Structure and Properties of Talc-Filled Polyethylene and Nylon 6 Films

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Synopsis

Water vapor transmission rates can be reduced by as much as 50% in polyethylene by using talc as a filler. The oxygen permeability as well as water vapor transmission rates are similarly reduced by talc in nylon 6 films. The films show low elongation at break and reduced breaking strength in the presence of talc. The yield strength and the modulus increase with the amount of talc, whereas the elongation at yield decreases. The mechanical and the barrier properties change with the size of the filler, the smaller size being more favorable. Talc probably acts as a nucleating agent and increases the crystallinity in polyethylene and nylon. Polyethylene unit cells in talc-filled films are oriented with the (110) planes parallel to the (001) planes of talc. Nylon 6 crystals, which are in the α form in the presence of talc, are oriented with the hydrogen bonded sheets, the (002) planes, parallel to the (001) planes of talc. In both polyethylene and nylon 6, talc is oriented with the c-axis normal to the plane of the film, i.e., with the broad faces of talc flakes in the plane of the film. Lattice matching between the polymer and talc suggests epitaxy to be a contributing factor for the observed orientation of polyethylene and nylon 6 crystals.

INTRODUCTION

Various additives and fillers are widely used in polymer processing. Cost, improvement in mechanical, electrical, thermal, and barrier properties, appearance, and the nucleating ability of the additives are some of the reasons for using fillers. Processing engineers have studied the effect of filler on the processibility and properties of such polymers as poly(vinyl chloride), polyamides, polypropylenes, epoxy, and polyester resins. Although the addition of fillers to polyethylene has been primarily to lower the cost, plate-shaped fillers have been shown to improve the barrier properties.[1] Our purpose in the work reported here was to reduce the water vapor and gas transmission in polymer films by the addition of platelet type particles such as talc. We present a detailed analysis of the barrier and mechanical properties, and the structure of talc-filled, blown, polyethylene, and nylon 6 films.

EXPERIMENTAL

Polyethylene films were extruded at 216°C through a 3 in diameter tubular film die and blown into 5 in diameter, ~1.5 mil thick films. Nylon films were extruded at 266°C through a 4 in diameter tubular die and blown into 2 mil thick, 8 in diameter films. Polyethylene films were produced from Allied resins of three different molecular weights with melt indices

of 0.7 (PE7), 0.3 (PE3), and 0.07 (PE07). Loading of 20–60 parts per hundred (phr) of talc with the diameter of the plates varying from 1.5 to 14 μm was used. The talc used was Pfizer MP-10-52. One experimental run was also made with aminosilane coating (Cyprobond).

Flat-plate X-ray diffraction (XRD) photographs were obtained using a Unicam camera with nickel-filtered copper radiation. Diffractometer scans obtained in the transmission mode on a Philips goniometer were used for quantitative analysis. Crystallinity measurements were made from "fast-rotational" scans (the sample spinning at 70 rpm in its own plane while 2θ is scanned at 2°/min.) so as to randomize orientations present in the plane of the film. Scans were made from $2\theta = 12$–30° and a crystalline index (CI) was calculated from the relative areas of the crystalline peaks and the amorphous halo. The orientation of the talc platelets (f_p) was determined by making azimuthal scans of the XRD photographs taken with the X-rays incident parallel to the plane of the film (transverse and machine direction photographs). These scans were done on a Joyce-Loebl (MK III CS) microdensitometer. f_p values were calculated from the average cosine squares, $\langle \cos^2 \phi \rangle$, for the normals to the flat faces of the talc flakes using the (002) or the (004) reflections and the relation $f_p = (3\langle \cos^2 \phi \rangle - 1)/2$, where ϕ is the azimuthal angle.

Water vapor transmission (WVT) rates were determined gravimetrically in accordance with ASTM E96A. Gas transmission rates of O_2 were measured using ASTM D1434. The tensile properties of the film were determined in accordance with ASTM D 882-67 using an Instron testing device and ASTM type IV specimens.

RESULTS AND ANALYSIS

XRD in Polyethylene. Figure 1 shows the XRD photographs of a polyethylene film with X-rays along the normal, machine, and transverse directions [N, M, and T; see Fig. 3(b)]. Such patterns are commonly observed
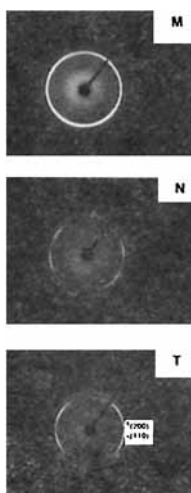

Fig. 1.   X-ray diffraction (XRD) photographs of blow-molded polyethylene with a melt index of 0.07. The three photographs were obtained with X-rays along the machine direction (M), normal direction (N), and tranverse direction (T).

