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Peelback of highly oriented cellulosic fibres

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An original study of peelback of cellulosic fibres spun using the N-methylmorpholine N-oxide (NMMO) process was performed. 13 micrometre diameter fibres were peeled under a microscope. Due to the high orientation of the material, the rupture could propagate in the centre of the fibres. Fibres presenting very different Fibrillability Index (FI = 0 or FI = 5) and hydration (swollen in water or freezedried) were studied. The resulting surfaces were analysed using Scanning Electron Microscopy (SEM). They showed the original formation of regularly spaced ribs corresponding to tearing of a homogeneous oriented material for the non fibrillable fibres. The structure of fibrillable fibres appeared through the creation of fibrils. Measurements of the energy release rate were performed with a set of each kind of fibres. Low values of this energy were obtained, corresponding to the formation of small ribs, due to the high orientation of the cellulose molecules. The energy values can be increased by the occurence of fibrils in the case of fibrillable fibres.

1. Introduction

The effect of orientation on the mechanical properties of polymeric materials has been widely studied during the last twenty years. Many of these studies were concerned with the improvement of the tensile mechanical properties but the transverse behaviour of oriented materials has received less attention [1, 2]. The transverse modulus of filaments was measured by compression of a single filament [3] or more recently by an ultrasonic immersion technique of packed fibres [4]. However, no experiment has been performed to evaluate the energy dissipated during peelback of fibres [5]. Transverse tearing experiments have only been performed on oriented films [6].

The study of the transverse mechanical properties of cellulosic fibres is interesting as they are assumed to induce the behaviour of the fibrillar structure during the fibrillability test consisting of a mechanical stirring. Indeed the traditional way of manufacturing regenerated cellulose is the Viscose process but this is very polluting and is being progressively replaced by the utilisation of N-methylmorpholine N-oxide [7, 8]. One of the characteristics of these new fibres is their possibility to be surface fibrillated [9a, 9b]. For use in textile fibres this behaviour is harmful to the stability of the staining and the fibrillability has to be reduced as much as possible. Textile companies worked significantly on this subject [10a, 10b] and the possibility to fibrillate is now well controlled. On the other hand, the creation of fibrils on the surface seems to be interesting to enhance the reinforcement of composites by these fibres [11]. A better understanding of the origin of fibrillability is important. Previous studies showed that the fibres are homogeneous [12] and we can assume that their fibrillability depends on the cohesion of the fibrillar structure, which can be analysed using a peelback test of the fibres [13].

In this study, such a peelback test is carried out in order to observe the surfaces (using SEM) resulting from the rupture of highly oriented material. At the same time, the energy release rate was determined. The study was limited to the comparison between four different samples. Fibres made from the same cellulose but presenting two very different degrees of fibrillability were peeled either in the hydrated state or after freeze-drying. Processing of fibres as well as the techniques used are described in the experimental section. In the following section, SEM analyses of the fibres subjected to the peelback test are shown as well as measurements of the energy release rate, in order to relate these values to the different degrees of fibrillability.

2. Experimental part

2.1. Fibre preparation

The regenerated cellulose fibres were spun at the CERMAV Laboratory in Grenoble. The cellulose used was V60 from Buckeye (England). The pulp with an average-DPv of 600 was dissolved at a concentration of 10 wt% in NMMO monohydrate using an IKA-Laboratory kneader HKD-TO.6. To prevent cellulose degradation, 0.1wt% propylgallate was added as an

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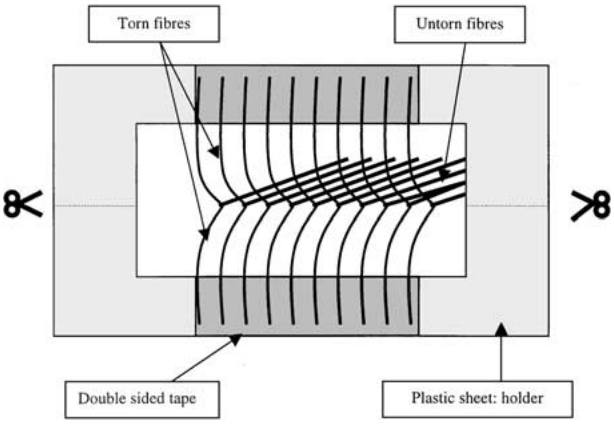

