Microfiber Formation: Immiscible Polymer Blends Involving Thermoplastic Poly(vinyl alcohol) as an Extractable Matrix

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SYNOPSIS

The utilization of polymer-blend technology to prepare microfibers via extraction of one of the components is known technology. Achieving fibrillation (microfiber formation) is not an *a priori* consequence of polymer blends exposed to a shear or elongational flow field. The viscosity ratio, concentration ratio, interfacial tension, and second normal stress function have all been noted to be important factors in achieving fibrillation in polymer blends. It has been found that thermoplastic poly(vinyl alcohol) is particularly effective in this technology, yielding fibrillated systems that can be easily extracted to yield microfibers (0.1–5 μ diameter). Thermoplastic poly(vinyl alcohol) (PVOH) offers cold-water solubility, biodegradability, and fibrillation characteristics with many commodity polymers (polyolefins, polystyrene, scrap mixtures), thus offering advantages over previously investigated extractable polymers. In addition, the resultant microfibers via this process can be pulped and handled in paper-making processes. The process for microfiber formation, the process variables, the polymers applicable to the formation of microfibers using PVOH as an extractable matrix, and the properties of the resultant microfibers are discussed with emphasis on the characterization of the microfibers as a fibrous thixotrope additive. Potential utility of the microfibers via this process include polymeric paper and admixtures with cellulosic-based pulp, oil- or water-adsorbent mats, fibrous thixotrope additives, filters, filler retention and pitch control in paper applications, and ultralow denier fibers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The morphology of phase-separated polymer blends is an important factor relating to the properties of the blends. The ability to form structured polymer blends has been the subject of many investigations as noted in a review by Meijer et al.[1] Under specific conditions, the structure of polymer blends can be composed of microfibers of one polymer embedded in a matrix of another polymer. Upon extraction of the matrix, liberation of microfibers can be achieved with diameters smaller than those obtained via conventional melt spinning.

The fibrillation of polymer mixtures in elongational flow was initially reported by Miller and Merriam.[2,3] Typical mixtures employed included polystyrene/polyethylene, polyethylene/poly(vinyl acetate), nylon/polyethylene, and polychlorotrifluoroethylene/polyethylene with extraction of the matrix polymer with preferential solvents. The range of microfiber diameters of 0.1–5 μ was noted. Breen[4] discussed similar results with poly(ethylene terephthalate)/nylon 6,6 blends with microfibers of 0.01–3 μ where formic acid was employed to remove nylon 6,6. Polyethylene mixtures with poly(ethylene terephthalate) or nylon 6,6 were also noted where hot xylene was employed to dissolve the polyethylene matrix. The only reference related to poly(vinyl alcohol)[5] involved mixtures of PVOH with polyolefins in which the resultant pellets were sheared in an aqueous solution containing an inorganic salt to prevent foaming and dissolution of PVOH (along with high hydrolysis levels to also prevent dissolution of PVOH). The resultant product was formed

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into paper. In their work, the fibers were not liberated from PVOH, which is the essence of the study reported in this article.

In more recent references, Stueben and Sommer[6] investigated various polymer blends based on polysulfone as the desired microfiber. Only a few potential extractable matrix candidates were noted that offered proper fibrillation. Tsebrenko et al.[7] noted fibrillation of polyoxymethylene in blends with a copolyamide. The formation of liquid crystalline polymer fibrils in thermoplastic matrices via extrusion through a capillary die was noted by Bassett and Yee.[8] Weiss et al.[9] reported self-reinforced composites of polystyrene and a liquid crystalline polymer produced via an extensional flow. Blizard and Baird[10] reported on the fibrillation of a liquid crystalline copolyester in matrices of polycarbonate or nylon 6,6.

Only limited mechanistic studies or theoretical analyses for the fibrillation process noted above have been reported in the open literature. In a key article by Van Oene,[11] it was noted that mixtures of immiscible fluids subjected to shearing flow will achieve an equilibrium level of dispersion. The morphology produced can be (for the dispersed phase) spherical, ribbonlike, or fibrous. The shape of the dispersed phase in a flow field will be determined by the shear forces from viscosity and elasticity of the two fluids and the pressure distribution around the dispersed phase. It was noted that interfacial tension and differences in the viscoelastic properties of the fluids were key variables. The second normal stress function of the fluid was shown to be the key to the determination of droplet/fiber formation of one polymer in mixtures with another polymer (favoring droplet/fiber formation for the polymer with the higher value of the second normal stress function).

White and Min[12] reviewed the development of phase morphology in a stratified and two-phase flow of polymer mixtures. In the stratified flow, phase morphology variations were noted to be attributable to viscosity differences between the phases. For the disperse two-phase flow, the morphology is also influenced by the interfacial tension. Large interfacial tensions and high Taylor numbers were noted to yield coarse phase morphologies. (Taylor number $= \nu/\eta a\gamma$, where ν = interfacial tension, η = viscosity, a = droplet radius, and γ = shear rate.) Compatibilization agents were noted to be effective in reducing interfacial tension and thus yielding finer morphological structures. It was noted that with low viscosity ratios ($\eta_d/\eta_c < 1$) (d = dispersed phase; c = continuous phase) and low interfacial tensions the droplets would break up instead of elongating

into fibers. With high viscosity ratios ($\eta_d/\eta_c > 10$), the droplets did not deform. White and Min noted that for the formation of microfibers from polymer blends (via extrusion through a capillary die) the viscosity of the dispersed phase must be of the same order or lower than that of the continuous phase.

