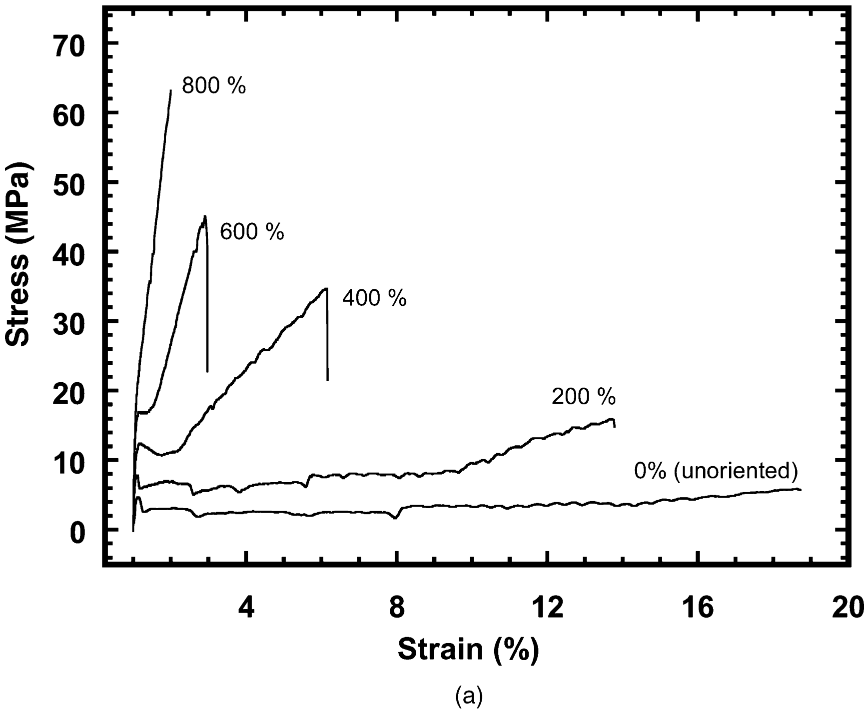


**FIGURE 5** (a) Effect of pre-orientation on the stress-strain isotherms for cross-linked films (entire curve); (b) Effect of pre-orientation on the stress-strain isotherms of the cross-linked films (expanded part of curve given in Figure 5a).