in blow-molded polyethylene films and are indicative of the uniaxial orientation. Similar uniaxial orientation has recently been reported for low molecular weight (melt index 0.98) polyethylene.[2] Our results show that this uniaxial orientation is obtained even with high molecular weight polyethylene with melt indices as low as 0.07. Although all our films consistently showed uniaxial orientation, this orientation is primarily a function of processing conditions. For example, Choi et al[2]. have reported both uniaxial and biaxial orientations for films blow molded under various processing conditions. The *b*-axes in all the samples are almost perpendicular to the machine direction and are uniformly distributed between the transverse and normal directions. The *a*-axis is uniformly distributed around the machine direction and exhibits maxima at ~45° to MD. The uniaxial orientation is further confirmed by the intensity distribution of the (110) reflection, which also showed uniform azimuthal intensity at ~60° around MD.

Figure 2 shows the XRD pattern obtained when polyethylene is blow-molded with talc. One obvious difference between the diffraction patterns with and without talc can be seen by comparing the diffraction photographs with X-rays along the machine direction [Figs. 1(M) and 2(M)]. Whereas in films without talc, the (110), (200) and (020) reflections show no orientation, they are oriented in films with talc. This might represent orientation of the polymer chains near the talc–polymer interface and can possibly be attributed to interfacial forces between the polymer and the rigid filler.

In the 11 samples studied, one consistent feature in talc-filled polyethylene films was the orientation of the (110) planes roughly parallel to the plane of the film. The results can be interpreted schematically as shown in Figure 3. These figures show the orientation of the *a*-, *b*- and *c*-axes of polyethylene crystallites with and without talc. Figure 3(C) shows the uniaxial orientation of blow-molded polyethylene films. Figure 3(D) shows the additional orientation in the presence of talc. It should be pointed out that polyethylene in the presence of talc is not exclusively in the orientation
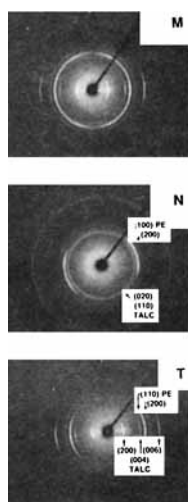

Fig. 2. XRD photographs of talc-filled blow molded polyethylene. M, N, and T refer to X-rays being incident along machine, normal, and transverse directions.
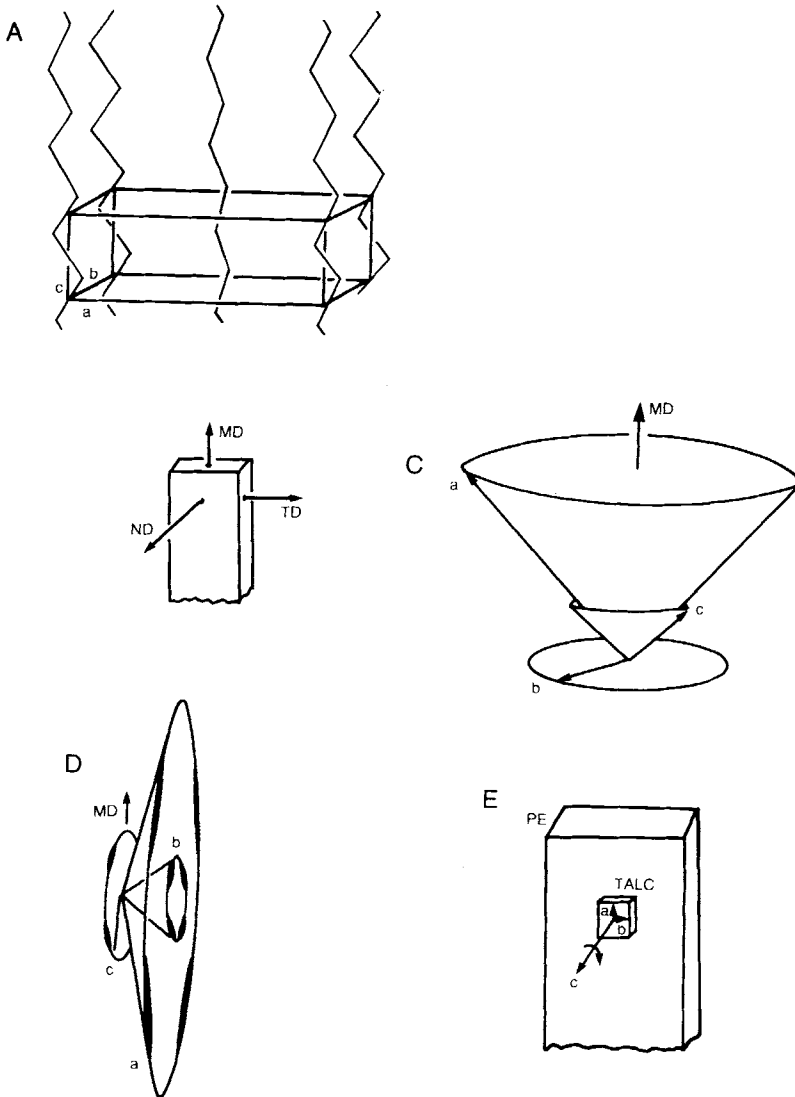
Fig. 3. A model for the orientation of the unit cell of polyethylene in blow-molded film: (A) orientation of the polyethylene chains in the orthorhombic unit cell; (B) definition of machine direction (MD), normal direction (ND), and transverse direction (TD) with respect to the blown film; (C) orientation of unit cell axis in the blown polyethylene film; (D) orientation of polyethylene lattice in the presence of talc; (E) orientation of the talc platelets in the film.