Figure 1 Schematic representation of the system used to measure the energy release rate.

antioxidant [14]. The solution was extruded with a Davenport Melt Indexer No. 3 fitted with a 130 micron one-hole spinneret operating at 100°C, using the conventional dry jet/wet spinning technique. After leaving the orifice the dope was stretched through an air gap before being coagulated in a water bath. All the fibres were prepared using a draw ratio equal to 10. The fibrillable fibres were obtained with a small air gap of 2 cm in air at $T = 20°C$ and a Relative Humidity (RH) around 50%. On the other hand the preparation of the non fibrillable fibres required the use of a larger air gap equal to 15 cm in which air at $T = 30°C$ with a RH = 90% was blown.

The fibres were torn using tweezers under a binocular microscope.

2.2. Scanning electron microscopy (SEM)

The surfaces resulting from the peelback of fibres were coated with gold and analysed using a JEOL jsm-6100 with a low tension to inhibit cellulose degradation.

2.3. Measurement of the energy release rate

The energy dissipated during peeling of the fibres was measured using an INSTRON Tester 4301 fitted with a 10 N load cell. In this configuration the apparatus presented a sensitivity of 1 gram (0.01 N) which induced the simultaneous study of at least 10 fibres to obtain significant experiments. Fig. 1 shows the system used to perform this experiment. 2 cm long fibres were torn over a length of 5 mm. Each torn part was stuck on one side of the holder. The latter, made of a plastic sheet, was cut after clamping to avoid the application of any stress which would lead to the rupture of the fibres. This geometry is analogous to a T-peel test such as those performed on adhesives [15].

3. Results and discussion

3.1. Observation of the surfaces of rupture using SEM

Since the experiments are very delicate to perform, we limited our study to fibres made from the same cellulose but presenting very different degrees of fibrillability in reference to a standard test [16]. They are either very fibrillable (Fibrillation Index = FI = 5) or non fibrillable fibres (FI = 0). Moreover, since the mechanical properties of cellulosic materials depend widely on their water content [17–19], experiments were performed using two very different degrees of hydration. The fibres were swollen in water and torn either in the hydrated state or after freezedrying. This way of drying was used because it allows the swollen structure to be kept.

3.1.1. Non fibrillable fibres

Fig. 2 shows that the peelback of a non fibrillable fibre in the hydrated state corresponds to the rupture of a homogeneous material. Indeed no fibrillar structure appears and we see on Fig. 3 that the peeling induces the formation of regular ribs. The presence of these ribs indicates an important mobility of the system for transversal deformations. This behaviour can be explained because the glass transition temperature of the system is lower than the ambient temperature. Indeed the results of Salmen and Back [19] for cellulose with this water content, estimated at 30% [20], give a glass transition temperature below 0°C.

The ruptures initiated in the centre of the fibres were very stable. The application of different peel rates (achieved manually) led to similar structures. Such structures can be observed in peeling tests carried out with uncross-linked adhesives in cohesive failure regimes [21, 22] where very regular ribs are present. This type of failure has also been observed using a tearing test on highly oriented linear polyethylene [6], or by peeling PET filaments [13], which appear as regular lines of material left on the surface. This explains clearly that these mechanisms are different from the ones observed for crazes, as described for example by Argon and Salama [23]. The latter authors showed evidence of fibrils which become thinner in section when moving to the crack tip, and are regenerated by meniscus instabilities.

Fig. 4 presents the surface of rupture for a non fibrillable fibre torn both in the hydrated state and after freeze-drying and confirms the large effect of the water content on the mobility of cellulose. Indeed as we can verify in Figs 5 and 6, after freeze-drying the surface of rupture still corresponds to the peeling of a homogeneous material but the plastic deformations induced are much lower. The application of different peeling rates always led to similar mechanisms. This kind of surface was observed for the rupture of well-oriented polyethylene films [6] which were also performed at a temperature 200°C lower than the glass transition [19]. It is noteworthy that the tearing of these freeze-dried fibres leads to unstable failure.

