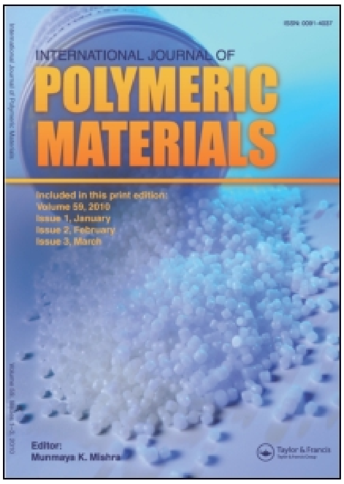

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Rolltrusion Processing of Polymers for Property Enhancement

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Rolltrusion is a single step solid state deformation process that has been successfully applied to many polymers and copolymers to produce unique properties. Property enhancement results in 3D mechanically improved behavior over the original workpiece without the need for cross-plying. Processing-structure-property relationships have been established. Rolltruded polymers are transparent since they are free of spherulites, rather they are comprised of anisotropic small crystallites formed from spherulites. The crystallites are crystallographically arrayed and interconnected by tie molecules that provide property improvement in three mutually perpendicular directions. Thin films have also been made and these may be used as membranes for the separation of small molecules. Permselective membranes so formed are pinhole free and very strong with a regulated 3D morphology. The rolltrusion technique is not restricted by the solubility constraints inherent in preparing solvent based thin films. Consequently, engineering plastics may be made into membranes without regard for their limited solvent solubility. Rolltrusion has now been established as a universal procedure for property enhancement of commercial and engineering polymers.

KEY WORDS Rolltrusion, 3D mechanical properties.

INTRODUCTION

Property enhancement through mechanical deformation has figured prominently in material property improvements for more than half a century. For several decades now, there has been considerable diversity in the techniques employed to create stronger and improved polymers. Many of these have been reviewed in the literature[1–5] and will not be mentioned further in this article. The goal of much of the experimental work is to produce polymers with mechanical properties approaching predicted theoretical tensile strength and tensile modulus. Although there has not been complete agreement on these parameters our knowledge has advanced considerably, but not without limitations. Some literature claims have placed the measured tensile modulus of polymers close to theoretical predictions. While this situation may be realized in fibers, it is unlikely to be reached in large polymer sections with significant polydispersity, where heterogeneities such as molecular chain length, microfibrils, macrofibrils, chain ends, various defects and kink bands in the crystalline phase are obtained. All of these and other features (see Figure 1) are important in relation to polymer property enhancement. Solid state factors must be less critical in rolltruded materials than in ultradrawn polymers where defects reduce the

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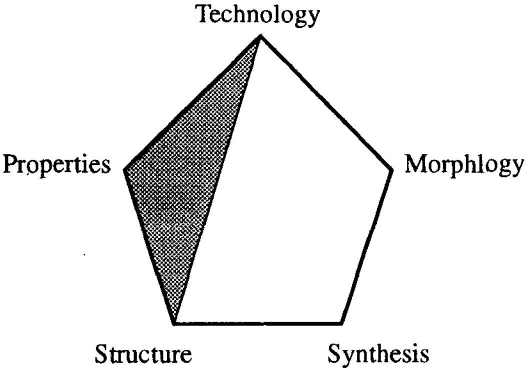

FIGURE 1 Interdependence of technology on primary parameters.