Tsebrenko et al.[7] studied blends of immiscible polymers that form microfibrils upon extrusion through an orifice. It was noted that the dispersed-phase particles elongate during flow into the entrance zone of the orifice and coalesce, yielding microfibrils. Meijer et al.[1] discussed various morphologies formed during the processing of immiscible blends. It was noted that under certain conditions the microfibrils formed can become unstable due to interfacial tension-driven Rayleigh instabilities, leading to the formation of ellipsoids.

Bentley and Leal[13] noted that at a low viscosity ratio (η_d/η_c) the drops were easy to elongate and, in shear flow, formed fibrils. At intermediate viscosity ratios, elongating drops tended to break up into short fibrils. At a high viscosity ratio, droplet deformation was not possible in a shear flow but was still possible in an extensional flow. Additional reviews of relevance to the subject matter of this article include references by Han,[14] Van Oene,[15] and Utracki.[16]

A unique application was proposed by Byck et al.[17] using a blend of polypropylene and a partially neutralized ethylene–acrylic acid copolymer. The blend was extruded into a thin tape followed by orientation. When placed in a hot alkaline bath, the tape was pulled transverse to the machine direction (orientation direction) of the tape. The ethylene–acrylic acid ionomer was extracted, leaving a fine fiber web with dimensions between the fibers similar to cell dimensions. Using cell cultures from the interior of blood vessels, a cell growth could be anchored on the web and present a blood-compatible surface.

A revolution in the fibers (fabrics) industry is presently occurring, referred to in the trade magazines as "microfiber fever."[18] Polyester microfibers with $\frac{1}{3}$ the thickness of cotton and $\frac{1}{2}$ the thickness of silk offer a considerably lighter and softer fabric than previously available. These microfibers are generally in the range of 0.4–0.8 denier (denier = grams/9000 meters). One of the present routes for producing microfibers involves splitting the feed to the spinneret into many sections and utilizing immiscible polymer streams to yield fine fibers of one polymer in a matrix of another polymer. With extraction of one of the polymers, finer fibers are obtained than previously possible with classical one-

component melt spinning. This process is referred to as "islands in the sea."

Fibrous thixotropic additives are commonly utilized to impart high, low shear viscosity and low, high shear viscosity to fluids. A thixotropic material exhibits gel-like properties at a very low shear rate, liquifies at high shear rate, and has its viscosity dependent upon its prior deformation history. Asbestos was a common thixotropic additive utilized to impart sag and drip resistance to fluids until replaced due to toxicity concerns. Melt-blown polymeric fibers (e.g., polyethylene, polypropylene) are presently utilized to achieve similar results. The microfibers described in this article offer significant potential as thixotropic additives and emphasis will be placed on these properties.

Poly(vinyl alcohol) offers attractive features for a matrix for microfiber formation. It is water-soluble, biodegradable, and immiscible with commodity polymers. As will be shown, a wide range of polymers form microfibers in admixtures with poly(vinyl alcohol) under shear or extensional flow. A key to the technology noted herein involves the recent development and commercialization of a thermoplastic version of poly(vinyl alcohol) (Vinex®) with a processing range similar to many commodity polymers. Vinex is covered by several patents issued to Air Products and Chemicals, Inc.[19,20]

EXPERIMENTAL

The basic process for producing the microfibers involves extrusion of a melt mixture of PVOH with an appropriate polymer (or polymers) (Fig. 1). The extruded blend is further oriented and chopped into pellets. The pellets are then added to a laboratory blender and agitated in water. After allowing the foam to destabilize, the fibers are filtered using cheesecloth or a mesh screen. The fibers are further
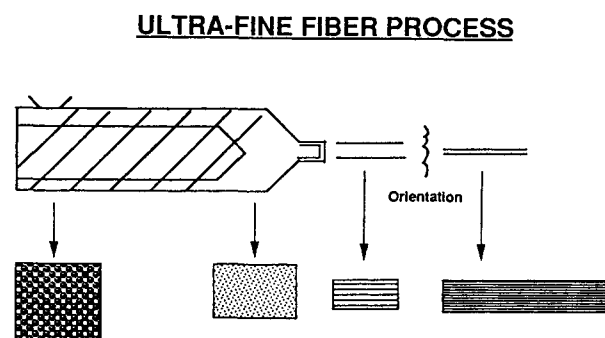
ULTRA-FINE FIBER PROCESS

Figure 1 Generalized process for the formation of microfibers.

agitated in water and filtered several times to remove residual PVOH.

The extruder used for most of the experiments noted herein was a 1 in. Killion extruder, 30 L/D, single-screw equipped with mixing sections (e.g., Maddox-type). The processing range for the thermoplastic PVOH variants was 170–230°C, with 200°C being the typical processing temperature chosen. The orientation step involved only hot drawing for most of the experiments with a draw ratio of 8/1 to 12/1 except where specifically noted.