In conclusion, the peelback of non fibrillable fibres, performed in both the hydrated and the dry state, induced a structure corresponding to the rupture of a homogeneous material and there was no appearance of any fibrillar structure. Since the method of determination of the fibrillation index consists of shaking fibres in water we expect to obtain a different behaviour with the fibrillable fibres.

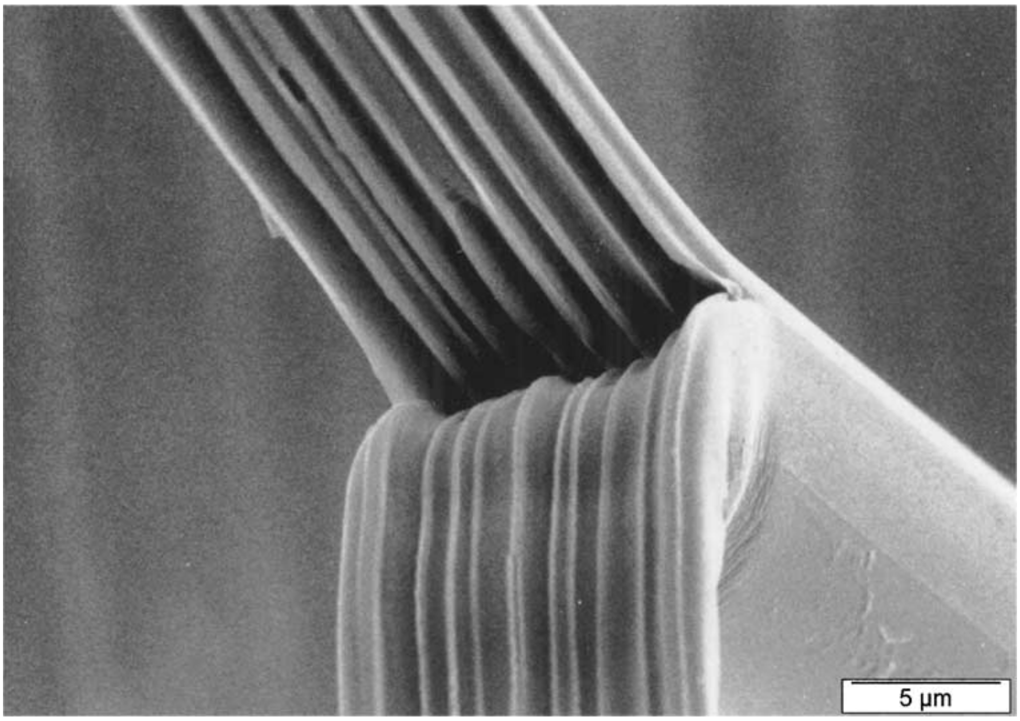

Figure 2 Peelback of a **non fibrillable hydrated** fibre.