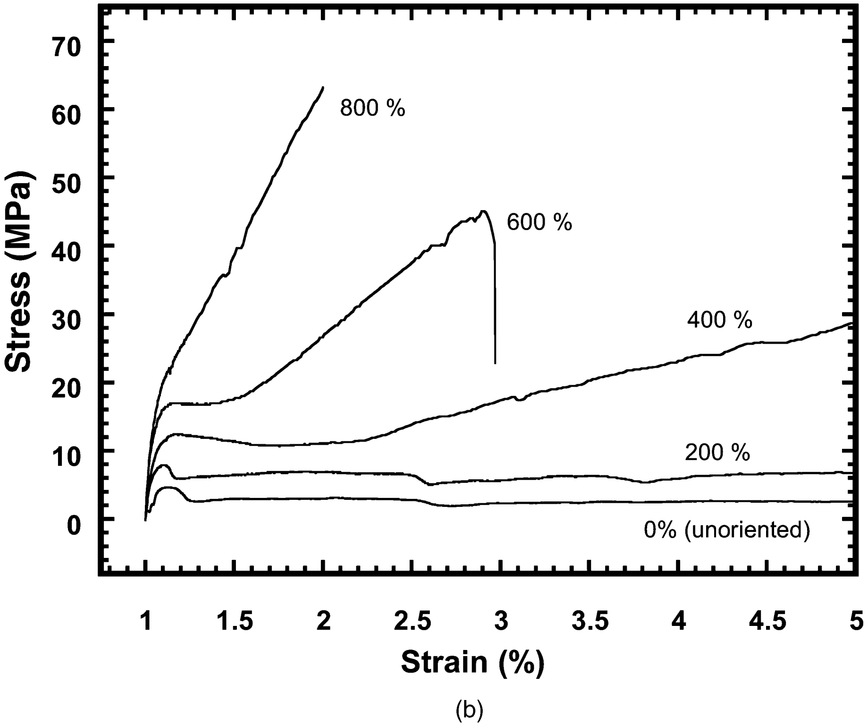


**FIGURE 5** Continued.

films [18,47–49]. This supports the fact that crosslinked Nodax films can not be pre-oriented beyond 800%, while uncrosslinked films were easily pre-oriented to 2000%, as reported in our previous studies [27,28]. This can be understood by the fact that crosslinking increases the connectivity of polymer chains and thus hampers chain movements during stretching. In other words, cross linking prevents the slippage of chain molecules past each other. Another way to explain this effect is the fact that cross links act as stress concentrators in the crystal lattice, and therefore their introduction may influence the tenacity of the crystalline fibers unfavorably [49,50]. This could also be a reason for decreases of the melting point and crystallinity with increases in the degree of crosslinking. A third reason for the decrease of the elongation at break ($\lambda_{max}$) could be modification of the chains with bulky benzoyl groups during measurements (which were done on un-extracted films). Possibly, bulky benzoyl groups could hamper network crystallization but their influence is believed to be small in comparison with the effects of the cross links [51].

Stress-strain isotherms at constant strain rate showed the existence of yield points, except for the case of the highly oriented sample (800%), as indicated in Figure 5b (which is simply a magnification of part of the entire curve given in Fig. 5a). For all the different extensions, only the sample with the lowest extension showed a plateau after the yield point similar to that for the unoriented sample. This indicates that an improved toughness as well as improved modulus was attained with orientation.

Pre-orientation has also shown a significant effect on the modulus and toughness (as defined by the area under the stress-strain curves given in Fig. 5a) of the crosslinked films, Figure 6. As would be expected, the pre-orientation resulted in much tougher films with higher values of the modulus, as compared to the original unoriented films. This was particularly significant for samples that had been pre-stretched 200–600%. After 600% pre-extension, toughness goes down while the modulus keeps increasing. Both the tensile strength (defined as the stress at break) and the yield stress were also increased with increase in the pre-stretching percent of the crosslinked films, as

