Wide-Angle X-ray Scattering Study of Crystalline Orientation in Reticulate-Doped Polymer Composites

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ABSTRACT: Reticulate doping consists of casting a composite film from a solution containing both a polymer and a charge-transfer complex (CTC) and allowing the conductive free radical salt to recrystallize as the solvent is removed from the polymer. In this study, a highly branched, low molecular weight polyethylene (PE) was doped with the CTC tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ). Wide-angle X-ray scattering (WAXS), conductivity, optical microscopy, stress relaxation, and differential scanning calorimetry (DSC) measurements were used to show the effect of the addition of filler and uniaxial orientation on the mechanical and electrical properties of the composites. It has been shown that increasing TTF–TCNQ concentration shifts the preferential orientation of the crystalline phase of the PE from slightly perpendicular to slightly parallel to the casting surface. WAXS measurements were made on samples that were uniaxially stretched at 80°C and cooled to room temperature. These experiments showed a smaller incremental increase in crystalline orientation with increasing TTF–TCNQ. This observation was consistent with a drop in initial relaxation times calculated from room temperature stress relaxation experiments. In the unoriented composites, increasing TTF–TCNQ loading had no effect on PE crystallinity; however, the increase in crystallinity caused by uniaxial stretching was decreased by the presence of TTF–TCNQ. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1785–1794, 1998

Key words: conductive polymer composites; reticulate doping; WAXS; relaxation; orientation

INTRODUCTION

Electrically conducting thermoplastic composites consist of a conductive filler supported by an insulating polymer matrix. The advantages of using thermoplastic composites versus other conducting materials include processibility, flexibility, ability to absorb mechanical shock, corrosion resistance, low thermal conductivity, ability to form complex parts, parts consolidation, and conductivity control.[1] Much of the research in conductive composites was initiated to find an inexpensive method for electromagnetic shielding of computers and electronic equipment as these devices moved from shielded rooms to desktops in homes and offices. Examples of other applications for conductive composites, both present and future, include conductive adhesives, energy storage devices, switching devices, static charge dissipating materials, and surge-protection devices.[2]

To achieve conduction in filled polymer systems, conductive pathways of filler particles must form throughout the matrix, allowing electrons to freely move from one side of the material to an-

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other.[3] Percolation statistics quantitatively relate the volume fraction of the filler to the electrical conductivity of the composite.[4,5] The critical volume fraction, V_c, also called the percolation threshold, is the lowest concentration of filler that forms continuous conductive pathways throughout the matrix. The composite conductivity increases slowly with increasing filler concentration until the critical volume fraction is reached.[6] At V_c a very sharp jump in conductivity is obtained over a very small range in concentration, referred to as the critical region. In the critical region the conductivity, σ, and concentration have a power law relationship as given by eq. (1),

$$\sigma \propto (V - V_c)^t \tag{1}$$

where V is the volume fraction.[7] The power law index, t, is a function of the interactions between the polymer and the matrix.[8] The critical region ends when all of the filler particles are involved in at least one conductive pathway, and higher filler concentrations only achieve moderate changes in conductivity.

The critical volume fraction can be reduced by increasing the degree of segregation between the conducting and insulating phases or increasing the aspect ratio of the filler.[9,10] Conduction is also affected by the interactions between the insulating polymer and the conductive filler. In systems with high polymer–filler adhesion, the polymer forms a thick film around the particle that limits the particle–particle contact; thus, the composite has low conductivity but good mechanical properties. In systems with weak polymer–filler adhesion, the particles have a higher probability of contacting, but the mechanical properties deteriorate due to the presence of the filler.[11] The intrinsic balance between conduction and mechanical properties has been a major stumbling block in bringing electrically conducting thermoplastic composites to many commercial markets.

Reticulate doping of polymers with an organic charge-transfer complex (CTC) allows the intrinsic balance between conduction and mechanical properties to be shifted by forming continuous conductive pathways at low volume fractions. Reticulate doping consists of casting a composite film from a solution of both the polymer and CTC and allowing the conductive salt to microcrystallize in the polymer matrix forming conductive pathways.[12] Most CTC form long rod-shaped crystals with high aspect ratios, thus conducting elec-

tricity at very low filler concentrations.[13,14] Because the filler concentration is low, the mechanical properties of the composite are similar to those of the unfilled polymer matrix. This effect can be enhanced by using polycrystalline polymers as the supporting matrix, because the filler particles are excluded from the crystalline regions.[15] This phase segregation increases the filler concentration in the amorphous phase, thus increasing the probability of forming conductive pathways, and lowering the critical volume fraction.