Characterization

The test procedure for fibrous rheology modification involved washing each fiber sample with distilled water to remove any residual poly(vinyl alcohol) followed by drying at room temperature overnight. The fibers were then mixed with either an epoxy resin (diglycidyl ether of bisphenol A) (Dow's DER 331) or glycerine at a fiber weight of 1.0 or 2.5% by weight. After mixing (by hand) with a metal spatula, the fiber–fluid mixture was degassed in a vacuum oven (50–70°C) overnight. The complex viscosity–shear rate data were obtained at 27°C on a Rheometrics RMS-605 mechanical spectrometer using a cone and plate fixture (cone angle: 0.106 radian; plate = 25.4 mm diameter; gap = 0.050 mm). A frequency range of 0.0628–99.54 rad/s was employed. Dynamic testing (using a strain of 100%) was utilized for all samples. All the measurements were made in a nitrogen atmosphere. Rheological data were collected at five frequencies for each decade of frequency.

Melt viscosity data on the polymers employed for the mixtures were determined on a Rheometrics Dynamic Analyzer (RDA II) using a parallel plate geometry in a dynamic mode at 200°C. The results are illustrated in Figure 2 for many of the polymer samples utilized in this study.

The surface area measurements were obtained from krypton adsorption at −196°C as per ASTM Method D-4780. Scanning electron micrographs were obtained using a JEOL 840 scanning electron micrograph operated at 5 kV. Specimens were conductively coated with gold/palladium prior to examination.

RESULTS

Polypropylene Microfiber Formation

The first series of experiments to be discussed involved investigations of the polymer variations that
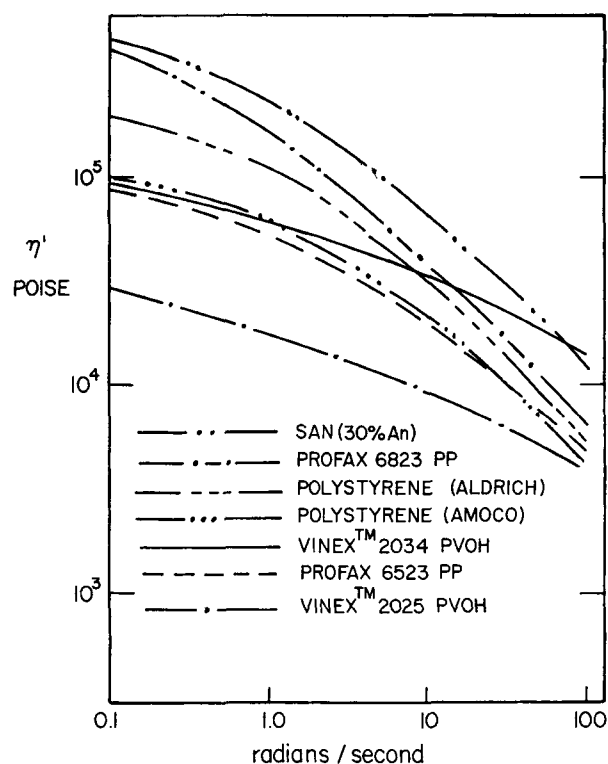
Figure 2   Melt viscosity data for polymers employed in this study.

Legend in figure:
- SAN (30% An)
- PROFAX 6823 PP
- POLYSTYRENE (ALDRICH)
- POLYSTYRENE (AMOCO)
- VINEX™ 2034 PVOH
- PROFAX 6523 PP
- VINEX™ 2025 PVOH

Axis labels: η' POISE (vertical), radians / second (horizontal)

Figure 3   Microfibers from Profax 6823 polypropylene.

are amenable to microfiber formation utilizing the process described above. It was found that polypropylene, polystyrene, polyethylene, poly(vinylidene fluoride), polymer mixtures, and even polymer scrap microfiber formation were quite amenable to this process. Figure 3 shows the microfibers produced from a 50/50 mixture of polypropylene (Profax 6823: Himont)/Vinex 2025 PVOH. The fiber formation via this process is evident; however, the fibers formed were rather coarse. It was subsequently found that finer fibers could be formed from a lower viscosity polypropylene (Profax 6523) or by incorporation of a more polar polyolefin (Surlyn 9020: ethylene–methacrylic acid ionomer: DuPont) to lower the interfacial tension. Optimum mixture compositions were in the range of 50/50 for polypropylene (PP)/PVOH blends although microfibers could be formed in the range of 70/30 to 30/70 by weight. Rayleigh instabilities were evident at the 30/70 range (see Fig. 4), and coarser, difficult to extract fibers were formed at the 70/30 composition.