shown in Figure 3(D). This is apparent, for example, by the presence of the (110) reflection in the normal photograph of talc filled film [Fig. 2(N)]. It is possible that polymer molecules near the surface of talc are oriented as in Figure 3(D), whereas those away from the talc surface are still in the orientation of unfilled polyethylene as in Figure 3(C).

Figure 2 also shows the reflection due to talc. The distribution of the talc flakes is cylindrically symmetric about the normal to plane of the film: (001) reflections show considerable orientation in both edge-on (machine

and transverse direction) photographs while (020) + (110) reflection appears as a ring in the normal photograph. This indicates that the c-axis of talc, which is also perpendicular to the broad face of the talc flakes, is oriented perpendicular to the plane of the film, and that the talc flakes or the talc crystallites are randomly distributed around the c-axis [Fig. 3(E)]. The degree of orientation (f_p) of the talc flakes relative to the plane of the film has an average value of 0.95.

XRD in Nylon 6. Figure 4 shows the XRD photographs of nylon 6 films produced by blow molding. This type of pattern is usually identified as due to the γ or the psuedohexagonal form of nylon 6.[3,4] The film is unoriented. However, when produced with talc, as can be seen from Figure 5, nylon 6 exists in the energetically most stable α form. More interesting is the planar orientation of these films; the (002) reflection is along the normal to the film, and the (200) reflection is unoriented in the plane of the film. This type of orientation is similar to that observed in doubly oriented nylon 6 films[5,6] and shows that not only the nylon 6 molecules lie in the plane of the film, but the nylon 6 chains which form a hydrogen-bonded sheet are parallel to the surface of the film.

As in the case of talc filled polyethylene, the talc platelets are randomly distributed in the plane of the film, and the flakes are oriented with their broad faces parallel to the surface of the film. This is seen in the oriented (001) reflections in the TD and MD photographs and the unoriented (020) + (110) reflections in the ND photograph (Fig. 5). As in the case of polyethylene, this shows that cylindrical symmetry of the talc flakes around the c-axis of the talc, and the orientation of this c-axis normal to the plane of the film. The orientation of the nylon 6 chains and the talc flakes is schematically shown in Figure 6.

As an extension of the studies on the orientation of nylon 6 films in the presence of talc, one of the talc-filled films (50% talc) was preheated at 290°F, stretched by a ratio of 1:4 at 325°F, heat set at 340°F, and then cooled. The orientation of the talc and nylon 6 molecules in this stretched film was very similar to that of unstretched talc-filled film, except that the normal photograph with X-rays along the normal to the film showed weak and oriented (200) and (020) reflections of the α-phase along with an intense
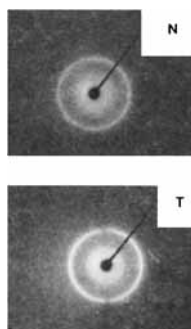

Fig. 4. XRD photographs of nylon 6 film produced without talc: (A) normal photograph, X-rays normal to the plane of the film; (B) transverse photograph, X-rays incident parallel to the surface of the film.
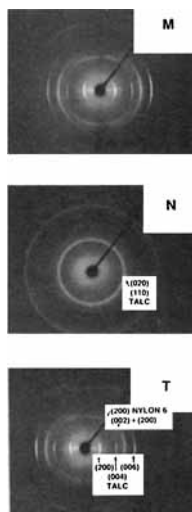
Fig. 5. XRD photograph of nylon 6 films produced with talc. M, N, and T refer to X-rays incident along the machine, normal, and tranverse directions.

unoriented (200) reflection. In unstretched talc-filled film, this in-plane (ND), photograph showed only the unoriented (200) reflection. This suggests that, in regions where the nylon molecules become oriented due to stretching of talc-filled films, the hydrogen bonded planes twist away from the plane of the film.