Studies of the conductivity of solution cast films as a function of casting temperature, solvent, and concentration of CTC in the solution have been carried out for free radical salts such as tetrathiothetracene–tetracyanoquinodimethane (TTT–TCNQ), tetrathiafulavalene–TCNQ (TTF–TCNQ), N-methyl Phthalazinum (TCNQ)$_2$ [mPht(TCNQ)$_2$], N-propyl phthalazenium (TCNQ)$_2$ [PrPht(TCNQ)$_2$], and 2,2'-Bipyrydylamine (TCNQ)$_2$ [BIPA(TCNQ)$_2$] in amorphous polymers, such as polycarbonate (PC) and polymethamethylacrylate (PMMA), as well as semicrystalline polymers such as polyethylene (PE) and polypropylene (PP).[16] The AC conductivity, thermopower, and magnetic properties of TTT–TCNQ and TTF–TCNQ films have been studied in order to obtain greater insight into charge transfer conduction mechanisms in reticulate-doped polymers.[17,18] In addition, Finter et al. have tested a modified method for reticulate doping of polymers by *in situ* complex formation and crystallization directly in the matrix as a method for producing films of insoluble charge transfer complexes.[19]

Often secondary shaping methods are required to obtain the necessary shape for a polymer composite application. Many of these processes change the morphology of the cast film and cause orientation of the polymer, which affects the relationship between CTC and the supporting matrix. This study looks at the effect of orientation via uniaxial stretching on the properties of reticulate-doped polymer composites. Uniaxially stretching a polymer composite aligns the filler particles in the stretching direction and creates internal stresses. The alignment of the anisotropic conductive filler increases conductivity in the stretching direction, due to an increased number of particle–particle contacts. However, the centers of the particles also become separated; hence, a plot of conductivity in the longitudinal direction vesus draw ratio generally shows a maxima due to these two competing effects. To further complicate

Figure 1 TTF–TCNQ.

this behavior, the internal stress can affect the efficiency of electron transfer from one particle to another, especially at low strains. Our experiments were not able to separate these complicated phenomena; rather, they indicated how these effects combine to change the conductivity in the stretching direction.

Composites of TTF–TCNQ supported by a highly branched, low molecular weight polyethylene (PE) were produced with varying filler concentrations and draw ratio. TTF–TCNQ, shown in Figure 1, was chosen as the CTC. TTF–TCNQ has a very high single crystal conductivity of approximately 500 S/cm, is well characterized and scatters at angles that do not overlap with scattering from PE in selected regions.[20,21] The PE used was chosen because it is often used as the supporting matrix in conductive thermoplastic composites. PE was a highly branched, low molecular weight polymer with a density of 0.906 g/cc. The weight average molecular weight was 35,000 g/mol, and the polydispersity index was 4.5. The melting point of the material was approximately 90°C and the melt flow index was 2250 g/10 min at 190°C. This particular grade of PE, while having a lower melting point and crystallinity than most commercial grades of low-density polyethylene, was chosen as the matrix because of its solubility in chlorobenzene at high polymer concentrations. WAXS experiments were done in conjunction with conductivity measurements, optical microscopy, stress relaxation measurements, and differential scanning calorimetry (DSC) to more fully understand the effects of TTF–TCNQ on the matrix morphology and bulk properties of reticulate-doped polymer composites.

EXPERIMENTAL PROCEDURES

Film Preparation

TTF was synthesized and purified by the procedure outlined by Narita and Pittman.[22] TTF was complexed with TCNQ (Aldrich) by crystallization from a solution of acetonitrile (Aldrich). The composite films were produced by making a 10 mM solution of TTF–TCNQ in chlorobenzene (Aldrich). PE (Aldrich) was dissolved by adding 10 mL of chlorobenzene for every gram of PE at 100°C. After both the TTF–TCNQ and PE were dissolved, the solutions were mixed and stirred at 100°C, then cast on a 70°C mercury surface. The films were covered with a with a film permeable to the chlorobenzene and left on the mercury for 48 h. The composite films were removed from the mercury surface and left under the hood overnight. Any residual solvent was removed by placing the samples in a vacuum oven at 70°C for an additional 24 h.

A motor-driven stretching apparatus built at The University of Oklahoma was used to uniaxially orient the samples parallel to the casting surface. Brittle failure of the highly filled samples was overcome by heating all samples to approximately 80°C before stretching. The samples were cooled under stress to room temperature by forced air.