ultimate properties in proportion to theoretical goals or limits. Rolltrusion was introduced initially to provide significant overall property enhancement at an affordable cost as a consequence of the unique periodic texture that is created in a single-step process.[6–11] The morphology is commensurate with a triaxial crystallite morphology where the crystallites are interconnected by variously stretched "amorphous" tie molecules that bridge them in three directions. This significant texture arises because of the considerable take-off tension that is simultaneously coupled with a very high compressive load applied to the workpiece in the roller nip region. As a result of this deformation mode the polymer workpiece, whatever its initial state, experiences a triaxial stress field that is responsible for its 3D morphology, has been verified through testing. Spherulitic as well as amorphous polymers have been rolltruded. The deformation conditions for each polymer must be established beforehand, so that the resulting workpiece becomes transparent, essentially free of voids and is comprised only of crystalline/amorphous inhomogeneities that are too small to scatter white light randomly.† Details of this morphology and its implications will be discussed later. Suffice it to point out here that our primary objective in the rolltrusion was to improve polymer properties so that they become far superior to the original commercial or starting plastics. Consequently, commercial plastics[8] of moderate molecular weight have been converted into quality materials with properties often comparable with some engineering plastics, except of course in respect of their inherently lower melting temperatures, which depends primarily upon the chemistry and bonding in the respective polymer system. From published results on rolltruded polymers the 3D texture that is created is unique and can be used to advantage to produce strong selective membranes[12] amongst other items for vapor and liquid transmission. Relatively thin transparent films may be produced without the use of solvents (noxious or otherwise), which is a considerable process advantage in membrane/film preparation.

EXPERIMENTAL PROCEDURE

This will only be described schematically (Figure 2) since we are merely concerned here

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† If the starting workpiece is amorphous and transparent it remains so after being processed as in the case of poly(ethyleneterephthalate) for example, in which a fully developed 3D structure is developed via rolltrusion (unpublished results).

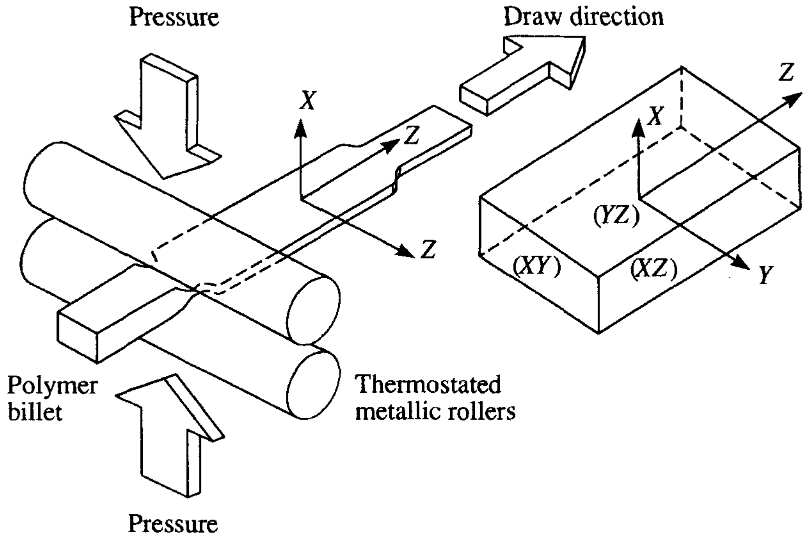

FIGURE 2 Scheme of the rolltrusion apparatus for double orientation. The coordinate insert illustrates the triaxial dimensionality of the processed workpiece.

with the basic features of rolltrusion and not the details of the existing automated computer controlled continuous process that is now operational.[13] Variously sized polymer billets of all kinds, and strips/rolls of different widths and thicknesses can be converted into very strong clear transparent sheets.† During processing the workpiece only becomes thinned in the thickness (compression) direction, there being little or no change in the width of the billet/specimen entering and leaving the rolls; hence there is the clear distinction with regular rolling *per se*. Rolltrusion of sheet-like polymer extrudates can also be converted into processed articles with improved 3D properties, without loss of transparency, and need for conventional cross-plying techniques often used to improve properties.

MORPHOLOGY OF ROLLTRUDED POLYMERS

The enhancement in properties arises as a result of well oriented crystallites‡ (in essence crystallographically oriented) within the workpiece interconnected essentially in three mutually perpendicular directions by tie molecules as illustrated in Figure 3. Mechanical properties of all rolltruded materials follows a general pattern for all polymers of moderate to high molecular weights. It has been established that the relative improvements in properties that occur with respect to the coordinates of the original workpiece such that $Z \gg Y > X$ direction (see insert in Figure 2). This pattern and resultant properties have been substantiated using conventional testing techniques that are commonly used for polymer characterization.

