

# Short Fiber Formation during Extrusion of Polyethylene–Sodium Lignosulfonate Blends

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## Synopsis

When extruding a blend of low density polyethylene (LDPE) and a technical grade of sodium lignosulfonate through a capillary it was observed that LDPE formed fibers in a matrix of the lignosulfonate. With short capillaries and low shear rates, short fibers of LDPE with lengths between 0.5 and 5 mm and with diameters in the range 2–20  $\mu\text{m}$  can be produced. Since sodium lignosulfonate is water-soluble, the LDPE fibers can easily be isolated. Such fibers can be used for synthetic wood pulp or in nonwoven types of applications.

## INTRODUCTION

The interest in polymeric blends and alloys with regard to their properties, processing, and morphology has been steadily increasing during the last decades.<sup>1,2</sup> The majority of the investigations has dealt with blends of two incompatible thermoplastics, e.g., polystyrene–polyethylene or polypropylene,<sup>3–11</sup> polyethylene–polypropylene,<sup>12,13</sup> polystyrene–poly(methyl methacrylate),<sup>7,14</sup> polyoxymethylene–copolyamides, or ethylene–vinyl acetate copolymers,<sup>15–18</sup> polyethylene–poly(ethylene terephthalate),<sup>19</sup> and polypropylene–polyamide.<sup>20</sup> In a number of these cases attention has been focussed on the formation during extrusion of long fibers of fibrils of one of the constituents in a matrix of the other. The rheological behavior of the two-phase melts as well as their morphology is, as can be expected, rather complex, and no general theory predicting which of the two materials will form the continuous phase (or if both will) has been presented.<sup>14</sup>

In the present work the rheological properties and the morphology in the solid state after extrusion of a two-phase material of a somewhat different nature are reported. One of the components used here is low density polyethylene (LDPE) and the other is a technical grade of sodium lignosulfonate, which normally is not considered to be thermoplastic. It has been shown earlier that polyethylene and polystyrene form long fibers in a matrix of lignosulfonate during injection molding and extrusion.<sup>21,22</sup> One of the primary aims of the present work was to investigate the possibility of producing short LDPE-fibers in a lignosulfonate matrix by extrusion. By short fibers we here mean fibers with lengths in the region 0.5–5 mm and with a diameter of 2–20  $\mu\text{m}$ . Such fibers, which can be used as synthetic wood pulp or in different nonwoven applications, are often produced by solvent-based processes.<sup>23,24</sup>

The sodium lignosulfonate matrix has the advantage of being water-soluble; the LDPE fibers are consequently easily extracted from the extrudate. Lignin-based materials have also a comparatively low price and are abundant and independent of oil. It should be pointed out that the idea of extracting fibers or fibrils from a two-phase extrudate is not new,<sup>10,20</sup> but the possibility of using a water-soluble matrix has apparently not been dealt with earlier.

Although a large amount of knowledge concerning the processing of two-phase systems is available,<sup>3-22</sup> the fact that some effects are unique to the specific combination studied cannot, at present, be excluded. Thus we cannot expect that the LDPE-lignosulfonate system should necessarily behave like the thermoplastic blends previously used. One of the reasons for this is the lack of thermoplasticity of the matrix material, another the fact that it is a technical grade, which contains various impurities, some of them volatile. However, the literature may provide some guidelines for production of short LDPE fibers in this type of matrix.

Throughout this work the two-phase blend was homogenized in a single-screw extruder and then fed into a capillary-type nozzle. The nozzle is mounted on the extruder and the length to diameter ( $L/d$ ) of the capillary region could be varied as well as the degree of convergence given by  $D/d$ , where  $D$  is the diameter of the cylindrical land at the capillary entrance. Also the entrance angle ( $\alpha$ ) of the convergence region was varied. This is described in greater detail in the next section.