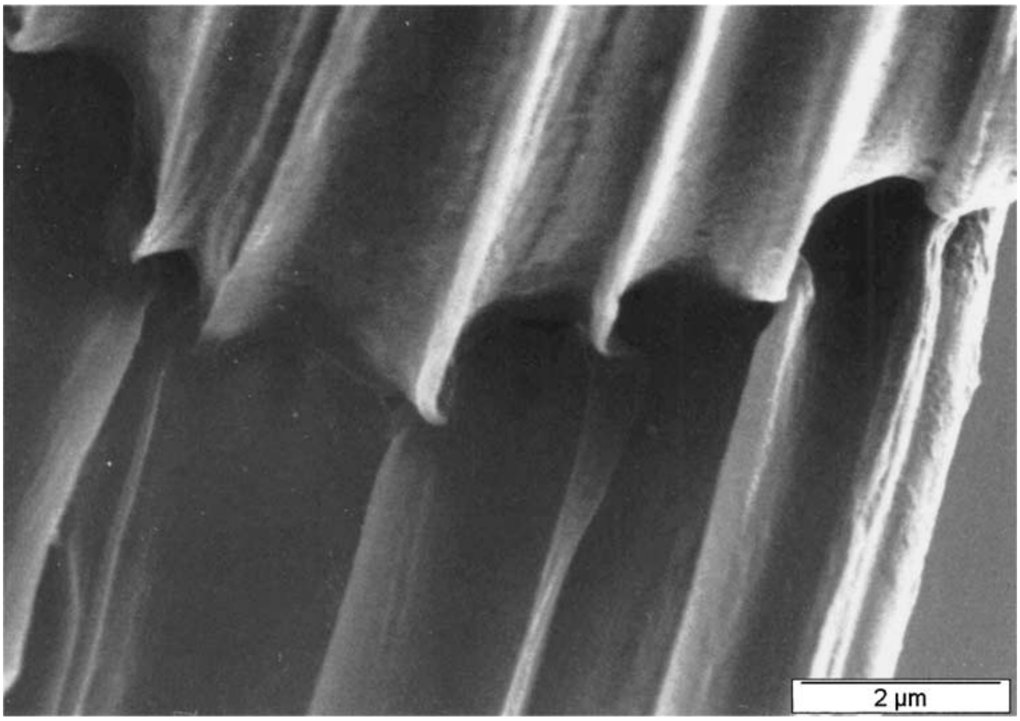

Figure 3 Formation of ribs during peeling of a **non fibrillable hydrated** fibre.

3.1.2. Fibrillable fibres

The rupture of fibrillable fibres in the hydrated state (Fig. 7) led to the appearance of fibrils. The formation of the fibrillar structure was limited to a few fibrils. As the peel rate increased these became more numerous but thinner. Fig. 8 shows that peeling still induced the development of ribs whose amplitude and thickness were smaller than the ones created with non fibrillable fibres. This behaviour corresponds to reduced entanglements in fibrillable fibres. This fact has also been observed in peeling experiments [22] when the reduced velocity $a_T V$ (a_T temperature dependent coefficient, V peeling velocity) is decreased, i.e. temperature T is increased, which again corresponds to an increase in the mobility. Pitman and Ward [24] found that the size of the crazes induced during the tearing of polycarbonate films increases with the molecular weight. Observation of Fig. 9 presenting the surfaces after a peelback test, performed first in hydrated and then in dry state, shows that the fibrillar structure appears even more after freeze-drying. We observe in Figs 10 and 11 that the peeling of freeze-dried fibrillable fibres