Another variation involving polypropylene microfiber formation involved the extrusion of a mixture of 50/50 PP/PVOH (Profax 6523/Vinex 2025) and a mixture of 40/50/10 PP/PVOH/ionomer (Profax 6523/Vinex 2025/Surlyn 9020) in a Killion 1 in. extruder (24/1: L/D) equipped with a variable
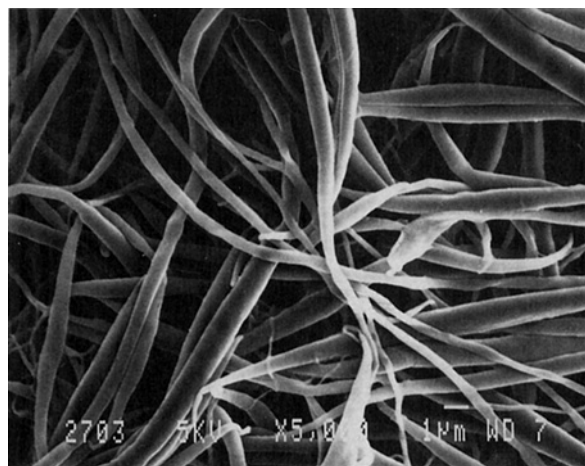
gap coat hanger slot die. The extruded films were oriented in the machine direction, cooled on a chill roll, and wound on a tension winder. The films quickly released poly(vinyl alcohol) upon immersion in water, leaving a nonwoven fine fiber (ribbon) web as shown in Figure 5 for the ionomer-containing sample. The fibers appear ribbonlike and continuous.

As has been noted in the Introduction, continuous microfiber production generally involves a specialized spinneret design to produce microfibers of one polymer encapsulated in a matrix of an extractable polymer. It has been found that this spinneret design may not be necessary, since a melt mixture of PVOH and polypropylene when extruded through a normal spinneret followed by orientation and extraction yields fine polypropylene fibers of ∼ 0.03 denier upon extraction with water. This was demonstrated by first preparing a 50/50 mixture of PP/PVOH (Profax 6723/Vinex 2025) in a 1 in. Killion extruder at 200°C. The pelletized mixture was then fed to a 1 in. 24/1 L/D extruder connected to a spin head with a 68-hole spinneret. The blend was extruded at 200°C and hot drawn at 110 m/min and then cold drawn on heated godets (100–110°C) at a draw ratio of 2.2×. The tensile strength of the fiber bundle was found to be 20,900 psi. The fiber before extraction is shown in Figure 6. After extraction, fibers of ∼ 1 μ (0.03 denier) were liberated (Fig. 7). Tensile strengths in the range of 20,000 psi were obtained (low, but reasonable, considering the limited orientation).

Polystyrene Microfiber Formation

In the evaluation of microfiber formation of various polymers via this process, it was found that poly-
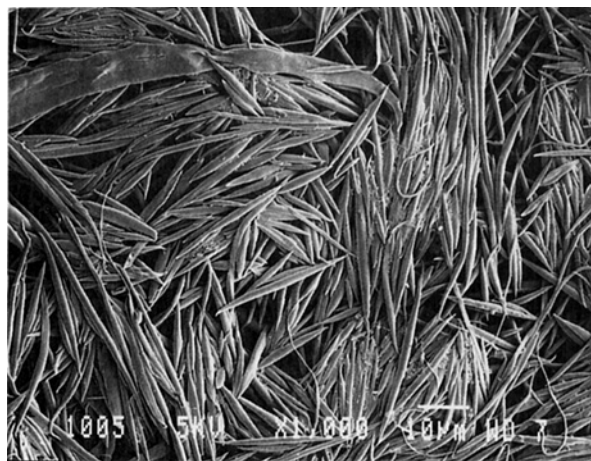
Figure 4 Microfibers from Profax 6523 polypropylene from 30/70 PP/PVOH blend.

Figure 6 SEM photomicrograph of a PVOH/polypropylene fiber blend produced via fiber spinning (prior to extraction).

styrene was particularly amenable to this process, easily yielding microfibers in the 0.5–1 μ range as shown in Figure 8. Styrene/acrylonitrile copolymer (30 wt % An) microfibers were also successfully prepared via this process, yielding microfibers in the range of 0.2–0.3 μ, as illustrated in Figure 9. A trend appears to exist with the fiber diameter in that as the interfacial tension of the polymer/PVOH mixture decreases (solubility parameter of the polymer increases) the microfiber diameter also decreases. It is also interesting to note that the polystyrene and styrene–acrylonitrile copolymer-based samples foamed more during the agitation stage of the extraction process than with polypropylene. Generally, foaming is not a problem with polystyrene or polypropylene in that the foam is not stable and can also be alleviated by the addition of defoamers. With the
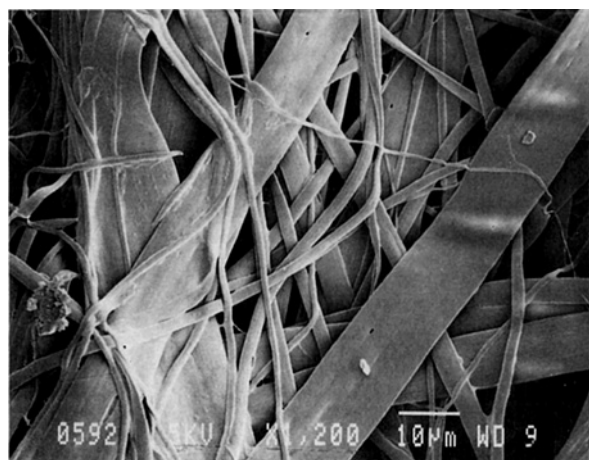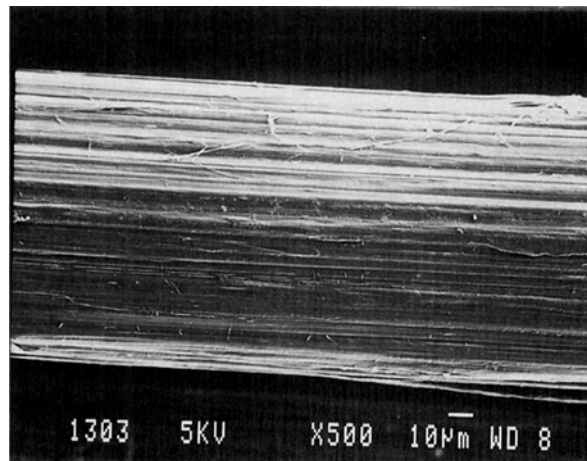
styrene–acrylonitrile copolymer, the foam was more stable and formed an emulsion-like product. This phenomenon appears to be related to the surface area of the microfibers. Another difference was noted with various polystyrene samples compared to polypropylene variants tested as polystyrene microfiber formation was possible at lower PVOH contents in the premix. Microfibers were obtained at PVOH levels as low as 20 wt %. This is, of course, partially due to density differences favoring polystyrene as the dispersed phase but also appears to reflect the higher viscosity of polystyrene relative to polypropylene at extrusion and orientation conditions. The higher viscosity of polystyrene would favor its pres-