The overall morphology, i.e., state and mode of dispersion of the phases in the extrudate depends on a number of factors, e.g., blend composition, initial size of the particles, the viscous and elastic properties of the constituents, the processing temperature, the surface tension of the interface, etc.<sup>8,10</sup> If fibers are formed, they are in many cases believed to form in the convergent entrance region of the capillary.<sup>15,16</sup> The initial droplets of one of the polymeric phases may in this region be elongated in the extrusion direction by elongational flow (cf. Refs. 7, 8, and 13). For a Newtonian drop in another Newtonian medium, the deformation and orientation of the droplets during flow is determined by the ratio between the viscosities of the two phases and the interfacial surface tension.<sup>7</sup> For droplet-fiber formation in viscoelastic fluids, Van Oene<sup>7</sup> also pointed out the importance of the initial size of the particles and the elastic properties of the polymers, and formulated requirements for obtaining a droplet-fiber morphology, viz., a stratified structure. Alle and Lyngaae-Jørgensen<sup>12,13</sup> suggested that if the polymer phase that formed the minor component in the blend was more viscous than the other, the minor component (in the form of droplets) was elongated in the inlet region of the capillary, i.e., formed fibers. Furthermore, the fibers became continuous through a coalescence process. The elastic deformation may then relax in the long capillary, the fiber structure becoming rather stable after the extrusion. Vinogradov and co-workers<sup>10,11,18</sup> noted that long fibers could be observed in a certain range of values of the ratio between the viscosities of the two polymers. This range depended on the shear stress, which Vinogradov considered to be another important parameter in conjunction with fiber formation during extrusion. From the literature it thus appears that the use of relatively short capillaries would be appropriate when short fibers are desired

since long fibers will not be produced to the same extent and nor will they coalesce as they might in a long capillary. This was the primary reason for working with short capillaries ( $L/d = 1-4$ ) throughout the present work. Such capillaries have also been reported to produce thinner fibrils<sup>9</sup> and to reduce the segregation of the phases (telescopic structures).<sup>15</sup> The die swell of polymer blends is also more pronounced at low values of  $L/d$ ,<sup>4,16</sup> which can be of importance when breaking up the fiber structure into shorter fibers.

It is reasonable to suppose that the morphology of the melt prior to the passage of the capillary should influence the final structure. It may also be reasonable to assume that if the fiber-forming phase is present in rather small entities this would be an advantage when aiming at producing short fibers using a short capillary. From the work of Han et al.,<sup>5</sup> it is clear that a static mixer produces an improvement in dispersion and breaks up the components into smaller units. All extrusion experiments reported below were therefore performed using a Kenics static mixer.

Before concluding this section, it is worthwhile to mention that since both polyethylene and polystyrene readily form fibers in the lignosulfonate matrix, it may be feasible to produce polymeric fibers using the two-phase extrusion method with polymeric waste material constituting the thermoplastic phase. Some preliminary experiments performed on blends modelling the composition of waste material are commented on in the last section.

## EXPERIMENTAL

### Materials

The low density polyethylene grade (Alkathene 017.040, ICI) had a density of  $0.917 \text{ g/cm}^3$  and a melt flow index of  $7 \text{ g/10 min}$  (190/2.16). It was delivered in the form of a powder with an average particle size of  $400 \mu\text{m}$ .

The sodium lignosulfonate was a technical grade (Wanin SR, Holmens Bruk AB, Vargön, Sweden) containing inorganic salts and sugars as impurities. The composition is given in Table I. Its particle size was  $30-100 \mu\text{m}$ . Prior to the processing its water content was ca. 8.5%.

The LDPE and Wanin SR were mixed manually at room temperature, ca. 300 g of the mixture being required for each experiment. Unless otherwise stated, the proportions of Wanin SR/LDPE (by weight) were 0/100, 25/75, 60/40, 70/30, or 80/20. In the majority of the experiments LDPE thus constituted the minor component.