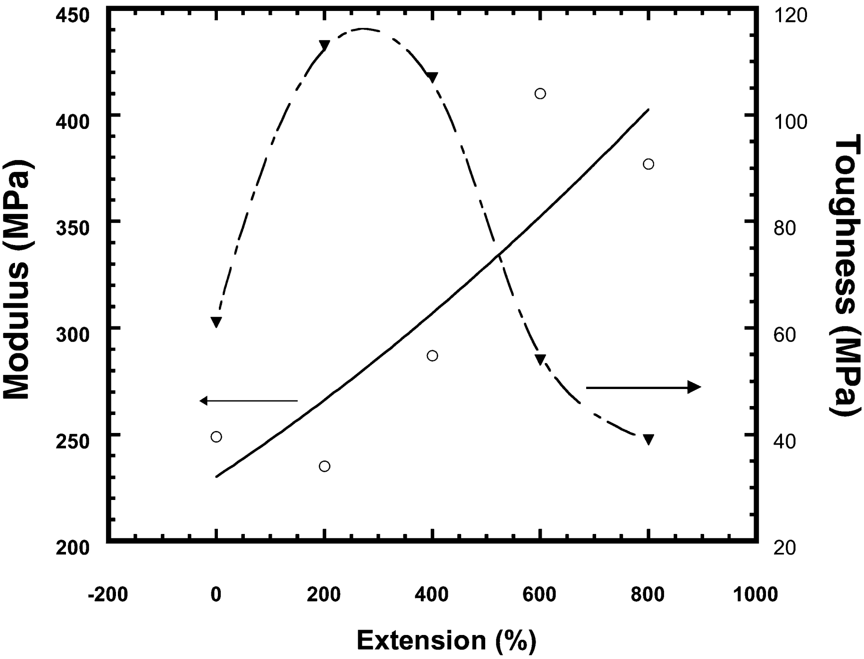


**FIGURE 6** Effect of pre-orientation on the tensile modulus and toughness of cross-linked films.

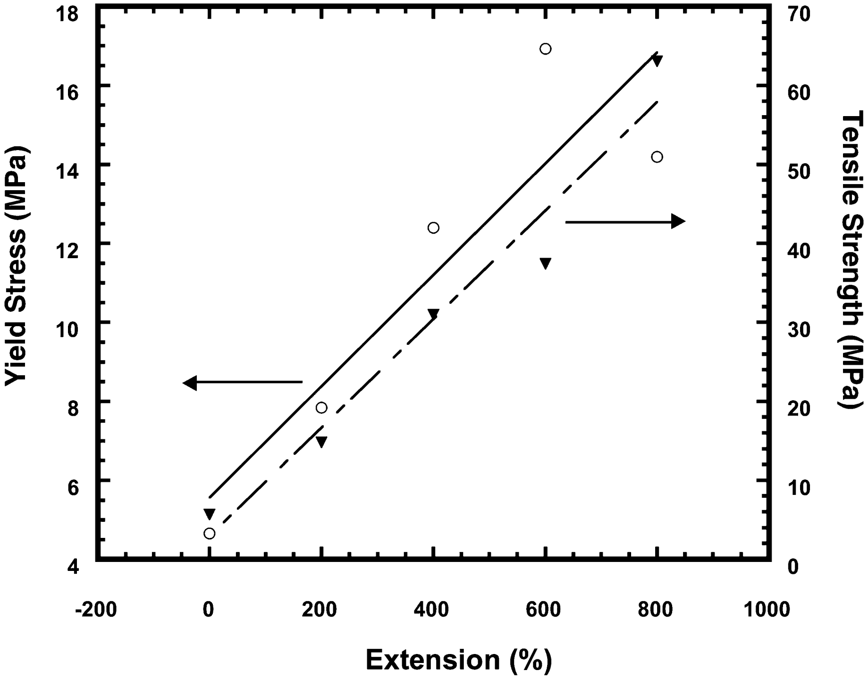


**FIGURE 7** Effect of pre-orientation on the tensile strength and yield stress of cross-linked films.

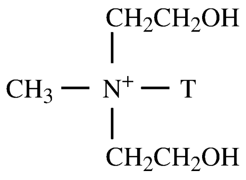
shown by Figure 7. This indicates the presence of higher level ordering at the higher stretching ratios [18].

Finally, these improvements in mechanical properties demonstrate the very desirable effects of pre-orientation techniques on mechanical properties. This behavior has been observed for the uncrosslinked Nodax films as well [27,28]. They provide interesting parallels to those obtained with biodegradable starch-ether [15,16,19] and poly(D,L-lactide) materials [23–25]. It is worth noting that pre-orientation of the films would give chains which are nearly perfectly oriented in the stretching direction, but such a material would be weak in the directions perpendicular to the stretching direction. A biaxial extension procedure applied to a film could give more useful materials that would be extremely strong in all directions within the plane of the film.

## 3. NODAX/CLAY NANOCOMPOSITES

Hybrids based on organic polymers and inorganic clay minerals consisting of layered silicates are considered to be very promising composite systems [52–61]. In favorable cases, the filler is present in the form of sheets one to a few nm thick and hundreds to thousands of nm long and wide. The earliest work of some Toyota Corporation researchers [53–56] has stimulated numerous subsequent theoretical and applied researches in this area. Such polymer layered silicate nanocomposites have exceptional physical property enhancements including improved barrier properties [62,63], higher mechanical properties [64–66], improved flame retardancy [67–69], increased dimensional stability [70–72], and improved solvent and UV resistance [73,74]. All of these benefits were obtained without significantly raising the density of the compound or reducing light transmission, and they are attainable at low filler levels [75]. These potential property enhancements have led to increased applications in various fields such as the packaging industry (for example, bottles, containers, and plastic films), the automobile industry (exterior and interior body parts and fuel tanks), the electronics industry (packaging materials and exterior parts of electronic devices), the coating industry (paints, wire enamel coatings, etc.), and the aerospace industry (body parts of airplane and exterior surface coatings) [61,68,75].