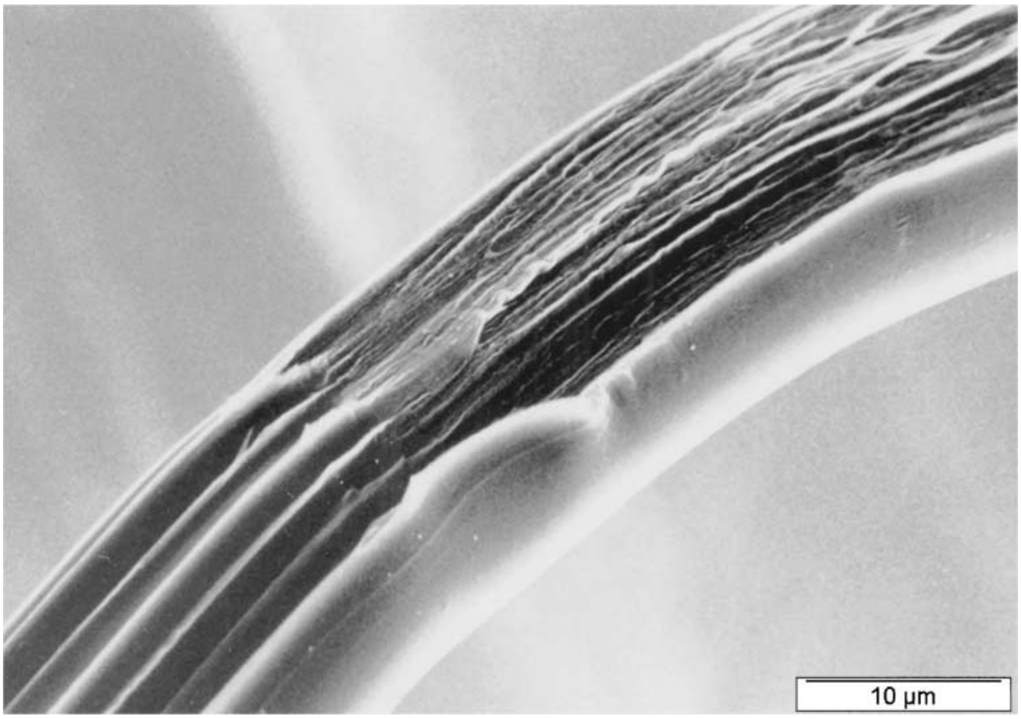

Figure 4 Surfaces resulting from peelback of a **non fibrillable** fibre in two different hydration states (left: hydrated; right: freeze-dried).

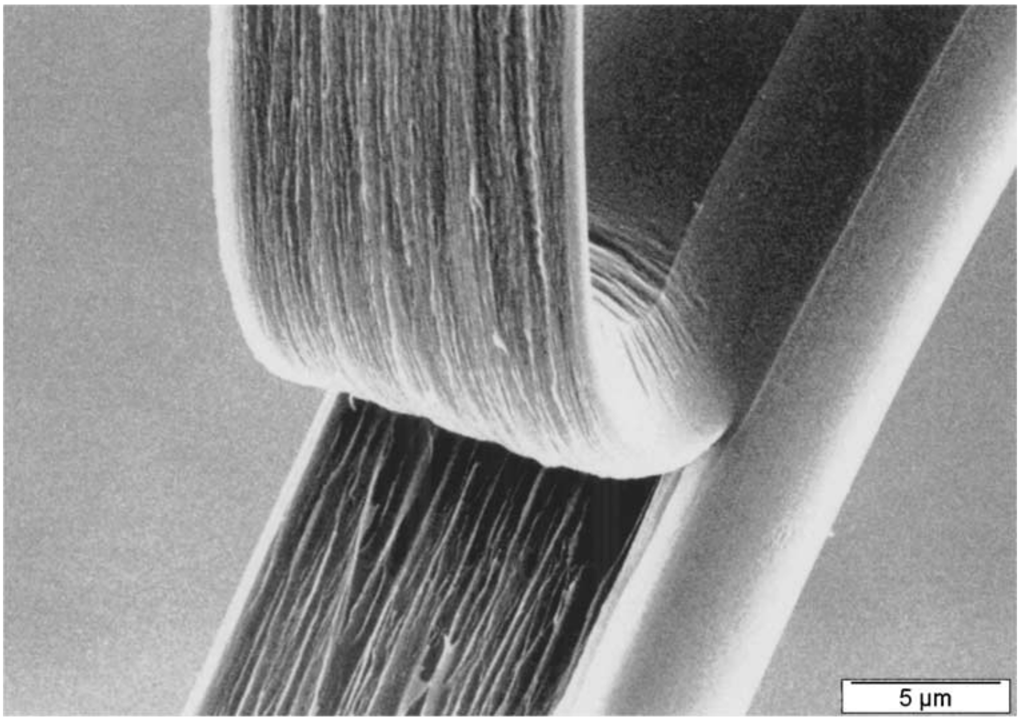

Figure 5 Peeling of a **non fibrillable freeze-dried** fibre.

led to the appearance of numerous fibrils. The study of the peelback of the cellulosic fibres after freeze-drying shows much more difference in the cohesion of fibrils between fibrillable and non fibrillable fibres than the study in the hydrated state. This could be explained by the use of the freeze-drying technique, which allows the fibres to be dried while keeping a swollen structure. This treatment permits only very localised rearrangements of the structure, which increases the heterogeneity of the material. Motion from less concentrated to more concentrated zones could create microscopic longitudinal holes, which are related to the appearance of a fibrillar structure during the rupture of highly oriented polyethylene films [6]. This idea is also related to a loss of entanglements by chain-breaking during void-tip advance at a craze interface [25]. The analysis of the surfaces resulting from the peelback of well oriented fibres seems to be a good way to investigate the fibrillar structure. Particularly, the study of freeze-dried fibres allows us to demonstrate the correlation between the cohesion of fibrils and their fibrillability.