TABLE I  
Approximate Composition of Wanin SR

	Percentage by weight
Sodium lignosulfonates	70
Salts	15
Sugar (as glucose)	12
Other substances	3

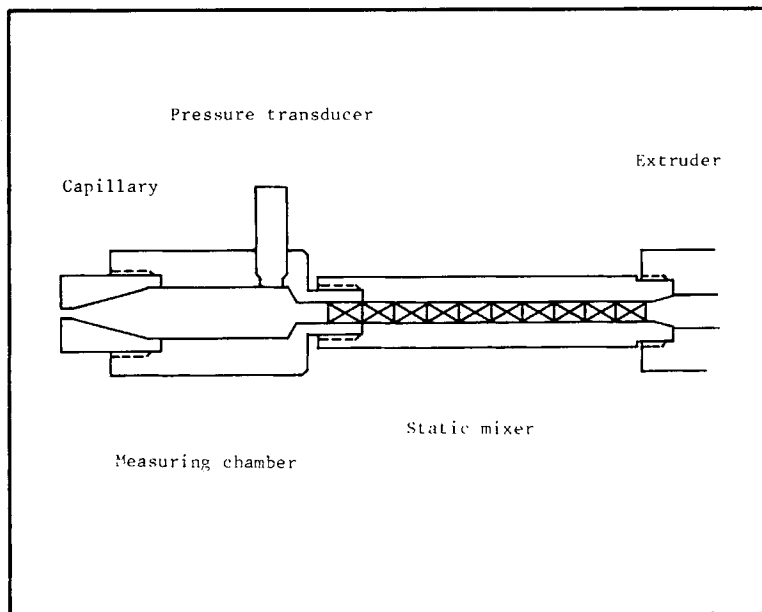


Fig. 1. Schematic diagram of the extruder, equipped with the static mixer, the measuring chamber, and the capillary.

### Extrusion of the Wanin / LDPE Blends

The blends were extruded at 180°C using a conventional single-screw extruder (Dolci, Estrusore 205), with a screw diameter of 19.8 mm and a length to diameter ratio of 24. Figure 1 shows schematically the experimental set up. The static mixer (Kenics mixer, Model 24-1950) is mounted in line with the screw, and is followed by a measuring chamber equipped with a pressure and temperature transducer (Dynisco, System 460, Model TPT 463E-10M-6/8). From the measuring chamber the material flows into the capillary (Fig. 1).

The capillary is shown schematically in Figure 2. In principle three different geometries differing in entrance angle ( $\alpha = 15, 30, \text{ or } 60^\circ$ ) were used. For each capillary with a given entrance angle, three different combinations of  $L/d$  and  $D/d$  were used, 4 and 20, 2 and 10, and 1 and 5. The diameter  $D$  was always 20 mm. A fourth capillary for characterizing the flow behavior of the blends was also used. The  $L/d$  ratio of this capillary was 32, the  $D/d$  ratio 20, and the entrance angle  $\alpha 45^\circ$ .

The screw speed was varied between 9 and 38 rpm which corresponds to shear rates within the capillaries of 10–6000  $\text{s}^{-1}$  (depending on the capillary).

### Morphological Studies

The Wanin SR component of the solidified extrudates was removed by immersion of the samples in water. The time required for dissolving Wanin SR was dependent on the capillary used, and on the composition of the blend. Those extrudates containing fibers dissolved more slowly than those con-