Orientation—WAXS

Orientation was measured as a function of draw ratio by wide-angle X-ray scattering (WAXS). Full characterization of the reticulate doped composites required measurements at different filler concentrations and different draw ratios. Each sample required data acquisition at two different scattering angles (2Θ). By carrying out these studies at Stanford Synchrotron Radiation Laboratory (SSRL), high photon flux synchrotron radiation allowed characterization to be performed quickly. The WAXS measurements were obtained using the coordination system defined in Figure 2(a). The Z axis is defined as the crystalline chain axis (the c-axis) and the angles α, β, and ε are the angles between the stretching direction, **S,** and the **X, Y,** and **Z** axes, respectively.[23] In Figure 2(a), the points a, b, and c form a crystalline reflection plane that has a unit vector, **N,** normal to the plane surface. The angle of orientation (ϕ) is the angle between $\underline{\mathbf{N}}$ and a unit vector, $\underline{\mathbf{S}}$, in the stretching direction.

Figure 2 (a) WAXS coordination system; (b) WAXS experimental geometry.

$$\underline{S} = \cos(\alpha)\,\vec{\imath} + \cos(\beta)\vec{\jmath} + \cos(\varepsilon)\,\vec{k} \qquad (2)$$

$$\underline{N} = \cos(E)\,\vec{\imath} + \cos(F)\,\vec{\jmath} + \cos(G)\,\vec{k}$$

$$\underline{N} = e\,\vec{\imath} + f\vec{\jmath} + g\,\vec{k} \qquad (3)$$

The coefficients of $\underline{N}$ are denoted e, f, and g to simplify the expressions below, and are determined from the reflection plane $[hkl]$ and the crystal structure. The angle ϕ is given by eq. (4).

$$\cos(\phi) = \underline{N}\cdot\underline{S} = e\,\cos(\alpha) + f\,\cos(\beta) + g\,\cos(\varepsilon) \quad (4)$$

Squaring and averaging eq. (4) gives eq. (5):

$$\begin{aligned}
\langle\cos^2(\phi)\rangle = {} & e^2\,\langle\cos^2(\alpha)\rangle + f^2\,\langle\cos^2(\beta)\rangle \\
& + g^2\,\langle\cos^2(\varepsilon)\rangle + 2ef\,\langle\cos(\alpha)\cos(\beta)\rangle \\
& + 2fg\,\langle\cos(\beta)\cos(\varepsilon)\rangle \\
& \qquad + \langle 2eg\,\cos(\alpha)\cos(\varepsilon)\rangle \quad (5)
\end{aligned}$$

To determine the average value of $\langle\cos^2(\phi)\rangle$ experimentally, the scattered intensity at a given 2θ was averaged over the azimuthal angle (χ), given by eq. (6):

$$\langle\cos^2(\phi)\rangle = \cos^2(\theta)\,\langle\cos^2(\chi)\rangle \qquad (6)$$

As shown in Figure 2(b), the sample was rotated in the azimuthal direction with the detector fixed at an angle 2θ to determine $\langle\cos^2(\phi)\rangle$ according to the expression above. The second term on the right side of eq. (6) was determined from eq. (7):

$$\langle\cos^2(\chi)\rangle = \frac{\displaystyle\int_0^{\pi/2} I(\chi)\cos^2(\chi)\sin(\chi)\,d\chi}{\displaystyle\int_0^{\pi/2} I(\chi)\sin(\chi)\,d\chi} \qquad (7)$$

where I is the intensity of the scattered X-rays. In practice, the integrals were replaced by sums as shown in eq. (8)[24]:

$$\langle\cos^2(\chi)\rangle = \frac{\displaystyle\sum_0^{\pi/2} I(\chi)\cos^2(\chi)\sin(\chi)}{\displaystyle\sum_0^{\pi/2} I(\chi)\sin(\chi)} \qquad (8)$$

Equation (5) has a total of six unknowns; hence, without further simplifications, at least five crystal planes would be required to determine the orientation functions in each direction. The orthogonality of the system provides the sixth equation.