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† About a dozen different polymers, copolymers and composites have been rolltruded successfully.

‡ Unless the polymer is not crystallizable under the designated rolltrusion conditions.

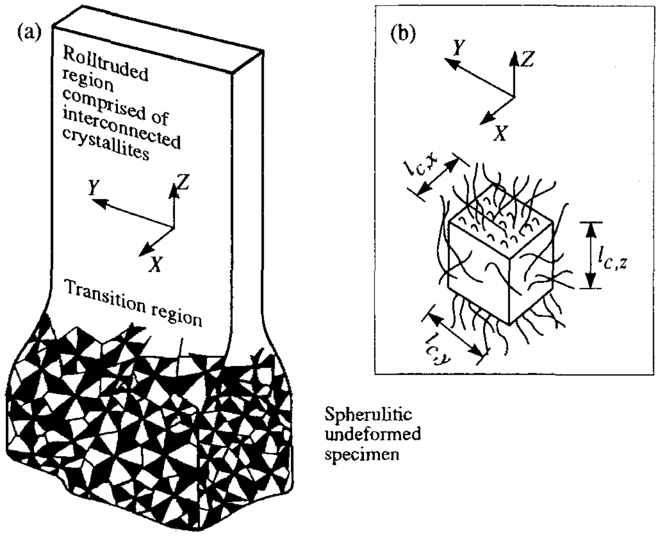

FIGURE 3 (a) Morphological model of unprocessed and rolltruded part of a polymer. (b) The enlarged view of a crystallite with tie molecules running in the X, Y, and Z directions to neighboring crystallites.

MECHANICAL PROPERTIES

Tensile tests on processed specimens have been made at 25°C up to the respective processing temperatures of the workspace using a Model (MTS 800) machine according to ASTM D–638 procedures. Unfortunately measurements can only be made in compression in the X-direction because of the thinness of the specimens. Still, high frequency sonic moduli tests[14] were carried out on selected polypropylenes when an improvement in modulus with draw ratio (DR) was noted. For test purposes sonic measurements were made in other specimen directions (Y and Z) and were found to match the ASTM tensile moduli measurements within 5–10% for deformation ratios as high as ×25, thus confirming the feasibility of the sonic technique.

THERMAL MEASUREMENTS

These were made using a Perkin–Elmer DSC2 calorimeter fitted with computer integration accessories. Baseline corrections were made for all thermograms whatever the test run conditions. Some of the difficulties and the significance of these measurements have already been addressed in the literature,[10] and will receive further attention elsewhere.

X-RAY MEASUREMENTS

Wide angle X-ray measurements (WAXS) were made in three directions X, Y and Z for each specimen using monochromatic CuK$_\alpha$-radiation with an XRD5 GE diffractometer fitted with a graphite monochromator. A Laué-type film camera (temperature regulated) using CuK$_\alpha$-radiation was employed for photographic recording purposes as seen in Figure 4

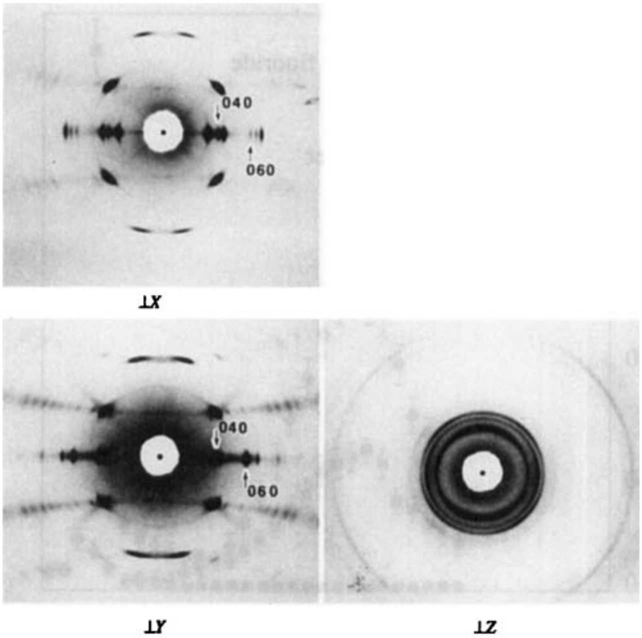

FIGURE 4 X-ray diffraction patterns of rolltruded polypropylene perpendicular to the X, Y and Z directions of the workpiece respectively. The main deformation is vertical, the others are mutually perpendicular to it.

for polypropylene.