In the present study, Nodax/clay nanocomposites were prepared by mixing the polymer in chloroform with Cloisite® 30B provided by Southern Clay products Inc. Gonzales, Texas [28]. The chemical structure of the clay modifier is given in Figure 8. The nanocomposites were thus prepared using an exfoliation-adsorption method. In our procedure, chloroform was used as a solvent since both the layered silicate and the polymer are completely dispersible in it. This procedure allowed the clay to be exfoliated into single layers. Because of the weak forces that stack the layers together, these silicates are well known to be easily dispersed into an appropriate solvent. The polymer then adsorbs onto the delaminated sheets. When the solvent is evaporated, the sheets reassemble, sandwiching the polymer to form, in the best cases, an ordered multilayer structure [76]. As expected from the



$$CH_3 - \underset{CH_2CH_2OH}{\overset{CH_2CH_2OH}{N^+}} - T$$

Here T is tallow (~ 65 % C18; ~ 30 % C16; ~ 5 % C14), Anion = Chloride

**FIGURE 8** Structure of the clay modifier used in the nanocomposites.

structure of the clay, (Fig. 8), it dispersed quite well into chloroform due to the presence of hydroxyl groups, and this was in fact observed during the preparation of the nanocomposites.

Diffraction patterns were obtained from wide-angle X-ray scattering (WAXS) measurements on the clay and the composites films. They provided information regarding the types of structure in the nanocomposites and whether the structures were affected by the clay. The patterns for various samples are given in Figure 9. There is clearly a disappearance of the clay peak at $2\theta = 4.79^\circ$ in samples with clay concentrations up to 5%. The peak started to appear at 7 and 10% clay loadings. Surprisingly, a sudden big shift towards lower $2\theta$ values and from 4.79° to 2.73° happened for the sample with 15% clay loading. At lower clay percents, an exfoliated structure was obtained. In this structure, diffraction peaks were not visible in the XRD diffractograms either because the spacing between the silicate layers was much too large (i.e., exceeding 8 nm in the case of ordered exfoliated

