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ESEM Study of Oil Wetting Behaviour of Polypropylene Fibres

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Résumé — Étude ESEM de la mouillabilité des fibres de polypropylène par l'huile — Les fibres de polypropylène ont été utilisées de manière conséquente dans les domaines relatifs à l'huile tels que les matériaux absorbants et coalescents à l'huile, les filtres à huile et les séparateurs d'huile. La mouillabilité des fibres par l'huile est particulièrement importante dans ces applications. La technique du microscope *environmental scanning electron (ESEM)* a été utilisée dans cette étude afin de comprendre la mouillabilité des fibres de polypropylène par l'huile. La mouillabilité a été observée par des mesures d'angle de contact avec l'huile. Les gouttes d'huile ont été ajoutées sur les fibres à l'aide d'une micro-pipette. Les angles de contact ont été mesurés à partir d'un micrographe ESEM utilisant l'analyse de l'image et l'approche théorique. L'observation ESEM révèle des fibres individuelles au niveau microscopique.

Abstract* — *ESEM Study of Oil Wetting Behaviour of Polypropylene Fibres — *Polypropylene (PP) fibres have been increasingly used in oil related areas, such as oil sorbents, oil coalescers, oil filters and oil separators. The wetting behaviour of the fibres by oil is of particular importance in these applications. The environmental scanning electron microscope (ESEM) technique was used in this study to investigate the oil wetting of polypropylene fibres. The wettability was investigated by contact angle measurements with oil. Oil drops were added onto fibres using a micro-injector. The contact angles were measured from ESEM micrographs using image analysis and theoretical approach. ESEM observation reveals the wetting of single fibres on a microscopic level.*

INTRODUCTION

Polypropylene fibre is one of the most important fibres in industrial textiles. The rapid increase in the range of applications of polypropylene fibres can be attributed to the excellent physical and chemical properties compared with other fibres: light weight, good mechanical properties, excellent chemical resistance and low moisture absorption (Koslowski, 2000). Polypropylene fibres have been increasingly used in oil related applications, such as oil sorbents, oil coalescers, oil filters and oil separators (Wei, 2003; Lebiedowski, 2001; Teas *et al.*, 2001). The wetting behaviour of the fibres by oil is of particular importance in these systems.

The wetting of fibres by a liquid is governed by the Young's Equation relating the interfacial energies between the three phases as illustrated in Figure 1:

$$\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl} \qquad (1)$$

where γ_{lv}, γ_{sv} and γ_{sl} refer to the interfacial energies of the liquid/vapour, solid/vapour and solid/liquid interfaces, θ is the contact angle.

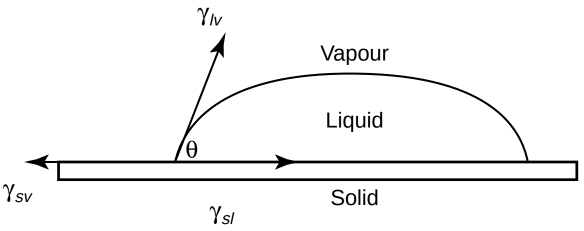

Figure 1

Contact angle.

ESEM provides a new tool for direct observation of wetting at a micron level (Wei *et al.*, 2002). The presence of liquid water in the ESEM specimen chamber allows the observation of wetting without the need for coating or drying of the sample. ESEM allows the high magnification observation of wet specimens with no damage to the material and its evolving microstructure. In this work a Philips XL30 field-emission environmental scanning electron microscope (ESEM-FEG) was used to study the oil wetting of polypropylene fibres.

1 MATERIALS AND METHODS

1.1 Materials

The PP raw material used was HF445J with a MFI of 19.0 g/10 min. The PP fibres were spun on a lab extrusion machine supplied by *ESL (Spares) Ltd.*, United Kingdom. The diameter of each hole in the spinneret was 0.4 mm. Barrel temperatures in the extruder were set at 215/225/230°C for the three zones, respectively. The spinning temperature was 230°C and the metering pump speed was 3 rpm. No spin finish was applied.