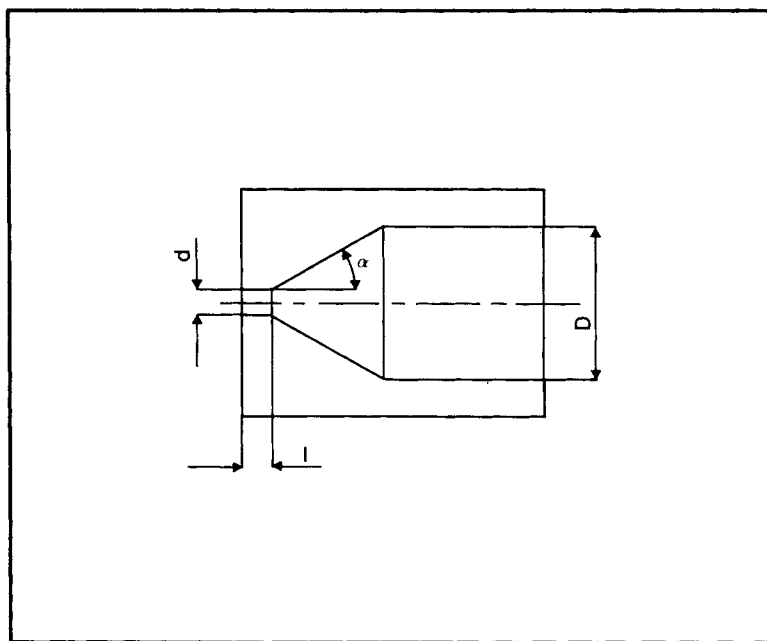


Fig. 2. Schematic diagram of the capillary unit. The entrance angle  $\alpha$  was 15, 30, or 60°, the  $L/d$  ratio could be varied between 1 and 4 and the  $D/d$  ratio between 5 and 10.  $D$  is 20 mm.

taining fragments and particles. Those blends with high LDPE content also dissolved slower than those with high lignosulfonate content. The resulting LDPE fibers were examined using an optical microscope. More than 100 samples were used in this analysis, and they were classified according to the quality of the fibers produced. Fracture surfaces of the extrudates were studied using a scanning electron microscope (Jeol JSM 35).

## RESULTS AND COMMENTS

### Rheological Properties

Figure 3 shows the viscosity ( $\eta$ ) vs. the shear rate ( $\dot{\gamma}$ ) for the Wanin SR/LDPE blends and for pure LDPE at 180°C. These curves were obtained with a capillary with a  $L/d$  ratio of 32; the corresponding shear stress range was 0.07–0.3 MPa. It should be pointed out that  $\eta(\dot{\gamma})$  curves for the same blends were also determined using an Instron capillary viscometer. These curves did not differ appreciably from those shown in Figure 3. In Figure 4 the viscosity of the blends has been plotted as a function of the weight fraction of Wanin SR at two different shear rates, 100 and 200  $\text{s}^{-1}$ .

From Figure 3 it is obvious that the viscous behavior can be described approximately by a power law relation of the type  $\tau = K\dot{\gamma}^n$ , where  $\tau$  is the shear stress and  $K$  and  $n$  are constants. It is also clear that the viscosity decreases when the amount of Wanin SR is increases. It appears that the lignosulfonate has a “lubricating effect” which is in agreement with earlier results.<sup>21</sup> The flow behavior shown in Figures 3 and 4 is also in accordance