Figure 5 SEM photomicrograph of extracted slot extruded film of a PVOH/PP/Surlyn blend.

Figure 7 SEM photomicrograph of polypropylene microfibers produced via extraction of PVOH/PP blend (see Fig. 6).

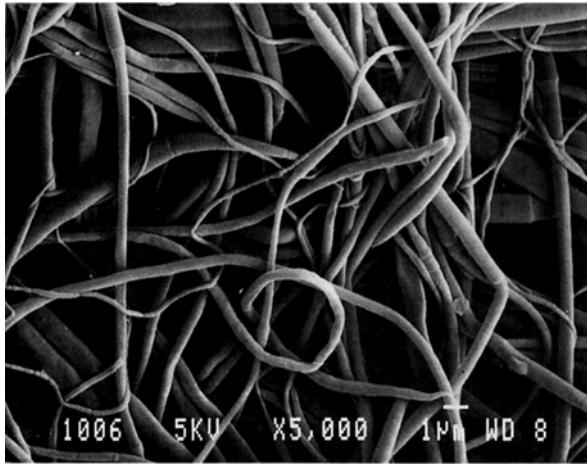**Figure 8** Polystyrene microfibers produced via PVOH blend extrusion/extraction process.

Figure 10 SEM photomicrograph of simulated polymer scrap microfibers mixture of PS/PP/HDPE/LLDPE.

ence in the dispersed phase at lower PVOH levels with other variables remaining constant.

In an additional variant of polystyrene utilization, scrap-foamed polystyrene was subjected to the same process. Microfibers with the same range of diameters were produced.

Polymer Mixture Microfiber Formation

In one of the earlier investigations in this program, polymer mixtures showed interesting results. A simulated polymer scrap composed of 50/10/10/20/10 PVOH/polystyrene/PP/HDPE/LLDPE yielded surprisingly uniform microfibers (Fig. 10).
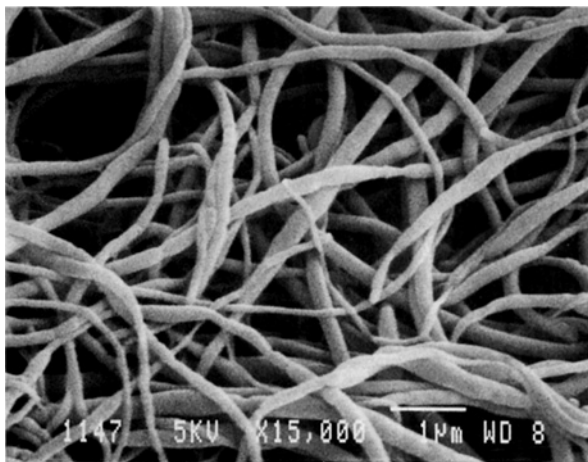
With this promising result, a sample of "real" polymer scrap was obtained from Rutgers University termed NJCT (New Jersey Curbside Tailings). NJCT consists of polymer bottles [from which poly(ethylene terephthalate) (PET) carbonated beverage bottles and HDPE milk containers have been removed as separate streams] primarily composed of high-density and medium-density polyethylene bottles, polypropylene bottles, some poly(vinylchloride) (PVC) bottles, and PET bottles not used for larger carbonated beverage bottles. This product (as proposed by Rutgers) is useful for plastic lumber and is described in Ref. 21. Two versions of this product were utilized in this evaluation. The first involved the washing of the NJCT in water followed by isolation of the floating particles, thus

Figure 9 Styrene–acrylonitrile Copolymer (30% AN) microfibers produced via PVOH blend extrusion/extraction process.