To compare the effect of oil properties on the wetting behaviour of the fibres, different types of oil were made in the laboratory. The crude oil was obtained from the North Sea. Samples of the crude oil were then weathered by heating on a hot plate at 50°C to make the evaporated oils with 25% and 50% weight loss respectively. The oil density and viscosity were measured using a digital density meter and dynamic viscosity meter, respectively. The measurements were run in triplicate and the mean value was reported. The oil properties are shown in Table 1.

TABLE 1

Oil properties

Oil type	Light	Medium	Heavy
Density (g/cm^3) at 20°C	0.814	0.849	0.890
Viscosity (mPa·s) at 20°C (shear rate 10.82 s^{-1})	18.7	54.8	631

1.2 ESEM

The field-emission environmental scanning electron microscope (ESEM) represents several important advances in scanning electron microscopy. ESEM allows the high magnification observation of wet specimens and even of the wetting process with no damage to the material. The ESEM column is equipped with a multistage differential pressure pumping unit. The pressure in the upper part is about 10^{-6}-10^{-7} torr, but a pressure of about 1-20 torr can be maintained in the observation chamber (Danilatos, 1993). Water is the most common imaging gas in the ESEM chamber. When the electron beam (primary electrons) ejects secondary electrons from the surface of the sample, the secondary electrons collide with water molecules, which in turn function as a cascade amplifier, delivering the secondary electron signal to the positively biased gaseous secondary electron detector (GSED). The water molecules are ionised, and the positively charged ions are attracted toward the specimen to neutralise the negative charge produced by the primary electron beam on the specimen surface. Therefore, in contrast to traditional scanning electron microscopy, ESEM can be used to examine uncoated, nonconductive specimens.

The ESEM has a large specimen chamber and some accessories can be added into the chamber to expand the observation capacity. A Philips XL30 ESEM equipped with a Peltier cooling stage and a micro-injector was used in this study.

1.3 Experimental Procedure

The micro-injector was mounted in the ESEM chamber before examination of a specimen. The micro-injector consists of three major parts: injection needle, liquid container and needle position adjusting screws. The fibres were placed on the specimen holder as shown in Figure 2. The injection needle was adjusted just above the fibres. Wet mode was selected from the ESEM controller. Samples can be examined uncoated in this mode, with a GSED, within a gaseous environment. This is particularly suited for the examination of wet samples, where it is desirable to observe the sample in its natural state.

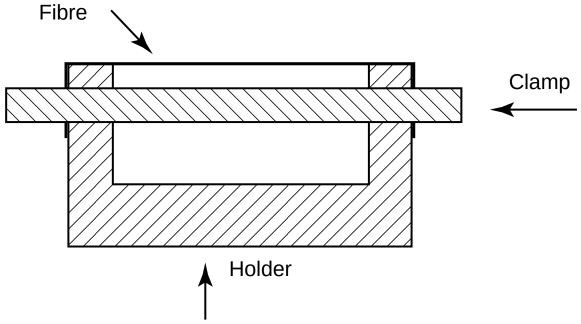

Figure 2

Sample holder.

The oil was placed onto fibres by pressing the syringe during the examination. After the oil was applied, the system was stabilised for 60 s. The specimen temperature was set at 5°C. Micrographs were taken at 20 kV and 4.9 torr (667 Pa).

2 RESULTS AND DISCUSSION

2.1 Wetting Process

When oil was applied to the fibres, they were wetted immediately. Oil droplets formed on the fibre surface in a very short time. A typical ESEM image is shown in Figure 3. The ESEM images also showed that the shape of the oil drops formed on fibre surfaces did not change with time. It can be seen that the oil droplets on polypropylene fibres appeared elliptical. In this case, the tangent method (Sawada *et al.*, 1978) is very difficult to apply because of the meniscus curvature at the three phase contact line. Hence direct measurement of the contact angle is not suitable.

2.2 Droplet Shape

The oil droplets on a fibre surface adopt shapes which conform to the Laplace law if the droplets are sufficiently small, that the gravity effects can be ignored. In this study the oil droplets observed in the ESEM were in the range between 50 μm and 100 μm, therefore the gravity effects could be ignored. The following analysis shows the balance between the force of gravity on an oil droplet and the force due to surface tension.