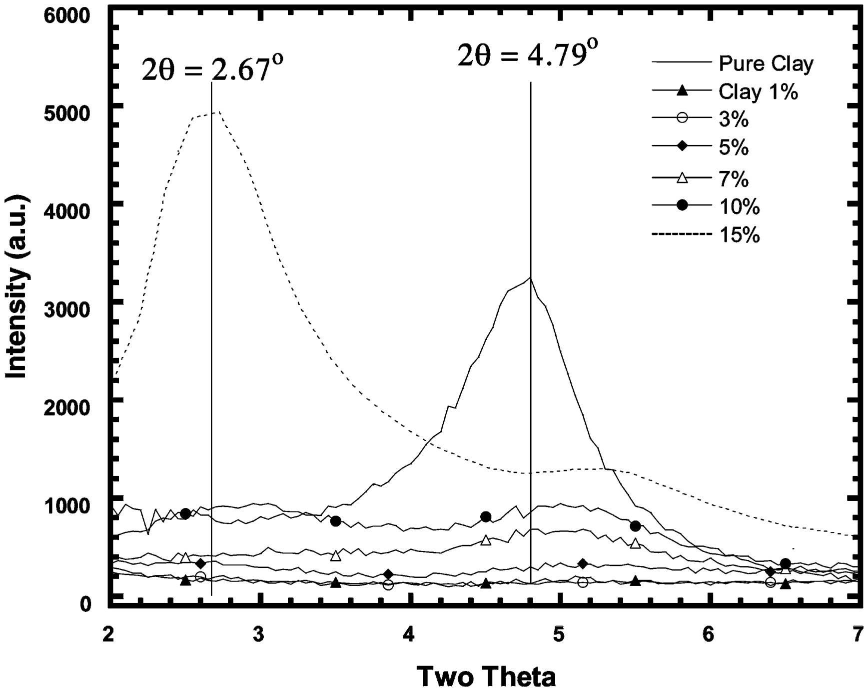


**FIGURE 9** X-ray diffraction patterns for Nodax/clay nanocomposites with different clay loadings. Also shown are the values of two theta for peaks of pure clay modifier and the sample with 15% clay.

structure), or because the nanocomposite did not have ordering [76]. With increase in the clay loading, there might be a transition from the exfoliated structures to the intercalated ones. This could have resulted in smaller peaks at the same value of $2\theta$, as can be seen from the peaks for the 7 and 10% samples. As the clay percentages are increased, intercalated structures would become more likely. In these structures, the polymer chains usually increase the interlayer spacing, in comparison with the spacing of the organoclay use (leading to shifts of the diffraction peak towards lower angles). This could be an explanation for the shift observed with the 15% clay loaded sample. Similar behavior was reported for clay nanocomposites with Nylon-6 [57] or PDMS [77].

The stress-strain behavior of the samples was surprisingly not very promising. As can be seen from Table 1, there is a substantial improvement in the Young's modulus at the expense of toughness with the addition of clay to the unfilled polymer. A large decrease in the elongation at break reflects how the toughness was affected with addition of the clay. In all the filled samples, average toughness value was around 0.63 MPa. This is a very surprising result when compared to 66 MPa for the unfilled sample. Increasing the modulus with an increase in organoclay content may have resulted from the decrease in exfoliated particle fraction at higher filler contents. It was reported that the material becomes stiffer whatever the method of preparation [76,54].

The thermal stability of the Nodax/clay nanocomposites was improved, according to the thermogravimetric analysis (TGA) measurements shown in Figure 10. The TGA trace shows a relatively small shift of the weight loss towards higher temperature with a

**TABLE 1** Mechanical Properties of the Nodax/Clay Nanocomposites

| % Clay | Young's modulus (MPa) | Tensile strength[a] (MPa) | Elongation at break |
|---|---|---|---|
| 0* | 267 | 5.99 | 11.5 |
| 1 | 154 | 4.07 | 1.1 |
| 3 | 386 | 14.7 | 1.05 |
| 5 | 534 | 13.7 | 1.06 |
| 7 | 648 | 8.64 | 1.05 |
| 10 | 689 | 13.1 | 1.04 |
| 15 | 221 | 5.92 | 1.34 |

*Unfilled sample was measured at 40 mm/min strain rate while the other samples were measured at 5 mm/min.

[a] Tensile strength is given by the stress at break.