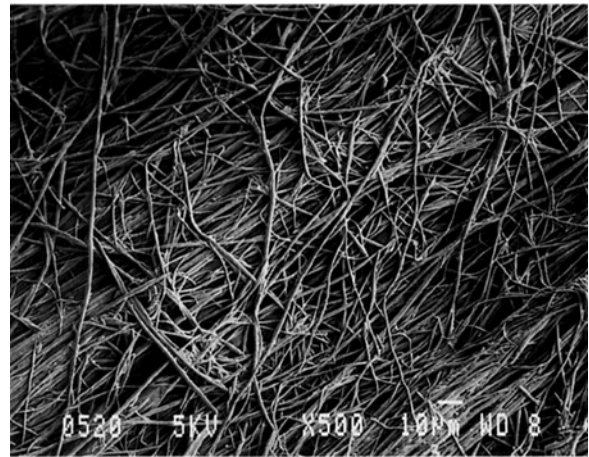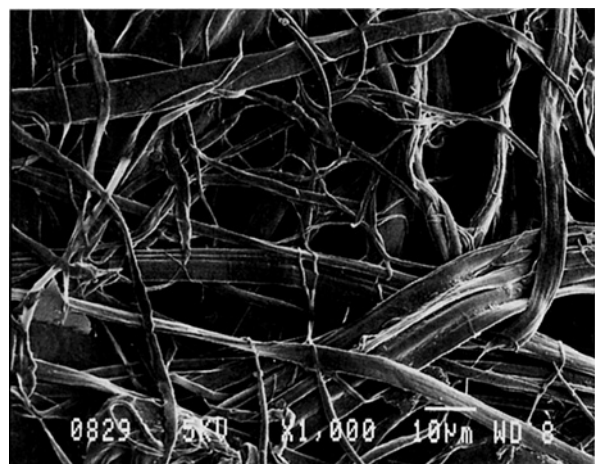**Figure 11** SEM photomicrograph of NJCT microfibers.

Table I   Complex Viscosity–Shear Rate Data

			Complex Viscosity (η) (Poise at 27°C)			
	Addition	Surface Area		Shear Rate (rad/s)		
Sample Designation	Level	(m²/g)	0.0628	0.6280	6.281	62.81
Epoxy Control (DER-331)	—	—	220	125	120	120
PE pulp TA-12	1%		1,410	495	280	195
PE pulp TA-12	2.5%		5,780	1,460	555	315
Pulpex EDH	1%		980	380	245	185
Polypropylene microfibers[a]	1%	0.3	2300	610	315	220
Polypropylene microfibers[a]	2.5%	0.3	11,000	2,030	600	330
Polypropylene microfibers[a]	2.5%	—	11,800	2,550	715	365
PP/PS 50/50 microfibers	2.5%	1.5	12,400	2,590	755	365
PP/ionomer 80/20 microfibers	2.5%	0.7	11,000	2,190	645	340
NJCT microfibers	2.5%		6,800	1,640	610	340

PE pulp TA-12, melt-blown fibers (polyethylene). Pulpex EDH, melt-blown fibers (polyethylene).

[a] Microfibers extracted from Vinex 2025/Profax 6523 (50/50 blend).

[b] Microfibers extracted from Vinex 2025/Profax 6523 (70/30 blend).

removing the PVC and PET that sank to the bottom of the container. The floating particles were dried, mixed with PVOH, and extruded, oriented, pelletized, and extracted. The resultant microfibers are illustrated in Figure 11. Although coarser in appearance than the other samples shown, they demonstrated the properties (e.g., fibrous thixotropy) expected of microfibers. Another procedure involving grinding the NJCT in liquid nitrogen followed by extrusion with PVOH, orienting, pelletizing, and extraction also yielded microfibers. It must be

Figure 12   Complex viscosity vs. shear rate for selected microfibers as thixotropic additives to epoxy resin (DER-331).

pointed out that the orientation stage was not as facile as with virgin polymers; however, streamline dies or tape orientation could alleviate this problem.

Other Microfibers

The process utilizing PVOH as an extractable matrix for the production of microfibers appears particularly suited towards polypropylene, polystyrene, and polyethylene and mixtures thereof. Other polymers have been investigated with some success. Poly(vinylidene fluoride) microfibers were capable of being formed with diameters in the range of ~ 0.5 μ at lower (< 40 wt %) PVOH levels. Very fine elastomeric fibers were capable of being formed using a poly(butylene terephthalate)–polytetrahydrofuran block copolymer (Hytrel 4056: DuPont). Cellulose proprionate was capable of being fibrillated via this process to yield very fine fibers; however, cellulose triacetate was not successful. PMMA was also not particularly successful due to a high level of dispersion but could be incorporated into polymer mixtures. Poly(vinyl alcohol) microfibers were prepared via extraction of the oriented PVOH/polystyrene blend with either toluene or methylene chloride. Fibers in the range of a 2 μ diameter were obtained.
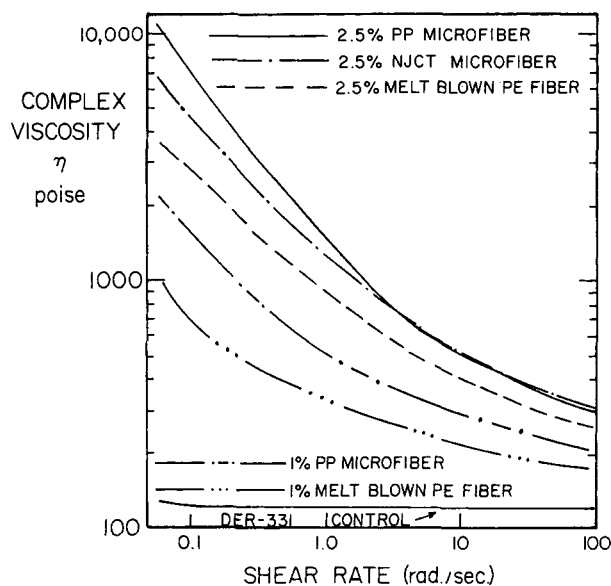
Fibrous Thixotropy Characterization