Small-angle X-ray diffraction (SAXS) measurements were carried out using:

(i) a Rigaku–Denki, 6 kW generator fitted with a small-angle camera with a vacuum path,

(ii) selected measurements were also performed (in collaboration with Dr. J. S. Lin) on the 10 m SAXS facility at the National Center for Small Angle Scattering, Oakridge, Tenn.

Agreement between instruments was good and the diffraction patterns were consistent with an electron density fluctuation in the three mutually perpendicular directions of the rolltruded samples, in line with the 3D model proposed (see Figure 5 for PVDF).[15]

BIREFRINGENCE MEASUREMENTS

Thin sections were cut from rolltruded specimens for deformation ratios ranging from ×1 to almost ×30 for regular polyethylene. The birefringence was measured with a calibrated Berek compensator perpendicular to the X, Y, and Z coordinates of selected specimens. Combining these results with WAXS measurements made under similar conditions, the crystalline and amorphous orientation factor f_c and f_a respectively, were calculated according to the recommended procedure treating the rolltruded specimens as two phase in nature (which is an assumption that is not truly valid for the tie molecular intercrystallite regions for any polymeric material that is well oriented, whatever way it is prepared). The amorphous phase is not random.

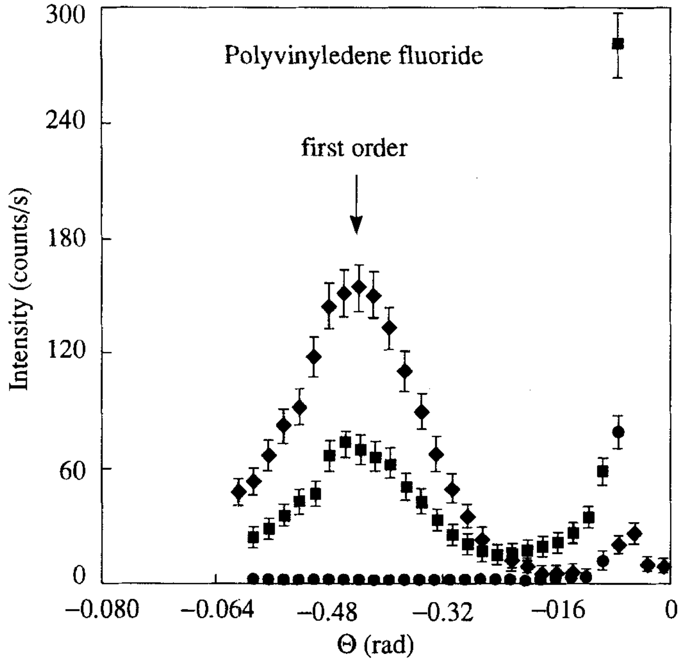

FIGURE 5 SAXS intensity versus scattering angle for rolltruded PVDF polymer. The scattering intensity ratios are $I_z : I_y : I_x = 1 : 25 : 82$. X-ray beam is parallel to X (♦), Y (■), and Z (●).

WEAR MEASUREMENTS

These were conducted as a function of deformation ratio on several polymers using standard techniques described elsewhere.[16] Wear rates were measured in plane perpendicular to X, Y, and Z respectively over a wide range of deformation ratios. Results in 3D were established for the first time, correlating directional wear rate with processing for three polymers. Other tests are still under review.