Barrier Properties. The reduction in the permeability in polyethylene and nylon 6 due to the increase in the volume fraction of talc is shown in Figure 7. The rates of WVT decreases by as much as 60% in both polyethylene and nylon 6, and the results are similar to that of Arina et al.[1] This reduction can be readily attributed to talc acting as a mechanical barrier and creating a highly tortuous path for the water molecules. An interesting observation is the change in WVT as a function of particle size. It can be
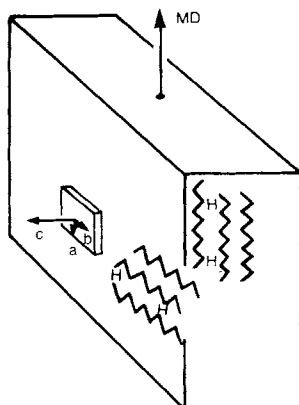

Fig. 6. Schematic representation of the orientation of the nylon 6 molecules and talc flakes in nylon 6 films.
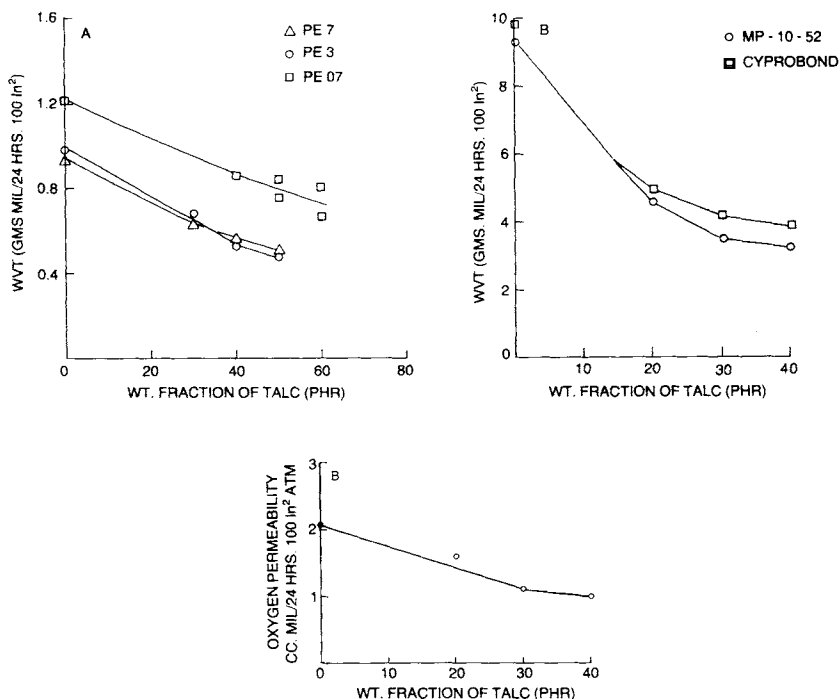
Fig. 7. Water and oxygen permeability as a function of talc concentration (in parts per hundred, phr): (A) water vapor transmission (WVT) rates in three polyethylene films with melt indices of 0.7 ($\triangle$, PE7), 0.3 (0, PE3) and 0.07 ($\square$, PE07); (B) WVT in nylon 6 films for two types of talc flakes, MP-10-52 (O) and Cyprobond ($\triangle$); (C) oxygen transmission rate through talc-filled nylon 6 films as a function of the talc content.

seen from Table I that the WVT is lowest in polyethylene films filled with talc of size (diameter of the flakes) less than 3 μm.

Mechanical Properties. Figures 8 and 9 show the changes in the mechanical properties in talc-filled polyethylene and nylon 6. The changes in the mechanical behavior of polyethylene and nylon 6 in the presence of talc are similar. Elongation at break and the break strength decreases with the addition of talc. The increase in the modulus with the addition of talc is the normally expected filler effect.[7] Similar observations have been made with other fillers such as wollastonite and mica in polyethylene.[1] The result from PE07 film (Fig. 8) which shows an increase in tensile strength differs from the data obtained with other films. This increase is probably due to the different processing conditions. Interfacial strength between the polyethylene molecules and the talc particles may also be different in this PE07 film. The aminosilane coating (Cyprobond) on the talc used in one nylon 6 film does not result in strengths higher than for the nylon 6 in which uncoated talc was used (Fig. 9). It is probable the smaller particle size of uncoated talc (MP-10-52) already provides good bonding between nylon 6 and talc, and the coating does not improve this bonding any further. It is, however, not possible to draw any general conclusions with the data currently available to us.