The nature of the microfibers described herein suggest their utility as fibrous thixotropic additives, thus warranting their evaluation vs. conventional fibrous

Table II   Complex Viscosity–Shear Rate Data

Sample Designation	Addition Level (%)	Surface Area (m²/g)	Complex Viscosity (η) (Poise at 27°C)			
			Shear Rate (rad/s)			
			0.0628	0.6280	6.281	62.81
Glycerine control	—	—	—	—	10	9
Polystyrene microfibers (1)	1	1.9	3,070	295	55	19
Polystyrene microfibers (1)	2.5	1.9	14,600	1480	235	53
Polystyrene microfibers (2)	1	11.6	875	98	25	13
Polystyrene microfibers (2)	2.5	11.6	11,800	1070	170	44
Polypropylene microfibers (1)	1	2.2	735	100	28	16
Polypropylene microfibers (1)	2.5	2.2	10,700	1150	180	40
Polypropylene microfibers (2)	1	0.6	1,300	175	33	13
Polypropylene microfibers (2)	2.5	0.6	6,620	770	115	29

Polystyrene microfibers (1) = extracted from 40/60 Vinex 2025/polystyrene (Aldrich Mw = 280,000). Polystyrene microfibers (2) = extracted from 50/50 Vinex 2025/polystyrene (Aldrich Mw = 280,000). Polypropylene microfibers (1) = extracted from 50/50 Vinex 2025/Profax 6523 PP. Polypropylene microfibers (2) = extracted from 50/50 Vinex 2025/Profax 6723 PP.

materials employed as thixotropic additives. Using the test protocol noted earlier, complex shear viscosity data as a function of shear rate were obtained (Table I) for a series of microfibers produced via the extrusion/extraction process described in this article. The polymeric microfibers yield very high viscosity at low shear at very low levels of addition, even surpassing the melt-blown fibers chosen for comparison. Even microfibers from the scrap product NJCT offer the desired high viscosity at low shear rate and low viscosity at high shear rate. Selected samples are compared in Figure 12.

Polystyrene microfibers appeared to be plasticized/partially dissolved by the epoxy resin, thus another fluid was chosen for viscosity measurements (glycerine). Glycerine has a much lower viscosity than that of the epoxy resin (9 vs. 120 poise at high shear rate). The viscosity data at various shear rates are tabulated in Table II and illustrated in Figure 13 for selected samples.

Process Variations

The majority of the studies reported here involved experiments in which the process variables were held constant and the polymer microfiber precursor was varied. Several experiments were run to look at process variables including blend ratio, draw ratio, and PVOH recycle. The viscosity results were utilized for comparison purposes.

The blend ratio for the PVOH/PP blend was investigated using equivalent processing conditions. The viscosity results (as per fibrous thixotropy measurements) are listed in Table III. At 50% PVOH and higher, the viscosities at various shear rates were equivalent.

At a constant PVOH/PP blend ratio (50/50 by wt), the orientation level (hot drawing) was varied from 3.8 to 18.2 by variation in the extruder rpm (thus feed rate). The strand pelletizer take-up speed was held constant. The surface area and viscosity data (using the previously described fibrous thixotropy test) are listed in Table IV. It is interesting to note that the viscosity imparted by the microfiber was virtually constant above a draw ratio of 3.8. The surface area also reached a plateau value at a higher draw ratio. These results are unexpected and indicate that a possibly limiting morphology is reached above which further drawing occurs in the matrix
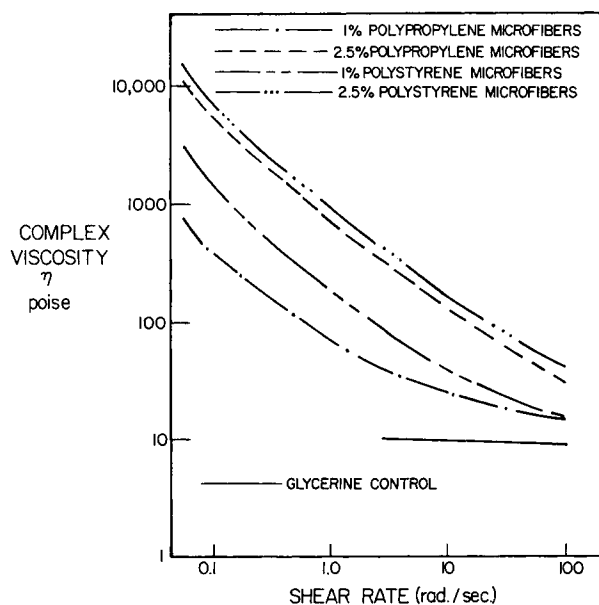

Figure 13   Complex viscosity vs. shear rate for polystyrene microfibers as thixotropic additives to glycerine.