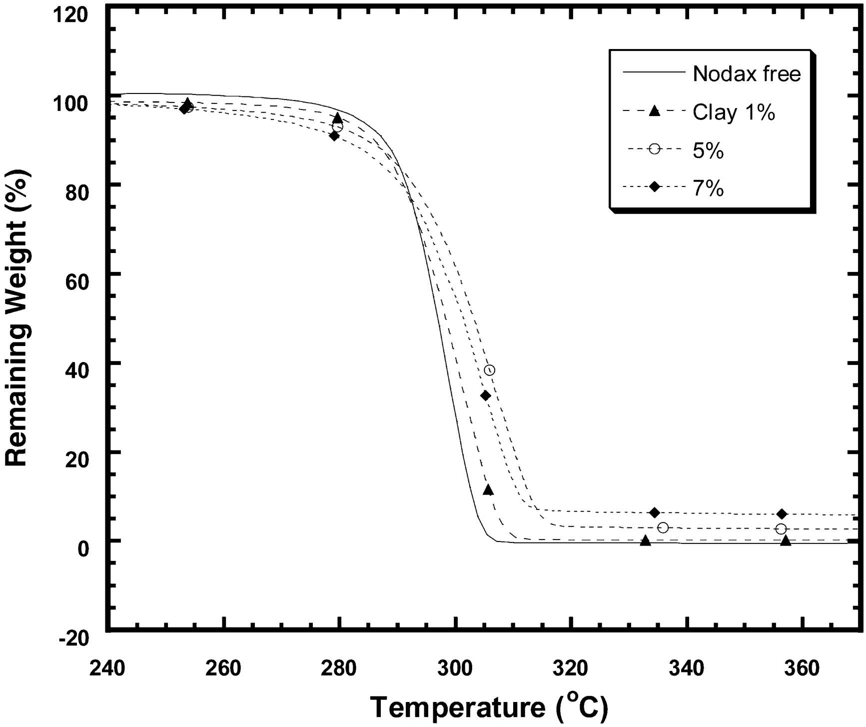


**FIGURE 10** Thermogravimetric analysis curves for some Nodax/clay nanocomposites.

stabilization as high as 6°C at 50% weight loss. Values of the temperature stabilization attained at 50% weight loss for each sample are given in Table 2. There is an increase to a maximum at 5% clay loading, followed by a pronounced decrease with further increase in clay content. Such behavior could be explained by changes in the relative proportion of exfoliated and intercalated species with filler content. At low filler contents, exfoliation dominates but the number of exfoliated particles is not high enough to promote thermal stability through char formation [76]. When the filler content is increased, more exfoliated particles are formed, char forms more easily and increases the thermal stability of the nanocomposite until 5% of nanofiller is reached. At higher levels, the equilibrium between exfoliation and intercalation is drawn towards intercalation and, even if char is still formed in high quantity, the morphology of the nanocomposite does not give improved thermal stability [76]. This explanation may apply to our system but may not be valid for other polymeric systems.

**TABLE 2** Thermal Stabilization of the Nodax/Clay Nanocomposites

| % Clay | Degradation temperature maximum (°C) |
|---|---|
| 0 | 297 |
| 1 | 298 |
| 3 | 301 |
| 5 | 303 |
| 7 | 301 |
| 10 | 299 |

The chemical nature of a specific material and its degradation mechanism play an important role in its thermal stabilization in clay nanocomposites. For example, a study on poly(etherimide) nanocomposites demonstrated that intercalated nanolayers were found to be better thermal stabilizers than exfoliated ones [78].

## 4. OTHER NODAX-LAYERED SILICATE HYBRIDS

Some of the benefits of using clays in these nanocomposites should also be attainable or even surpassed by the use of other layered fillers, such as mica or graphite. Such work is in progress.

## 5. CONCLUSIONS

Pre-orientation was found to improve the modulus, tensile strength, and yield stress as well as increasing or at least maintaining the toughness of uncrosslinked and crosslinked Nodax films. These improvements presumably resulted from increases in the crystallinity with orientation, a conclusion that was supported by increases in the intensity of X-ray diffraction patterns of the pre-oriented samples relative to those of the unoriented ones. Pre-orientation techniques could therefore be very useful in processing such materials for industrial applications. Such improvements in the mechanical properties of Nodax will certainly be of great importance with regard to their industrial end-use applications. These improvements in the mechanical properties for the crosslinked as well as uncrosslinked Nodax films should help in the production of high-performance materials from such biodegradable polymers.

Addition of organoclay to Nodax was found to improve its thermal stability. This improvement most probably resulted from changes in the nanocomposites structure from exfoliation at low clay content to intercalation at higher contents. This transition in structures was proved by the change in the intensity of X-ray diffraction peaks with changing clay contents. At lower clay contents, a decrease in the intensity of the clay peak was observed due to exfoliation. At higher clay contents, a shift in the peak intensity toward lower values was observed due to intercalation. The major benefit was increases in the modulus with increases in clay content. Improvements in other mechanical properties will require additional experiments on the effects of clays in these types of materials.

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