The effect of particle size on the mechanical properties of polyethylene

TABLE I

Water Vapor Transmission and Mechanical Properties of the Talc-Filled Polyethylene as a Function of the Size of the Talc Particles at a Loading of 40% Talc[a]

Sample	Machine direction						Transverse direction				
	WVT	ϵ_y	ϵ_B	σ_y	σ_B	M	ϵ_y	ϵ_B	σ_y	σ_B	M
Control PE 07	0.93	11.6	580	3.10	5.00	1.60	4.4	7.1	3.22	2.88	2.47
3 μm	0.44	7.5	460	3.14	4.52	2.80	2.2	4.0	2.82	2.62	2.87
5 μm	0.50	8.0	480	2.94	4.13	2.41	3.1	5.0	2.85	2.61	2.71
8 μm	0.52	7.5	350	2.78	2.83	2.42	2.4	5.0	2.04	2.21	2.60
14 μm	0.77	7.8	90	1.95	1.85	1.71	2.2	4.0	1.48	1.42	2.18

[a] WVT = Rate of water vapor transmission (g mil/24 h 100 in²), ϵ_y = elongation to yield (%), ϵ_B = elongation to break (%), σ_y = yield strength × 10⁻³ (psi), σ_B = break strength × 10⁻³ (psi), and M = modulus × 10⁻⁵ (psi).
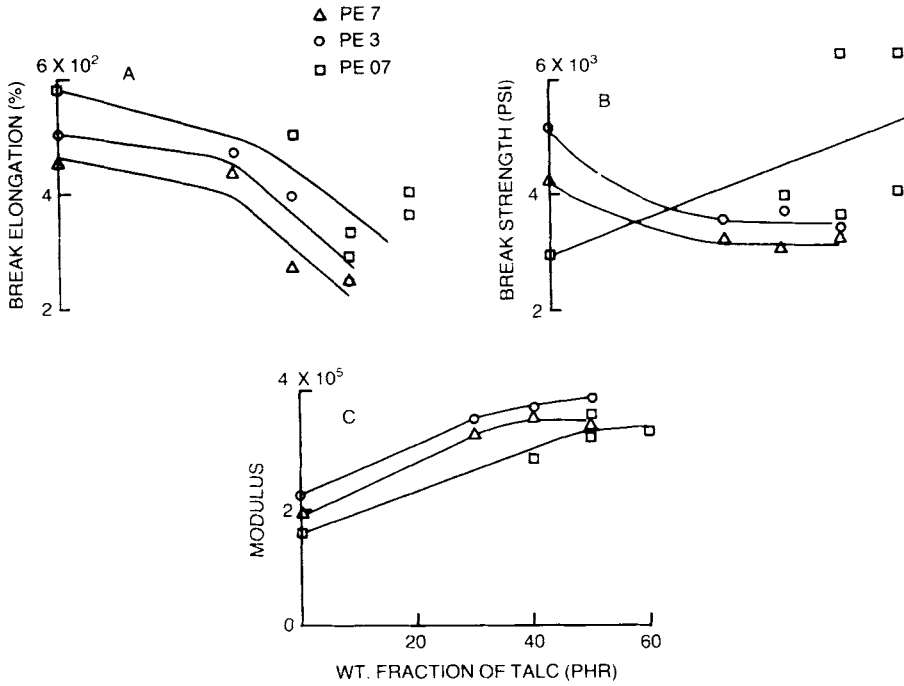
Fig. 8.   Variation in the mechanical properties of talc- (MP-10-52; equivalent diameter d of flakes = 1.34 μm; d_{max} = 9.31 μm; d_{min} = 0.09 μm) filled polyethylene along the machine direction as a function of talc concentration (in parts per hundred, phr): (A) elongation to break; (B) break strength; (C) modulus; ($\triangle$) PE7 (melt index, MI=0.7); ($\bigcirc$) PE3 (MI=0.3); ($\square$) PE07 (MI=0.07).
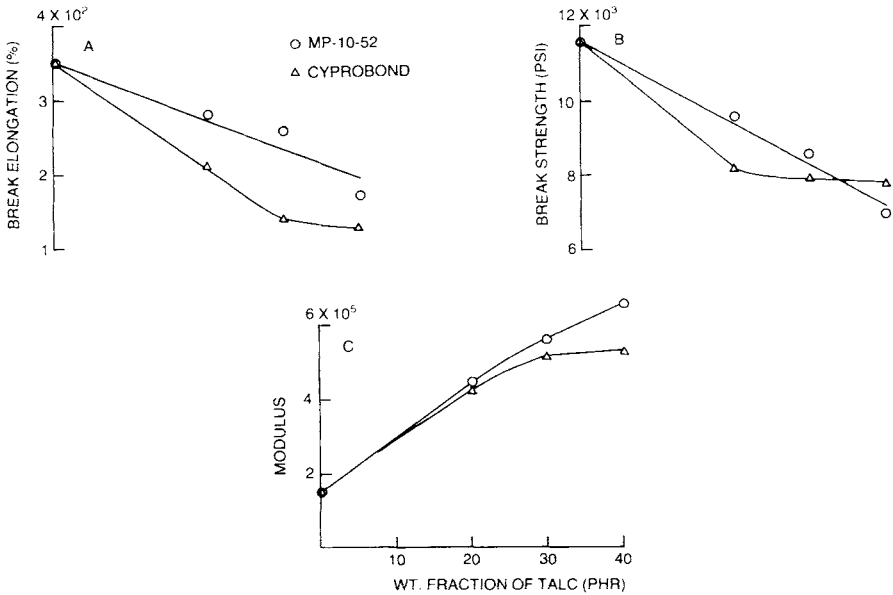
Fig. 9.   Mechanical properties of talc-filled nylon 6 along the machine direction as a function of talc concentration: (A) elongation to break; (B) break strength; (C) modulus; ($\bigcirc$) MP-10-52; ($\triangle$) Cyprobond.