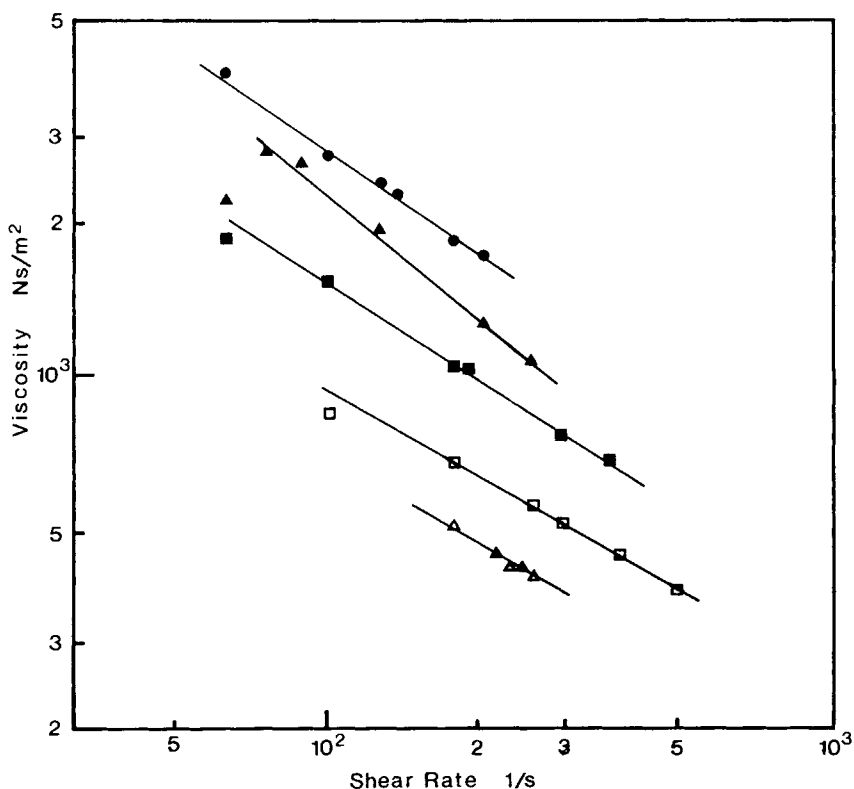


Fig. 3. Viscosity ( $\eta$ ) vs. shear rate at 180°C for the Wanin SR/LDPE blends: (●) 0/100; (▲) 25/75; (■) 40/60; (□) 60/40; (△) 80/20 Wanin SR/LDPE.

with the idea that it is the component with the highest viscosity (in this case LDPE) that forms the fibers.<sup>13</sup> In no case is any pronounced extreme point in the  $\eta$  (% Wanin SR) curves noticeable. Such extreme points are sometimes encountered with certain types of polymer blends.<sup>15</sup>

It was not possible to process Wanin SR at 180°C more than once due to thermal degradation. The flow properties of this material are very difficult to determine with sufficient accuracy due to its instability at elevated pressures and temperatures. Furthermore, it is likely that the water content of Wanin SR has a pronounced influence on the flow behavior of the blends. It is known that moisture has a strong effect on the softening behavior of lignosulfonates, an increase in moisture content reducing the softening temperature.<sup>25</sup> In the present work it was noted that a decrease in water content of Wanin SR was paralleled by an increase in viscosity of the blends.

### Short Fiber Formation during Extrusion

Before discussing production of short LDPE fibers in the Wanin SR matrix, it should be mentioned that long polymeric fibers may readily be produced in the same type of matrix in a capillary with a sufficient length. The  $D/d$  ratio should be rather low as well as the shear rate. This was usually the case during the viscosity measurements in the extruder and in the Instron capillary

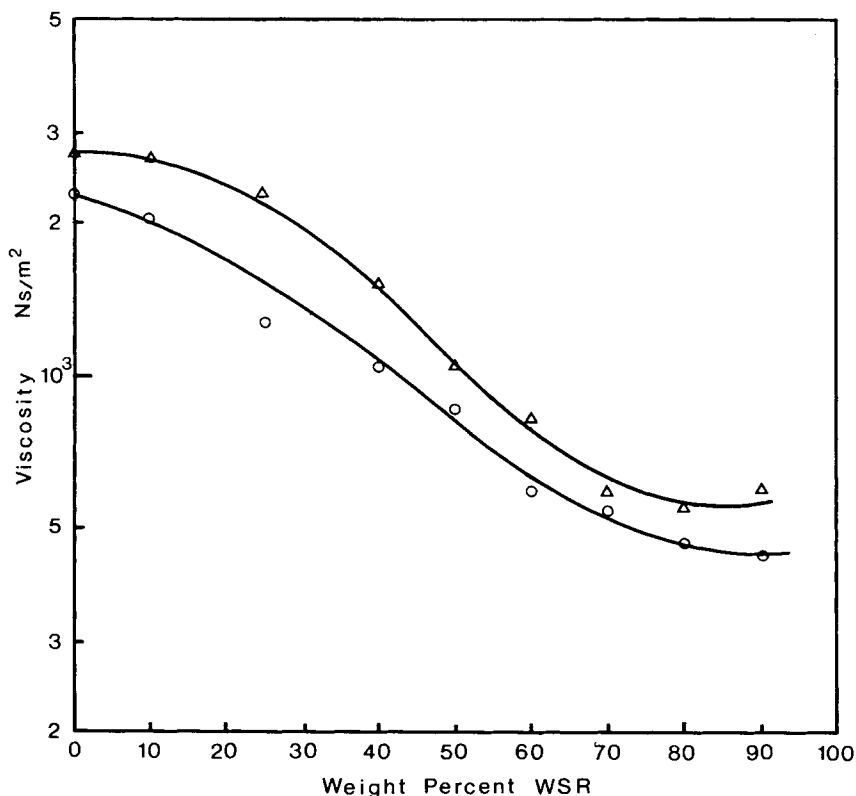


Fig. 4. Viscosity ( $\eta$ ) at 180°C vs. the amount of Wanin SR at ( $\Delta$ ) 100 s<sup>-1</sup> and ( $\circ$ ) 200 s<sup>-1</sup>.

viscometer. In many cases, however, segregation and “telescopic” structures were encountered. By using short capillaries, a static mixer, and a powder grade of LDPE, such problems have been minimized.