$$\cos^2(\alpha) + \cos^2(\beta) + \cos^2(\varepsilon) = 1 \qquad (9)$$

The angles α, β, and ε are evaluated from eq. (5). If the pure axial crystal plane reflections can be obtained then only three planes need to be studied and eq. (5) simplifies, as shown in eq. (10):

$$\langle\cos^2(\phi_{h00})\rangle = \cos^2(\alpha)$$

$$\langle\cos^2(\phi_{0k0})\rangle = \cos^2(\beta)$$

$$\langle\cos^2(\phi_{001})\rangle = \cos^2(\varepsilon) \qquad (10)$$

Another simplification can be made for particular crystal structures allowing fewer than five reflection planes to be required. Because PE has an orthorhombic crystal structure the crossproduct terms in eq. (5) are zero, as shown in eq. (11), and only two reflection planes were required for characterization[24]:

$$\begin{aligned}
\langle\cos^2(\phi)\rangle = {} & e^2\,\langle\cos^2(\alpha)\rangle + f^2\,\langle\cos^2(\beta)\rangle \\
& + g^2\,\langle\cos^2(\varepsilon)\rangle \quad (11)
\end{aligned}$$

PE [110] and [200] reflection planes, at 21.4° and 23.7°, respectively, were used for characterization of the crystalline orientation.[25,26] The values of e, f, and g for the [110] reflection plane are 0.554, 0.832, and 0, while those of [200] are 1, 0, and 0, respectively. Figure 3 shows 2Θ from 20° to 25°, the region of interest for the orientation studies, for both the TTF–TCNQ and the PE, and indicates that there is no significant scattering of

Figure 3   WAXS comparison for TTF–TCNQ and PE.

the TTF–TCNQ at either [110] or [200] PE reflection planes.

Conductivity Measurements

Depending on the filler loading of the composite, two different methods were used to measure the DC electrical conductivity. Conductivity measurements on samples with high filler content were done in a four-point probe geometry, while samples with low filler loading were measured in a sandwich geometry. Copper electrodes were attached using a silver conductive epoxy (TRA-CON, BA-2902). A INSTEK Model PS-6010 Power Supply was used to induce the current, and a Keithly 197A multimeter was used to measure the voltage. Further details about both the four-point probe and sandwich geometry are given in ASTM standards D-4496 and D-257, respectively.

Stress Relaxation Measurements

The stress relaxation properties of the composites were measured with an Instron TT-C-L tensile tester with a specially designed computerized data acquisition system. An initial strain rate of 2.1% induced at a rate of 2.54 cm/min was used. The samples were produced with a ASTM Standard D-1708 die.

Crystallinity

The crystallinity was determined by differential scanning calorimetry using a Perkin-Elmer DSC II calorimeter at a scanning rate of 10°C/min and a computerized data acquisition system designed at the University of Oklahoma. Fractional crystallinity, X, was calculated as shown in eq. (13),

where ΔH_f is the measured heat of melting and ΔH_f^0 is the heat of melting for a pure crystalline material, which is given in the literature as 282 J/g[24]:

$$X = \frac{\Delta H_f}{\Delta H_f^0} \qquad (12)$$

RESULTS AND DISCUSSION

As expected, reticulate doping of polymers allows conductive pathways to be formed at very low volume fractions due to the formation of micro-crystallites inside the matrix.[27,28] Figure 4 shows the percolation diagram for the unstretched PE composites. The conductivity profile should follow an S-shaped curve where the percolation threshold is the point of the upturn in the diagram. The lack of an upturn in Figure 4 indicates that the critical volume fraction is below 2.5% by volume (4.5% by weight). The percolation threshold for the TTF–TCNQ composites is much lower than that of conventional fillers such as carbon black and metal powders, which have critical volume fractions of 10 and 30%, respectively.[6,29] The critical region ends when the conductivity is no longer a strong function of volume fraction which, for the TTF–TCNQ–PE system, is between 5.0 and 10.0% by volume (8.8 and 17.0% by weight).

Figure 5 contains two photos from a Nikon Optical Microscope of the TTF–TCNQ both at 320× (a) showing the long rod-shaped particles, and at 800× (b) showing the branching from one particle. Optical microscopy showed that there

Figure 4   Percolation diagram for TTF–TCNQ–filled PE.