somewhat parallels the dependence of WVT on the size of the talc (Table I). The modulus increases when the particle size is 3 μm and then begins to decrease as the particle size is increased. The yield at elongation remains fairly constant as the particle size is increased beyond 3 μm. All the other parameters, the elongation yield and at break, as well as the break strength, show a steady decrease as the particle size is increased. This series also showed considerably lower elongation at break in the transverse directions, suggesting that the material has poor tear resistance along the machine direction.

DISCUSSION

An understanding of the interactions between the polymer and the solid filler is of considerable interest from a commercial as well as a scientific point of view. Orientation of the talc flakes with their broad faces parallel to the surface of the film can be readily attributed to mechanical forces on the talc particles during processing and the platelet morphology of the talc. But the orientation of the polymer chains in the presence of talc needs to be studied carefully.

Polymer–Substrate Interactions. Our results show preferential orientation of the polymer chain molecules in the presence of talc. The orientation of the film is affected not only by the filler, but by the processing conditions as well. We notice that the (110) planes of polyethylene and the (002) planes of nylon 6 are parallel to the (001) planes of talc. Such an orientation of the crystallographic planes can probably be explained by the mechanical force on the polymer chains at the talc–polymer interface. One can also speculate if such orientation can be attributed to epitaxy. By examining the electron micrographs of fractured surfaces, ultra thin films, and free surfaces of filled samples, Rybniker[8] has shown that polyethylene-crystallized expitaxially on basal planes of sheet silicates in such a way that a system of parallel lamallae, oriented perpendicular to the basal planes of the substrate (polymer chain between the folds parallel to the basal plane) grows out from the filler surface. Our results on talc filled polyethylene are consistent with these findings. It is possible that the planar orientation of the nylon 6 in talc-filled nylon film can also be interpreted as being due to substrate-induced orientation of the nylon 6 chains.

The epitaxial relationship between the polymer and substrate can be analyzed in detail by comparing the various distances on the substrate and in the polymer lattice. The lattice mismatch is 2.4% between the interchain distance of 4.48 Å in the (110) plane of polyethylene and the separation of the (020) planes of talc (4.59 Å). The mismatch is 1.1% if we compare the 4.48 Å chain separation in the polyethylene (110) plane with a distance of 4.53 Å between the (110) planes of talc. This small lattice mismatch suggests that the polymer chains might lie on basal planes of talc, such that the (110) planes of PE are parallel to the (00h) planes of talc and the (001) planes of PE are parallel to (100), (110) or (1T0) planes of talc (Fig. 10). This is confirmed by the experimentally observed orientation of the (110) planes of PE in the presence of talc.

A similar comparison can be carried out on nylon 6 as well. When various interchain distances in nylon are compared with the ($hk0$) distances in talc,
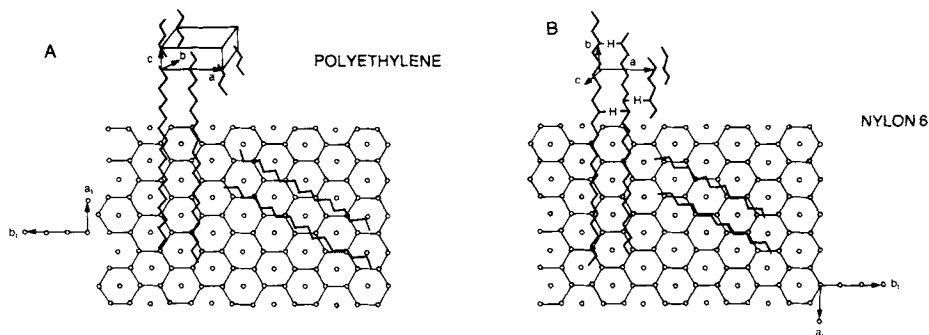
Fig. 10.   Schematic representation of the epitaxial orientation of polyethylene chains (A) and nylon 6 chains (B) on the talc lattice. Talc lattice is represented by axes a_t and b_t. Polyethylene and nylon 6 lattices are shown by a, b, and c axes.