The extrudates had a more or less foamed structure. The foaming can be traced to Wanin SR which contains some water and also other substances which may volatilize during extrusion at 180°C. The blend which consisted of 25% Wanin SR and 75% LDPE did not contain any fibrous material at all. Instead the LDPE phase formed a continuous, foamed network. This blend also exhibited more scatter in the measurement of the viscosity, as is evident in Figure 3. The slope of the viscosity curve is also affected.

The die swell for this blend was comparatively large, of the order 5–7; for the other blends it was significantly lower, 1.4–1.7, and independent of the composition. The blend 25/75 Wanin SR/LDPE is thus not considered in the following.

The extrudates had always a thin LDPE skin on their surface. The thickness of this skin layer increased with increasing entrance angle. It was smaller than 0.05 mm when  $\alpha$  was 15° and ca. 0.1 mm at 60°. It is possible that the dispersed phase migrates towards the surface of the extrudate during processing.<sup>9</sup> At higher entrance angles there may be some accumulation of LDPE close to the capillary region which may yield an increase in skin thickness. A low value of  $\alpha$  apparently produces a thin LDPE skin.

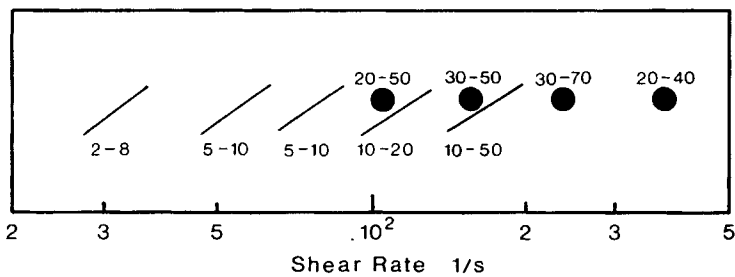


Fig. 5. Schematic illustration of the effect of the shear rate ( $\dot{\gamma}$ ) on the fiber formation. The numbers indicate the diameter of the LDPE fibers or the fragments (upper numbers) formed.

The capillaries with different  $D/d$  ratios produced flows with different shear rates. At  $D/d = 20$  ( $L/d = 4$ ) shear rates between 1200 and 5700  $s^{-1}$  were obtained, at  $D/d = 10$  ( $L/d = 2$ ) between 180 and 950  $s^{-1}$ , and at  $D/d = 5$  ( $L/d = 1$ ) the corresponding range was 10 to 120  $s^{-1}$ . Examination of the optical micrographs indicated that fibers were formed to an appreciable extent only at shear rates below ca. 100  $s^{-1}$ . Between 100 and 300  $s^{-1}$  fibers were formed together with fragments of LDPE, and at still higher shear rates only fragments and particles were observed. This is schematically shown in Figure 5 where also the diameter of the fibers is indicated. There is a tendency for thinner fibers to be formed at lower shear rates (cf. also Ref. 9). As long as LDPE constitutes the minor component of the blend, the blend composition had no influence on the shape and size of the fibers. The length of the fibers is difficult to determine accurately since the fibers are entangled, but in general the length ranges from 0.5–5 mm.

At shear rates higher than ca. 100  $s^{-1}$  fibers may, however, be formed in the capillary inlet but can then be broken up into fragments by the shear field (cf.



Fig. 6. Optical micrograph of LDPE fibers formed at  $\dot{\gamma} = 84 s^{-1}$  using a capillary with  $D/d = 5$  and  $\alpha = 15^\circ$ . The blend is 70/30 Wanin SR/LDPE.