COMPUTER MODELING

Using a modified commercial software package termed ABAQUS (initially formulated for metal working technology) the rolltrusion process was simulated for several deformation ratios in the deformation range ($< \times 10$). Simulated deformed grid patterns consistent with experimentally measured workpiece deformations were obtained. Besides, useful computer plots for trends in strain and stresses with processing time (distance along workpiece) were obtained for several temperature and deformation conditions.[17] Simulation of the role of tie molecules connecting crystalline blocks (at low 2D deformations) is featured in the literature.[18] Strengthening tie molecule connections, as well as increasing their numbers, reinforces mechanical properties. Further work on these topics will appear later.

In rolltruded specimens it is likely that there are some incorporated fully extended chains but all the experimental evidence indicates that model (Figure 3) is preferred since significant necking and elongation occur when the workpiece is oriented in the Y direction. The crystallites rotate and transform in this operation from 3D to 1D (uniaxial) overall according to X-ray diffraction measurements conducted during different stages of orientation. This behavior is consistent with the fact that tie molecules must interconnect crystallites in the Y direction.

DISCUSSION

Property enhancements and improved changes in rolltruded plastics have been well documented even though a considerable amount of work remains unpublished. A self-consistent model of the processed workpiece (Figure 3) embodies all the experimental evidences obtained so far for deformed samples. In essence, the process produces specimens that have a 3D morphology from semicrystalline or amorphous potentially crystallizable polymers.†

Actually, the high stresses which the polymer is subjected to in the roller nip region transform spherulites (for example) comprised of radiating lamellae connected by tie molecules to provide strength enhancement according to their physical nature and abundance, and commensurate with intercrystallite reinforcement in the direction: $Z \gg Y > X > XYZ$ of initial workpiece. XYZ denotes the starting sample. The special network[19] produced by rolltrusion is one in which the crystallites function in a sense as fusible but ordered branch points (akin to a cross-linked system in its function i.e., load-bearing capability). Jet they are thermotropic in the sense that a whole system is fusible and recyclable too.

Table I illustrates measured improvements in tensile modulus and tensile strength for variously rolltruded polymers. A standard tensile test made on bulk specimens points to a considerable improvement in mechanical properties in the Z and Y directions with corresponding enhancement in the compression X direction of the rolltruded specimens. Sonic measurements point to a moderate increase in tensile modulus (up to ×1.5) for deformation ratios up to ×20 in polypropylene.

The changes (enhancements) in strength without complete chain extension throughout the processed sample are supported by X-ray measurement. WAXS determines that there is a rapid improvement in f_c for deformation ratios less than ×10 and even much lower depending upon the specific polymer being processed. The crystallites are crystallographically aligned with only the c axis aligned in the main (Z) direction of the highest strength and modulus. That the crystallite orientation is triaxial or uniplanar, unidirectional is born out by the single crystal-like diffraction pattern shown in Figure 4 for example for polypropylene. Figure 5 clearly illustrates that there are discrete diffraction peaks and there must be a periodic fluctuation of alternating 3D ordered crystallites interconnected by less dense tie molecules between them. Nylon-66 is a good example (see Figure 6).

Within a given polymer the long period in the X, Y, and Z direction of a rolltruded specimen depends upon processing conditions, particularly the processing temperature especially. The intercrystallite tie molecular region is typically 25–30% of the overall long period dimension. In PVDF for example the dimensions are similar in all directions (Figure 5). A systematic study of the effect of processing conditions has been made for several polymers and co-polymers and will be reported on whenever all the analyses are

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† Note however that completely glassy unoriented polymers can be rolltruded although the internal textures lacks crystallites that function as linchpins-pins that hold the structure intact.