the best match is obtained with the interchain distances in the (002) plane (hydrogen-bonded sheet) of nylon 6. When this interchain distance of 4.78 Å is compared with the 4.59 Å separation of the (002) planes and the 4.53 Å separation of the (110) planes of talc, the mismatch is respectively 4.12% and 5.5%. Thus, it is probable that nylon 6 chains crystallize on the talc basal planes so that the nylon 6 chains which form the hydrogen-bonded sheet, i.e., the (002) planes, are parallel to the (001) planes or the broad faces of talc and the (oko) planes of nylon 6 are parallel to (100), (110) or (1To) planes of talc (Fig. 10). This is confirmed by the orientation of the (200) and (002) reflections of nylon 6 and the (001) reflections of talc. Similar results have been reported for epitaxially crystallized nylon 6 on KCl.[9]

The mismatch calculated here between talc and polyethylene, and talc and nylon 6 is less than what is usually regarded as accepted limits of ±15%,[10] and shows that lattice matching may be responsible for the specific orientation of the polymer crystals. We thus have indirect evidence for epitaxy in extruded polymer films. It should be mentioned that such oriented growth of polymer chains may not exist in the entire bulk of the film. It is possible that the polymer molecules are well oriented near the surface of the talc crystallites and undergo a continuous transition from the orientation of the filler surface to that existing in the bulk of the polymer matrix away from the filler surface.[8] Such a phenomena can explain the absence of complete biaxial orientation, especially in polyethylene (Fig. 2).

Barrier Properties. Although the polymer molecules are biaxially oriented in talc-filled films, this alone cannot give rise to the considerable reduction in the observed gas transmission rate, especially in polyethylene. The reduction in gas transmission rates in talc-filled films can be explained by the effective decrease in the diffusion constant due to the increased path length and the amount of permeant dissolved per unit volume. Model calculations of thin platelets in a regular array[11] show that a large reduction (nearly 10-fold) in permeation can be achieved with filler volume fractions in the 5–20% range (Table II). The reduction in the apparent diffusion constant is, however, sensitive to the distances between particles. With increasing imperfections in the array the diffusion constant quickly approaches the limiting value predicted by model calculations of a random array of particles. Calculations of the possible reduction in the permeation

TABLE II
Sample Calculations for a 50-μm Membrane ($x = 50$)[a]

v_d	d (μm)	b (μm)	t_d (μm)	t_m (μm)	n	h (μm)	$\overline{D}/D_m$
0.05	5	0.5	0.1	1.56	30.2	1.65	0.07
0.05	5	0.5	0.5	7.76	6.0	8.25	0.13
0.05	5	1.0	0.1	1.29	36.0	1.39	0.12
0.05	5	1.0	0.5	6.46	7.2	6.94	0.24
0.10	5	0.5	0.1	0.73	60.5	0.82	0.04
0.10	5	0.5	0.5	3.64	12.1	4.13	0.11
0.10	5	1.0	0.1	0.64	72.0	0.69	0.07
0.10	5	1.0	0.5	3.23	14.4	14.40	0.19
0.20	5	0.5	0.1	0.31	1.2	0.41	0.02
0.20	5	0.5	0.5	1.57	24.2	2.07	0.08
0.20	5	1.0	0.1	0.32	144.0	0.35	0.04
0.20	5	1.0	0.5	1.24	28.8	1.74	0.14

[a] v_d = volume fraction of filler, d = dimensions of a rectangular parallelepiped in the platelet plane, b = gap distance between the plates in the plane of the platelet, t_d = thickness of plates, t_m = separation between plates, n = number of layers of plates, h = factor related to distance between plates, $\overline{D}$ = diffusion coefficient of the composite, D_m = diffusion coefficient of the matrix, and $x = n(t_d + t_m)$.

rates using literature suggested models[12-14] for random arrays are shown in Figure 11. Possible reductions of 60–70% are indicated at prohibitively high filler volume fraction of 40% (about 65 wt % of talc in polyethylene).