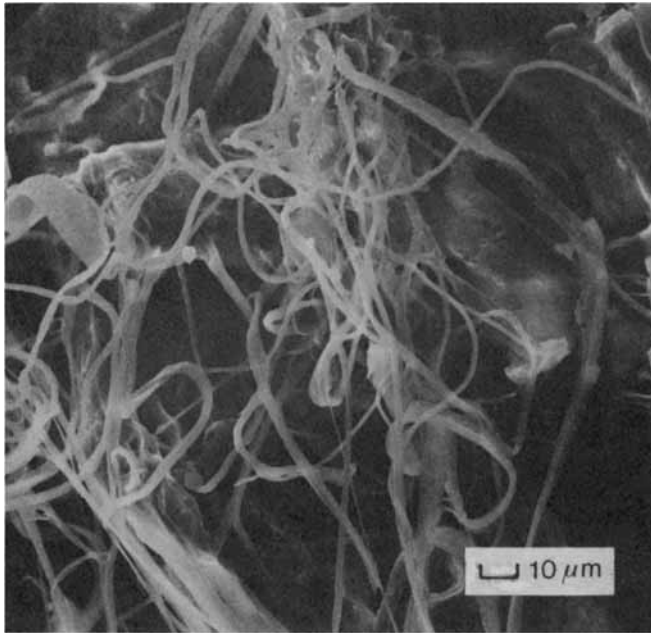


Fig. 7. Scanning electron micrograph of LDPE fibers produced with the same capillary as in Figure 6 but at  $\dot{\gamma} = 64 \text{ s}^{-1}$ . The blend is 60/40 Wanin SR/LDPE.

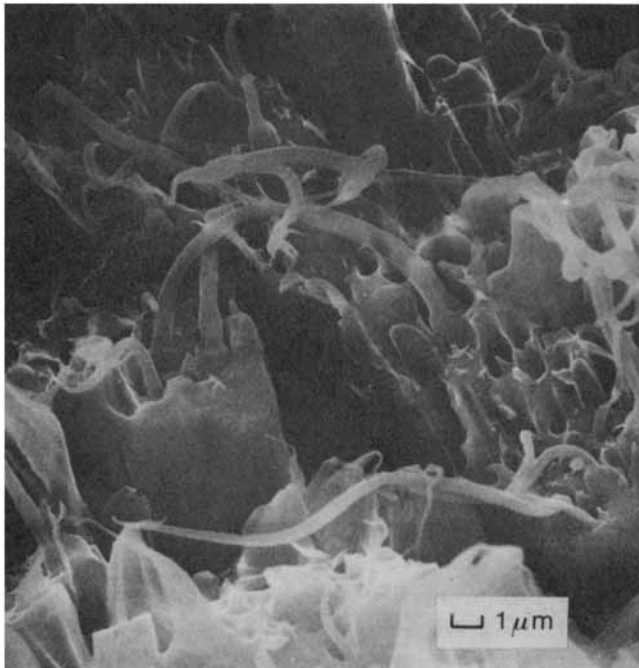


Fig. 8. Fracture surface of an extrudate produced using a capillary with  $D/d = 10$  and  $\alpha = 60^\circ$ . The shear rate was  $720 \text{ s}^{-1}$ , and the blend was 60/40 Wanin SR/LDPE.

Ref. 7). According to Vinogradov et al.,<sup>10</sup> they are disintegrated due to unsteady elastic turbulent flow at high shear stresses. It cannot be excluded that fiber formation is prevented due to the large acceleration of the melt in the entrance region of the capillary when  $D/d$  is high.

Figure 6 shows an optical micrograph of the extracted LDPE fibers produced with a capillary of  $D/d = 5$  and  $\alpha = 15^\circ$ . The shear rate was  $84 \text{ s}^{-1}$ . This is a rather typical picture of the formed fibers. Figure 7 is a scanning electron micrograph of fibers produced with the same capillary but at  $\gamma = 64 \text{ s}^{-1}$ . Figure 8 is a scanning electron micrograph of a fracture surface of an extrudate produced using the capillary with  $D/d = 10$  and  $\alpha = 60^\circ$ . Virtually no fibers can be detected, only fragments of LDPE.