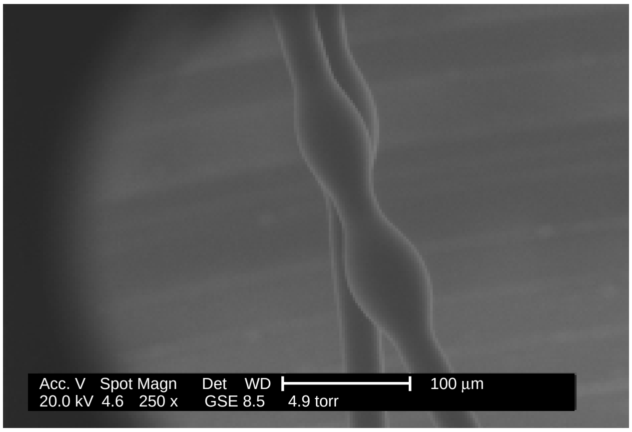

Figure 3

Oil droplets on fibre surface.

Force of gravity:

$$2\,Rg\rho \tag{2}$$

Force of surface tension:

$$2\,\gamma/R \tag{3}$$

where R is the radius of a droplet; ρ is the density of oil; g is 9.81m/s^2 and γ is the surface tension of oil.

In case:

$$2\,Rg\rho > 2\gamma/R \tag{4}$$

The gravity exceeds the surface tension only for droplets with a radius $R > 1.89$ mm (*e.g.*: ρ = 0.85 g/cm^3; γ = 0.030 N/m at 20°C), but in ESEM the oil droplet diameters are less than 100 μm.

The oil droplets formed on a fibre surface can be considered in terms of the Laplace equation:

$$\Delta P = \gamma_{lv}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{5}$$

where ΔP is the pressure difference between the two sides of a curved interface, γ_{lv} is the interfacial energy between liquid and vapour, R_1 is the curvature along the fibre axis and R_2 is the curvature across the fibre axis. For complete wetting by a fluid on a flat surface this pressure difference can be reduced toward zero by simultaneously increasing both R_1 and R_2.

However, in the case of fibres, R_1 and R_2 can not simultaneously be increased because of the radius of curvature of the fibre itself.

2.3 Contact Angle Measurement

The axisymmetrical barrel shape droplets on a single fibre observed in the ESEM can be further analysed using Carroll's approach (Carroll, 1976). This approach for the calculation of contact angles of barrel shape droplets on cylindrical solids comprises an analytical expression relating droplet length L, maximum drop radius x_2 and the fibre radius x_1 as shown in Figure 4.

$$\frac{\bar{L}}{2} = aF(\varphi_1, k) + nE(\varphi_1, k) \qquad (6)$$

where $\bar{L} = L/x_1$, $n = x_2/x_1$, $a = (n \cos\theta - 1)/(n - \cos\theta)$. k and φ_1 are defined as: $k^2 = 1 - (a^2/n^2)$, $\sin^2 \varphi_1 = (n^2 - 1)/(n^2k^2)$, $F(\varphi_1, k)$ and $E(\varphi_1, k)$ are elliptic integrals of the first and second kind, respectively.

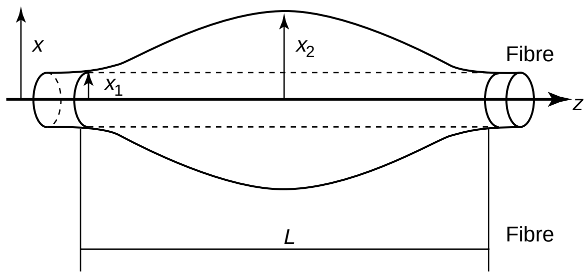

Figure 4

Oil droplet profile.

2.4 Image Analysis

In the contact angle calculation, the measurement of droplet shape and fibre diameter is of importance. In this study, the ESEM photographs were saved as 8-bit images. Using computerised image analysis, these images were digitised and the droplet profiles were detected. From the digitised images, the fibre diameter and droplet sizes could be obtained for each contact angle calculation.