The reductions as high as 60% in the permeation rates of water vapor in polyethylene, and O_2 in nylon, on the addition of 30–40 wt % of talc, about 15 vol %, shows the distinct advantage of the oriented plate like particles of talc in these systems. The improved barrier properties with
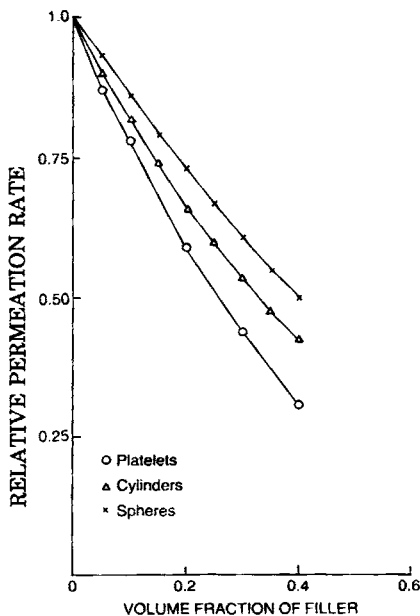

Fig. 11. The relative permeation rates predicted from model calculation of randomly oriented filler particles in heterogeneous media[12].

particle size reduction at a fixed talc fraction is a reflection of the increased diffusion path length resulting from the reduced probability of finding large distances between particles. With increased fractions of filler, there is a reduction in the effectiveness of the filler particle due to the increase in overlap between talc platelets in adjacent layers. It is also difficult to achieve good void free mixtures of high filler loadings greater than 30 wt % in plastics. These two factors lead to a leveling in barrier properties.

Mechanical Properties. The properties of the composite materials are obviously determined by the properties of the components. The mechanical properties reported here are in general agreement with the behavior expected of polymer composites with rigid fillers.[7] Since it is difficult to disperse fine particulate matter in viscous polymer melts and get good dispersion, the composites can have a range of stress–strain properties depending upon the processing conditions. Nearly all composites contain some amount of entrapped air and this, which is influenced by the processing conditions and the degree of dispersion of the filler, can greatly influence the mechanical properties of the composite. In spite of these variations, we can still get an idea of the effect of the size and the concentration of the filler on the properties of the composite.

The properties of the composites with fillers in the form of flakes have been discussed in the literature (see, for example, Ref. 7). The flakes are expected to produce unusually large increases in the modulus, especially, as in our case, if the flakes are oriented predominantly in the plane of the film. However, even though in theory flake composites could have very high strengths, these strengths are difficult to achieve in practice. This is borne out by our results. It is probable that the flakes are not perfectly aligned or there may not be an optimum overlap of one flake over another. Poorly aligned or stacked flakes act as stress concentrators and reduce the strength of the composite. We also noticed, especially in polyethylene, that the addition of talc resulted in poor tear resistance along the machine direction. If the filler is coated with a liquid, such as ethylene oxide oligomer, elongation to break increases considerably, but will decrease the modulus of elasticity of the filled polymer.[15]

The modulus of the polymers increases with rigid fillers, and this increase is determined by the concentration of the filler, shape of the particle, relative modulus of the components, and the packing of the fillers. Nature of the interface and the degree of adhesion, which may not be very important in determining the elastic modulus, can have a significant effect on the strength and stress–strain behavior of the composites. Although theories indicate that the elastic moduli of a composite material should be independent of the size of the filler particles, our results (Table I) show an increase in the modulus as the particle size decreases. It is possible that the polymer is changed in some manner at the interface, as by adsorption, and therefore the properties such as modulus change with the particle size since smaller particles have larger surface area for the same filler concentration.

Generally fillers cause a dramatic decrease in elongation to break and often decrease the tensile strength of the polymer (Figs. 8 and 9). The decrease in elongation to break is because in polymers filled with rigid particles, all the elongation occurs in the polymer phase. The actual elon-

gation experienced by the polymer is much greater than the measured elongation of the specimen.

As seen in Table I, the tensile strength increases as the particle size decreases. This again is probably due to the increase in interfacial area per unit volume of the filler as the particle size decreases. Also, even though the stress fields near a particle are independent of the size of the particle, the volume of the polymer that experiences a given value of stress concentration increases with particle size, so that the probability of finding a large flaw in this volume also increases, thus contributing to the decreased tensile strength of the film.

To summarize our observations on the mechanical and barrier properties of the talc-filled films, an optimum reduction in the rate of vapor transmission can be obtained with small talc particles (less than 3–8 μm in diameter) or less and at a loading of $\approx$30 percent by volume. Epitaxial relationship between the polymer and the substrate, and the higher local deformation of the polymer chains at the talc–polymer interface may be responsible for the orientation of the polymer in talc filled films.

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