In summarizing, it has been found that in a capillary with a  $D/d$  ratio of 5 and  $\alpha = 15^\circ$  short fibers with diameters of 2–20  $\mu\text{m}$  are formed to an appreciable extent, provided that the shear rate is below  $100 \text{ s}^{-1}$ .

### FINAL REMARKS

It has been shown that in short capillaries and at low shear rates, LDPE forms short fibers in a matrix of sodium lignosulfonates. The two-phase extrusion procedure thus may provide an alternative route for producing polyethylene-based synthetic wood pulp and similar products. It should be stressed that the fiber forming tendency is a general property of thermoplastic polymers and that amorphous materials like polystyrene have also been found to yield fibers in a matrix of sodium lignosulfonate.<sup>21</sup>

As evident from the preceding sections, the LDPE–Wanin SR system exhibits some similarities with other two-phase thermoplastic systems. Another example of this can also be mentioned. Vinogradov et al.<sup>10</sup> have studied the fiber formation of polyethylene (PE) in polystyrene (PS) and established the ranges of shear stress and viscosity ratios between PE and PS for which formation of perfect fibers is possible. In our case  $\log(\eta_{\text{PE}}/\eta_{\text{W}})$  is of the order 0.2–0.6 ( $\eta_{\text{W}}$  denotes the viscosity of Wanin SR obtained by extrapolation of the curves in Fig. 4). In this range, formation of fibers is possible according to Vinogradov et al.<sup>10</sup> In our case fibers did not form at shear rates higher than  $100 \text{ s}^{-1}$ . This corresponds to a shear stress of ca. 0.1 MPa. This critical shear stress is in good agreement with the ultimate shear stress found in Ref. 10 for PE/PS blends before disintegration of the fibers begins. This agreement is probably a coincidence, but it underlines the similarity between LDPE/Wanin SR and more conventional thermoplastic blends.

A few experiments relating to extrusion of blends of 60% (by weight) Wanin SR, 26% high density polyethylene, and 14% polystyrene have also been performed. These experiments were intended to model extrusion of Wanin SR and plastics waste. As shown in Figure 9, the thermoplastic fraction forms some fibrous material also in this case, although not to the same extent as in the case of pure LDPE. The reduced fiber forming tendency may be due to the use of pellets instead of powder. Nevertheless, the results indicate that it may be possible to produce short fibers from mixed plastics waste by extrusion together with a water-soluble material like lignosulfonate.

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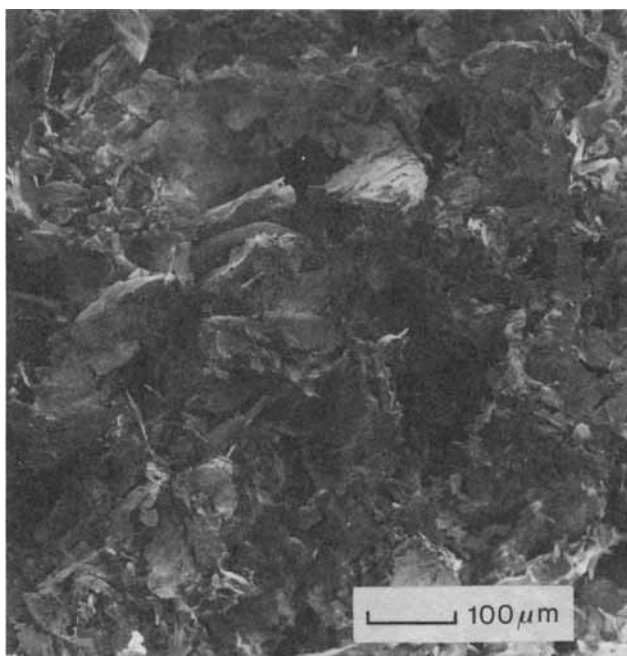


Fig. 9. Fibrous material produced by extrusion of a blend of 60% Wanin SR, 26% high density polyethylene, and 14% polystyrene at 180°C. The capillary had a  $D/d$  ratio of 5 and an entrance angle of 15°. The shear rate was  $15 \text{ s}^{-1}$ .

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