(a)

(b)

Figure 5   Optical microscopy of TTF–TCNQ particles: (a) 320× magnification; (b) 800× magnification.

was a large distribution of aspect ratios of the TTF–TCNQ for a given volume fraction, and both the maximum and average aspect ratios were drastically affected by the volume fraction of filler. The maximum aspect ratio, shown in Figure 6(a), was largest for the TTF–TCNQ cast onto a surface with no matrix and consistently decreased as a function of TTF–TCNQ volume fraction in the reticulate doped composites. The average aspect ratio, shown in Figure 6(b), decreased rapidly in presence of the matrix, but was constant at high filler loading. Metal fibers with a similar aspect ratio still required at least 5% by volume to create a continuous conductive network, a much higher volume fraction than found in this study for TTF–TCNQ.[30] There was a significant amount of branching of the TTF–TCNQ particles, which probably decreases the percolation threshold by acting as an interconnect for TTF–TCNQ.

The orientation of the composite films was quantitatively characterized as $\cos^2(\varepsilon)$, where ε is the angle between the stretching direction, **S,** and the polymer chain axis, shown as the **Z** axis in Figure 2(a). The value of $\cos^2(\varepsilon)$ can be between 0 and 1. If the orientation of the chain axis is perpendicular to the stretching direction, then $\cos^2(\varepsilon)$ is 0. If the chain axis is parallel to the stretching direction, then $\cos^2(\varepsilon)$ is 1. When the chain axis is randomly distributed, then $\cos^2(\varepsilon)$ is 1/3.

Figure 7 shows pole figures at a diffraction angle of 21.4° for 10% by volume TTF–TCNQ at draw ratios of 1.0 and 2.0, respectively. For perfectly unoriented materials the relative intensity would be constant. The slight increase in intensity with χ in Figure 7(a) indicates a slight preferential orientation in the unstretched composites, while in Figure 7(b) the sharper increase in intensity with χ shows much higher PE crystallite orientation. Figure 8 shows the orientation as a function of TTF–TCNQ volume fraction for the unstretched samples. In composites with TTF–TCNQ concentrations of 0, 2.5, and 5% by volume, the PE crystallites were slightly oriented perpen-

Figure 6   (a) Maximum aspect ratio of TTF–TCNQ as a function of TTF–TCNQ concentration; (b) average aspect ratio of TTF–TCNQ as a function of TTF–TCNQ concentration.

Figure 7 Chi scan at 21.4° for a 10% by volume TTF–TCNQ composite: (a) unstretched; (b) stretched to λ = 2.0. The solid lines have been added to help guide the eye and are not intended to indicate any functional form of the intensity.

Figure 9 Orientation of stretched TTF–TCNQ–filled PE as a function of draw ratio and filler volume fraction.

dicular to the casting surface. In samples with higher filler concentrations in the plateau region of conductivity, the crystallites were oriented slightly parallel to the casting surface. Reticulate doping has been shown to form long rod-shaped crystals with the conducting phase forming a two-dimensional network parallel or at small angles to the casting plane.[18,31] This network oriented the PE crystallites parallel to the casting surface, as indicated by the shift in initial orientation from slightly perpendicular to slightly parallel to the casting surface.

Figure 9 shows the orientation of the PE crystallites as a function of draw ratio for 0, 2.5, 10, and 20% by volume TTF–TCNQ. As expected, crystalline orientation in the stretch direction in-

creased with increasing draw ratio. The increase in orientation resulting from uniaxial stretching decreased with increasing filler concentration, i.e., the slope of the lines in Figure 9 were lower for higher TTF–TCNQ concentrations. One explanation for this behavior is that the addition of TTF–TCNQ to the polymer causes a decrease in the relaxation time. To test this hypothesis, stress relaxation measurements were performed.

Stress relaxation measurements were done at room temperature, while stretching was done at approximately 80°C. Thus, the relaxation measurements are not directly comparable to the stretching conditions, but give some insight into the effect of TTF–TCNQ on the relaxation process. Figure 10 is a plot of the first 30 s of the relaxation measurements for several different concentrations of TTF–TCNQ. The downward shift indicates faster relaxation for increasing TTF–TCNQ. This effect was quantified by fitting the experimental data to relaxation models to determine the relaxation time constants as a function of filler volume fraction. The simple Maxwell model shown in eq. (13), with one relaxation time, τ, was used to model the data, but this model had an average correlation coefficient of 0.845, and clearly did not fit the data.