Table III Complex Viscosity–Shear Rate Data

PVOH/PP Ratio	Surface Area (m²/g)	Complex Viscosity η (Poise) (2.5% Microfiber Additive to DER-331 Epoxy) at 27°C			
		Shear Rate (rad/s)			
		0.0628	0.628	6.28	62.8
70/30	0.3	11,800	2550	715	365
60/40	0.3	11,400	2440	680	360
50/50	0.3	11,000	2030	600	330
40/60	0.2	6,080	1100	435	285
30/70	0.1	Too coarse to test			

PVOH = Vinex 2025. PP = Profax 6523 polypropylene.

PVOH. It is also interesting that fibrous thixotropy (viscosity) is not a monotonic function of the surface area. This may be the result of incomplete fiber liberation and/or fiber bundles limiting full surface area utility.

For practical utility, recycle of, at least, part of the PVOH would be desired due to economic reasons based on both the cost of PVOH as well as the associated disposal costs. A blend of 50% PVOH (Vinex 2025) and 50% of polypropylene (Profax 6723) was extruded, oriented, and chopped into pellets. The pellets were extracted, and the extracted PVOH was devolatilized in an air-circulating oven at 80–90°C (several days). The second stage of the experiment involved repeating the experiment with 100% recycled PVOH and with 50% recycle and 50% new PVOH (Vinex 2025). The extracted fibers from the initial, 100% recycle PVOH and 50/50 recycle/new PVOH experiments were characterized in the fibrous thixotropy viscosity test with data shown in Table V.

Virtually no difference was observed between the initial control sample and the 50/50 recycle/new PVOH sample. The 100% recycle sample exhibits lower values but still useful fibrous thixotropy characteristics. The melt viscosity of the extracted PVOH was found to be identical with the control PVOH (Vinex 2025). Total recycle would not be feasible but at least partial recycle appears quite possible.

The melt viscosity for the thermoplastic PVOH employed in most of these studies (Vinex 2025) was lower than the polymers utilized for microfiber formation (see Fig. 2). At the higher frequencies (shear rates), the viscosity ratio (η_d/η_c) was in the range of 1–10, which has previously been noted to be the range where microfiber formation is favorable.

Additional studies were conducted relevant to areas where microfibers are commonly utilized. Promising results were obtained for oil and water sorption. Oil sorption is of significance as microfibers are utilized for oil spill pickup on water. Filtration tests demonstrated the utility of the microfibers noted here for removal of fine particles from water. Admixtures with cellulosic pulp were conducted, and uniform dispersion of the microfiber in cellulosic pulp-based handsheets was achieved. The microfibers can be pulped, and felt mats/paper were pre-

Table IV Complex Viscosity–Shear Rate Data

Draw Ratio	Surface Area (m²/g)	Complex Viscosity η (Poise) (2.5% Microfiber Additive to DER-331 Epoxy) at 27°C			
		Shear Rate (rad/s)			
		0.0628	0.628	6.28	62.8
3.76	0.3	Too coarse to test			
5.15	1.4	7810	1560	500	280
6.83	2.9	7450	1530	490	280
9.86	5.2	7550	1430	455	255
13.5	5.2	7460	1550	520	290
18.2	5.1	7270	1390	455	250

Microfibers extracted from 50/50 Vinex 2025/Profax 6523 (PVOH/polypropylene) blend.

Table V   Viscosity Data for Recycle Experiments

Sample Description	Complex Viscosity η (Poise) (2.5% Fiber in DER-331 Epoxy) at 27°C			
	Shear Rate (rad/s)			
	0.0628	0.628	6.28	62.8
Control Fiber (100% New PVOH)	6130	1410	460	265
Fiber using 50% new/50% recycle PVOH	5930	1370	470	275
Fiber using 100% recycle PVOH	4660	695	290	200

50% Vinex 2025/50% Profax 6723 blend.

pared using laboratory paper-making equipment. Additional areas of interest would include insulation and decrease of the "stickies" problem in paper manufacture and a filler retention aid in paper. The details of these studies will be reported in a later publication.

In summary, thermoplastic poly(vinyl alcohol) offers unique advantages as an extractable matrix for the formation of microfibers in the diameter range of 0.1–5 μ for many of the polymers of interest. These attributes include cold and hot water solubility, immiscibility and fibrillation with many commodity polymers (e.g., polyolefins, polystyrene), biodegradability (important for disposal problems), recyclability, and pulpability of the extracted microfibers. One of the attributes of microfiber utility involves asbestos replacement as a thixotropic additive. The microfibers of this process exhibit excellent thixotropic additive properties. Extrusion of the PVOH-based blend (PVOH/PP) using typical fiber spinning equipment followed by extraction of PVOH yields continuous microfiber tows of ~ 0.03 denier (an order of magnitude lower than conventional microfiber technology). An interesting aspect of this technology is the utility to convert scrap polymers into useful materials.

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