TABLE I
Mechanical property enhancement for rolltruded polymers

Polymer sample	Test direction	Maximum modulus		Maximum strength		Modulus enhance factor	Strength enhance factor
		(GPa)	(10^5 psi)	(MPa)	(10^3 psi)		
Orig. iPP	Z or Y†	0.7	1.1	27.6	4.0	1.0	1.0
	X	0.7	1.0	38.6	5.6	1.0	1.0
Oriented	Z	21.3	30.9	524.0	76.0	28.1	19.0
	Y	2.3	3.3	44.8	6.5	3.0	1.6
	X	2.1	3.0	104.0	15.1	3.0	2.7
Orig. P/E cop.	Z or Y†	0.8	1.1	20.7	3.0	1.0	1.0
	X	1.0	1.5	22.8	3.3	1.0	1.0
Oriented	Z	13.0	18.9	520.7	75.5	16.4	19.1
	Y	1.6	2.3	30.3	4.4	2.0	1.5
	X	2.0	2.9	88.3	12.8	2.0	3.9
Orig. PVDF	Z or Y†	1.2	1.8	46.2	6.7	1.0	1.0
	X	2.1	3.0	49.7	7.2	1.0	1.0
Oriented	Z	2.7	4.0	586.2	85.0	2.2	12.7
	Y	2.1	3.1	62.1	9.0	1.7	1.3
	X	1.8	2.6	137.9	20.0	0.8	2.8

† The original sample was unoriented so tensile properties show no directional dependence.

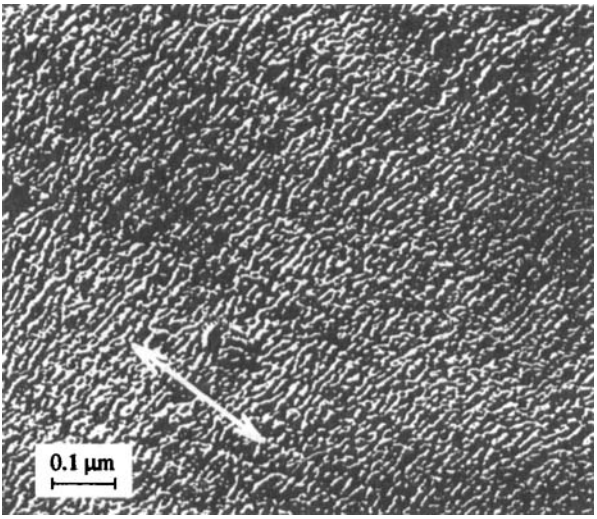

FIGURE 6 Replica of platinum shadowed, fractured (010) hydrogen bonded unetched surface of rolltruded nylon-66, showing crystallites oriented with their c-axes in the main deformation direction (direction and scale arrowed).

completed. Note that the prevalent notion or need for fully aligned chains to attain would negate the presence of a distinct small angle period (up to two or even three orders) for fully extended chain fibers or highly uniaxially drawn single crystals or reactor powders.

Again, significant support for the 3D or triaxial model (Figure 3) is obtained from the fact that tensile strength for large rolltrusion deformations (up to ×30) increases almost linearly[20] with f_a, not f_c (Figure 7). This may be interpreted simply that the load bearing

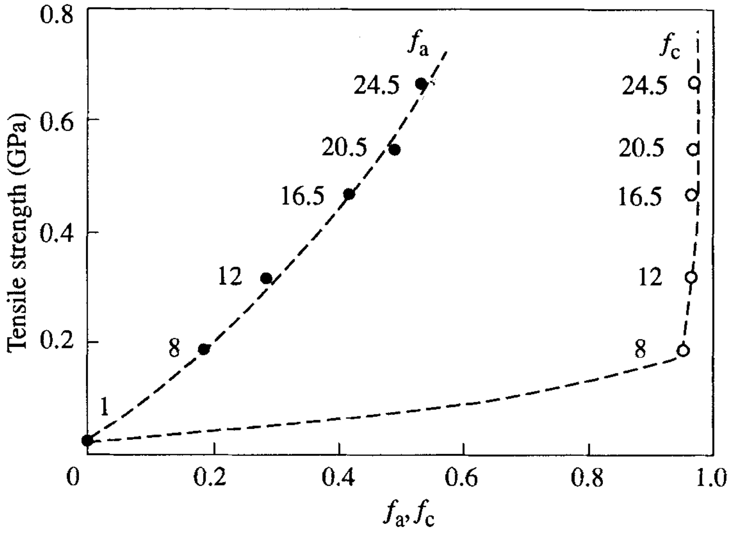

FIGURE 7 Tensile strength of rolltruded polyethylene as a function of crystalline orientation factor, f_c, and amorphous orientation factor, f_a, for different draw ratios shown in the diagram. Note that the tensile strength versus f_a plot is linear.