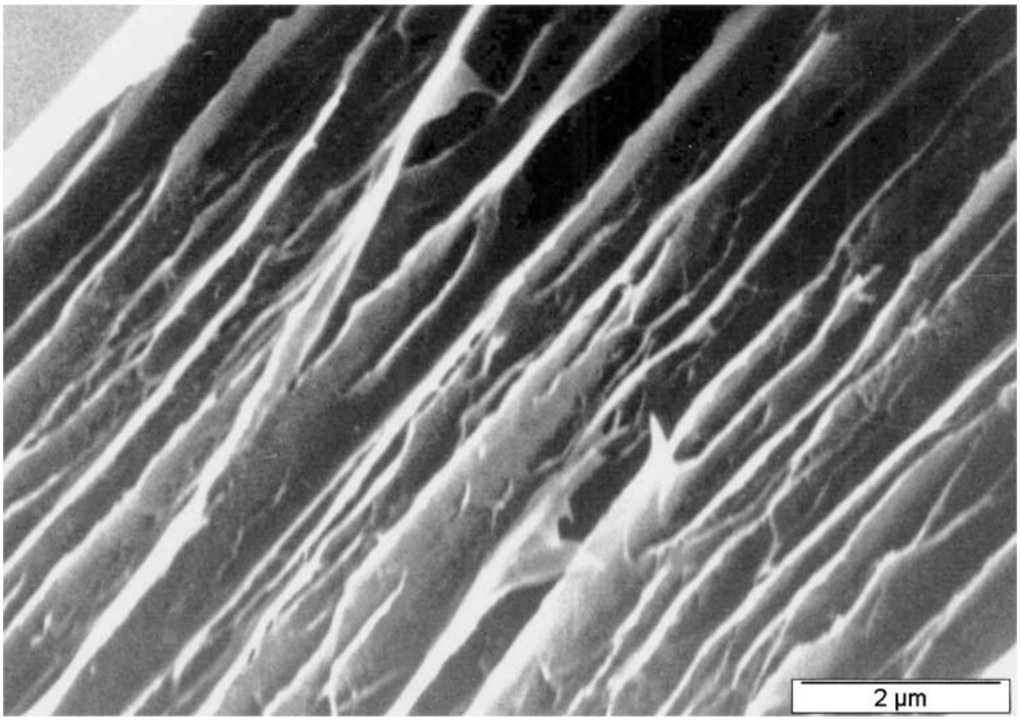

Figure 6 Formation of ribs during peeling of a **non fibrillable freeze-dried** fibre.