The oil contact angles on the PP fibres were analysed using Equation (6) and values for the contact angles are given in Table 2. Figure 5 illustrates the ESEM micrographs of the different oil types on the fibres. It can be seen that the contact angles calculated are between 15 and 25°, indicating the affinity of polypropylene fibres for oil. With increase in viscosity from light oil through to heavy oil, there is a small, but definite increase in contact angle.

TABLE 2

Oil contact angles

Oil type	Light	Medium	Heavy
Contact angle (°)	15 ± 2	18 ± 2	25 ± 3

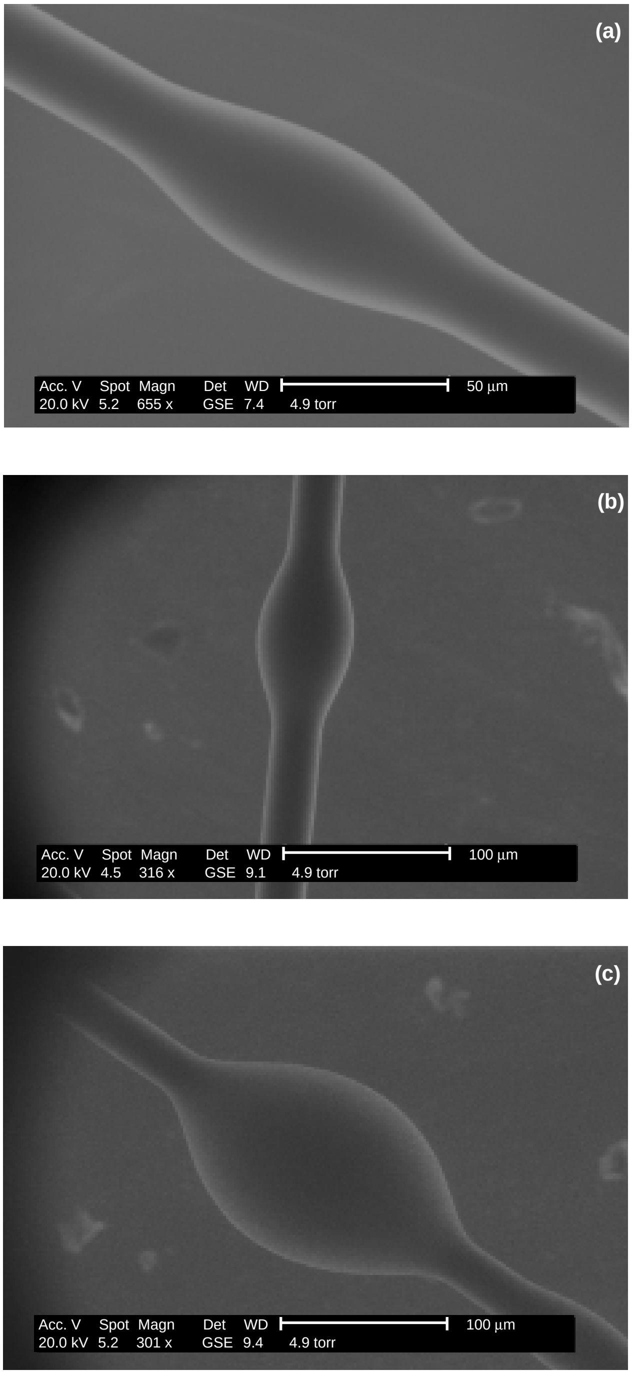

Figure 5

ESEM images of oil droplet on fibres. a) light oil; b) medium oil; c) heavy oil.

CONCLUSION

Polypropylene fibres have been increasingly used in many industries for a wide range of oil related applications. Wetting behaviour of the fibres by oil is of importance in these applications. ESEM observation revealed the different wetting behaviour of the material by oil, which would help researchers and engineers to better understand the wetting on a microscopic level and to improve the performance of the products made from these materials.

ESEM provides a new approach to the direct observation of wetting in a variety of environments. Additionally ESEM is able to examine samples under a range of gaseous environments, relative humidity and temperatures, thus making it a powerful tool to perform a wide range of observations within the ESEM chamber. The potential use of the ESEM in oil and gas related research and development is promising and significant.

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