elements of the system are the intercrystallite tie molecules, which are the main load bearing elements, that are variously extended during processing, as well as upon test conditions. Note that f_c under similar test conditions is far from linear for large deformations since the crystallites rapidly orient in the early stages of drawing (and this factor tends to unity at DR values well below ×10). Consequently, it provides a poor correlation with tensile strength (engineering properties) certainly beyond this "saturation limit" after which it asymptotically approaches unity, whilst in the tie molecule (amorphous) region tensile strength rises linearly with DR up to high values.

Likewise the wear properties (essentially a surface property) of rolltruded polymer show anisotropic behavior.

SUMMARY

Rolltruded polymers exhibit enhanced anisotropic properties in the X, Y, and Z directions of the workpiece compared to the starting material. A model for the rolltruded polymer is presented, based upon many experimental data obtained that substantiate it for property reinforcement.

References

1. A. Peterlin, *Ultra-High Modulus Polymers,* (Appl. Sci. Publishers, London, 1979), Chap. 10.
2. A. E. Zacharides and R. S. Porter, *The Strength and Stiffness of Polymers,* (Marcel Dekker Inc., New York, 1983), p. 1.
3. G. Capaccio and I. M. Ward, *Polymer,* **15,** 233 (1974).
   A. G. Gibson and I. M. Ward, *J. Polym. Sci., Polym. Phys. Ed.,* **16,** 2015 (1978).

4. A. J. Pennings, D. J. Dijkstra, A. R. Postema, M. Roukema, W. Hoogsteen, and H. Van der Werff, *Frontiers of Macromolecular Science*, Eds., T. Saegusa, T. Higashimura, and A. Abe, (Blackwell Scientific Publications, Oxford, 1989), p. 357.
5. V. A. Marikhin and L. P. Myasnikova, *Makromol. Chem., Macromol. Symp.*, **41,** 209 (1991).
6. M. J. Shankernarayanan, D. C. Sun, M. Kojima, and J. H. Magill, *J. Int. Polym. Proc. Soc.*, **1,** 66 (1987).
7. E. M. Berg, D. C. Sun, and J. H. Magill, *SPE ANTEC, Tech. Papers*, **35,** 625 (1989).
8. E. M. Berg, D. C. Sun, and J. H. Magill, *Polym. Eng. Sci.*, **29,** 715 (1989).
9. D. C. Sun, E. M. Berg, and J. H. Magill, *Polym. Eng. Sci.*, **30,** 635 (1990).
10. D. C. Sun and J. H. Magill, *Polym. Eng. Sci.*, **29,** 1503 (1989).
11. C. C. Lin, M. Kojima, and J. H. Magill, *J. Mat. Sci.*, **27,** 5849 (1992).
12. R. J. Ciora, Jr. and J. H. Magill, *J. Polym. Sci., Polym. Phys. Ed.*, **32,** 1035 (1992).
13. M. Rosner, *Materials and Processing Report*, **7,** 4 (1992).
14. K. Koyama and J. H. Magill, (unpublished results).
15. D. C. Sun, J. H. Magill, and J. S. Lin, *Bull. Am. Phys. Soc.*, **33,** 717 (1988).
16. H. Voss, J. H. Magill, and K. Fredrick, *J. Appl. Polym. Sci.*, **33,** 177, 1745 (1987).
17. D. C. Sun and J. H. Magill, (unpublished work).
18. D. C. Sun, E. M. Berg, and J. H. Magill, *Proc. Am. Chem. Soc., Div. Polym. Materials Eng. Sci.*, **61,** 555 (1989).
19. E. A. Egorov, V. V. Zhizhenkov, V. A. Marikhin, and L. P. Myasnikova, *J. Macromol. Sci. Phys.*, **B29,** 129 (1990).
20. J. H. Magill, D. C. Sun, and M. J. Shankernarayanan, *J. Appl. Polym. Sci.*, **34,** 2337 (1987).