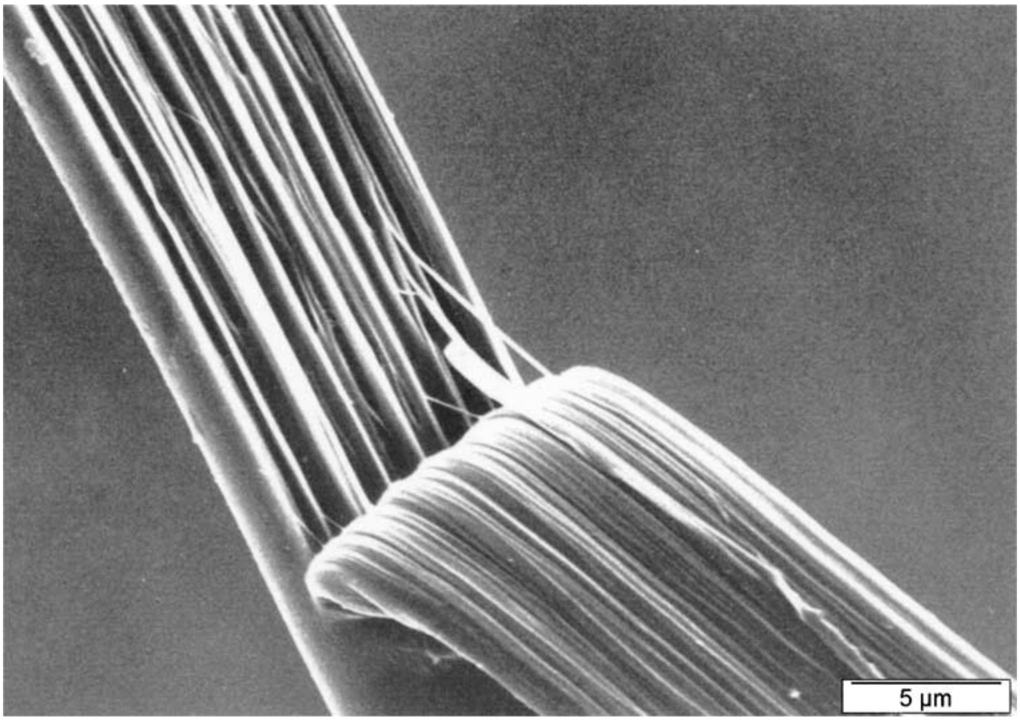

Figure 7 Peeling of a **fibrillable hydrated** fibre showing the apparition of fibrils.

3.2. Measurements of the energy release rate

Usually the characterisation of the mechanical properties of fibres relates to the tensile behaviour but in our case we are interested in the transverse properties which seem to be correlated with the fibrillability. Clements and Ward [6] showed that, for the rupture of highly oriented polyethylene films, the more fibrillar the structure, the smaller the energy release rate. We showed previously that it is possible to obtain a stable tearing along the fibre axis except for the freeze-dried fibres. This latter drawback prevented further experiments on freeze-dried fibres. We measured the energy release rate of fibrillable and non fibrillable fibres either in hydrated state or equilibrated in ambient air with $\mathrm{RH} = 30\%$. These produce stable failures.

The measured force (F) was around 3.10^{-3} N for one fibre. The energy release rate G is defined as $G = F/d$, where d is the fibre diameter. Since the fibres have a Young's modulus equal to 15 GPa the longitudinal strain should be around 0.3% during the tearing. This deformation is assumed to be negligible and all the