Figure 8 Orientation of unstretched TTF–TCNQ filled PE as a function of filler volume fraction.

$$\frac{E(t)}{E(0)} = e^{-t/\tau} \qquad (13)$$

The failure of the one parameter model was not unexpected because polymeric materials have several different relaxation processes occurring

Figure 10 Stress relaxation of TTF–TCNQ–filled PE as a function of filler loading.

simultaneously at different rates, such as segmental motion, chain coiling and uncoiling, and chain alignment.[32] Models with only one time constant are usually only valid over a very limited range of time, and real polymer systems often require the characterization of several time constants.[33] The Maxwell-Wiechert model, shown in eq. (14), was used to model the data.

$$\frac{E(t)}{E(0)} = \sum_0^\infty E_i e^{-t/\tau_i} \tag{14}$$

An acceptable fit with an average coefficient of determination of 0.970 was obtained with two

terms, and the equation was truncated after the second term as shown in eq. (19).[34]

$$\frac{E(t)}{E(0)} = E_0 e^{-t/\tau_0} + E_1 e^{-t/\tau_1} \tag{15}$$

E_i are the dimensionless relaxation moduli and τ_I are the relaxation times. E_0 and E_1 were 0.49 $\pm$ 0.03 and 0.34 $\pm$ 0.04, receptively, with no significant changes with volume fraction of TTF–TCNQ. The tensile modulus was 115 $\pm$ 16 MPa and was also not affected by the presence of the filler. Therefore, the constant tensile modulus is consistent with the observed constant relaxation moduli.

Relaxation times, however, were not constant with volume fraction, indicating that perhaps different relaxation times might account for the difference in orientation of stretched samples found in WAXS experiments. Figure 11(a) shows the relaxation time corresponding to the slower process, τ_1, may slightly decrease with increasing volume fraction, but the errors in measurement make it difficult to draw this conclusion with certainty. Figure 11(b) shows that the relaxation time corresponding to the faster process, τ_0, definitely decreased with increasing volume fraction and remained constant at filler loadings above the critical region. Figure 11 indicates that relaxation of the unfilled PE or low-volume fraction-filled polymers was slower than that of the highly filled polymer. Therefore, the initial hypothesis was

Figure 11 (a) Slower relaxation time as a function of volume fraction TTF–TCNQ; (b) faster relaxation time as a function of volume fraction TTF–TCNQ.

Figure 12 Composite conductivity as a function of volume fraction TTF–TCNQ and draw ratio.

Figure 13 Baseline subtracted DSC curves for stretched, 2.5% TTF–TCNQ composite films as a function of draw ratio.

confirmed: the addition of TTF–TCNQ causes a decrease in the relaxation time and may be the cause of the decrease in PE crystallite orientation in WAXS measurements.

Stretching the composites led to an initial increase in conductivity followed by a five-orders of magnitude drop in conductivity, as shown in Figure 12. Initial stretching caused an increase in conductivity, most likely as a result of TTF–TCNQ particles forming more linear conductive pathways. As draw ratio increases further, the conductive rods were either broken by the stress, or the rods were pulled apart, leading to fewer conductive pathways and a decrease in conductivity.

The fractional crystallinity of the unstretched material was determined by DSC to be 22.7 ± 1.6% and was unaffected by volume fraction of filler. Because this fractional crystallinity was extremely low for a polyethylene, the crystallinity was calculated from WAXS experiments to confirm DSC results. The fractional crystallinity from WAXS using the parameter B = 3.25 as reported by Kakudo and Kasai was 19.9% for the unfilled material, which is well within the normal differences found by these two methods.[23] Figure 13 shows the baseline subtracted DSC curves for the 2.5% TTF–TCNQ composites as a function of draw ratio. As expected, the crystallinity did increase with draw ratio, but the addition of TTF–TCNQ inhibited crystallization during stretching as shown in Figure 14. The incremental increase in crystallinity due to stretching declined with TTF–TCNQ volume fraction until the concentration was above the critical region, where no increase in crystallinity with stretching was observed.

CONCLUSIONS

Solution-cast films of PE showed orientation of the crystallite lamella perpendicular to the casting surface, but the addition of TTF–TCNQ microcrystallizing inside the matrix forced PE crystals to preferentially form parallel to the casting surface. Uniaxial stretching parallel to the casting surface increased the orientation of the crystallites along the stretching direction. The incremental increase in orientation with stretching was decreased with higher filler loading. The conductivity of the composites decreased by approximately five orders of magnitude by stretching to a draw ratio of 2.0. In addition, the fractional crystallinity of the PE was not affected by the volume fraction of TTF–TCNQ. The incremental

Figure 14 Crystallinity of TTF–TCNQ–filled PE as a function of volume fraction and draw ratio.

increase in fractional crystallinity attained by stretching decreased in the critical region, and above the critical region the fractional crystallinity was constant for all draw ratios tested.

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