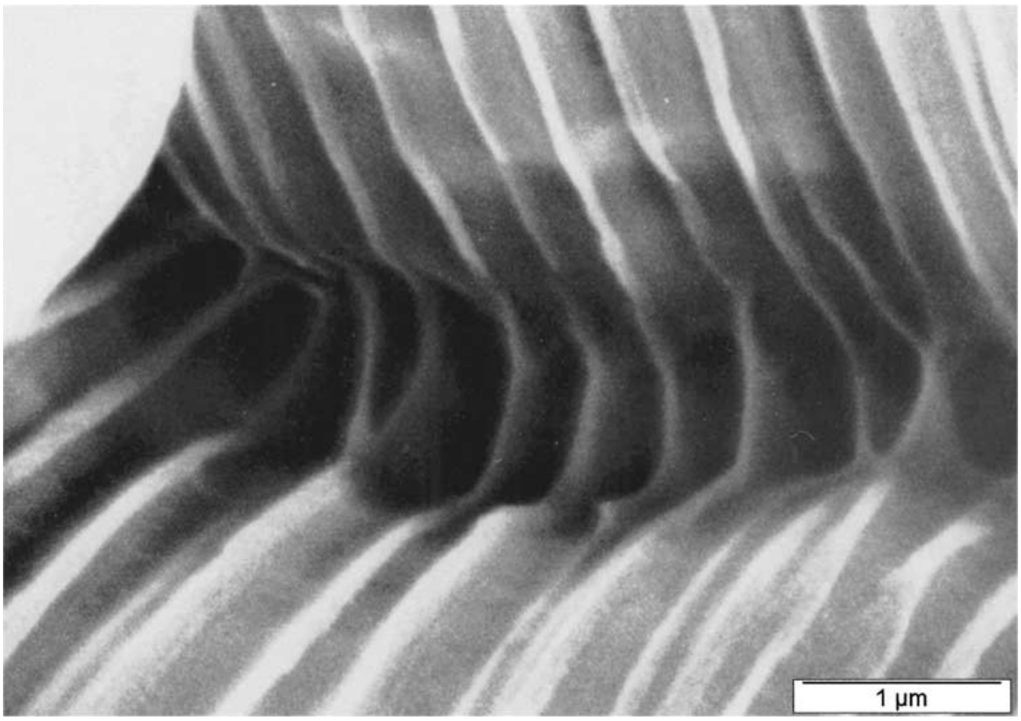

Figure 8 Formation of ribs during peeling of a **fibrillable hydrated** fibre.

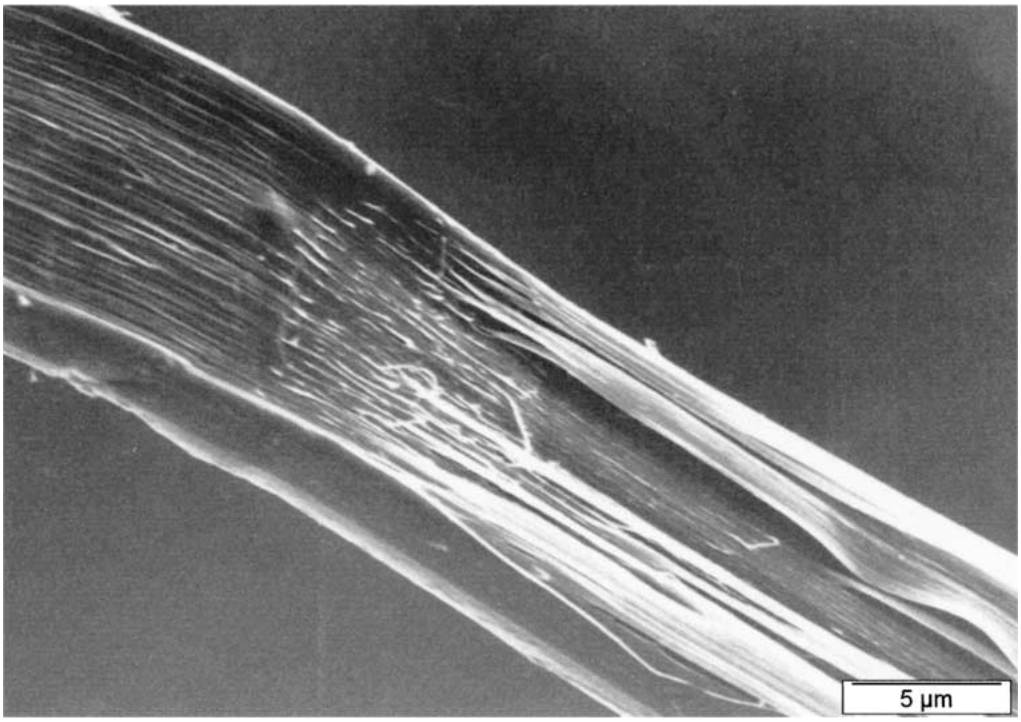

Figure 9 Surfaces resulting from peelback of a **fibrillable** fibre in two different hydration states (left: hydrated; right: freeze-dried).

energy required for peeling is assumed to be spent at the peeling front, as explained by Verdier *et al*. [22]. It comes mainly from the elongation of the ribs and from surface decohesion.

3.2.1. Non fibrillable fibres

Fig. 12 shows the stable evolution of the force needed for peeling hydrated non fibrillable fibres at 0.5 mm/min. The three curves obtained with rates of 0.05, 0.5 and 2 mm/min indicate very good stability confirming the propagation of the rupture in the centre of the fibre. The experiment at a rate of 5 mm/min (not shown) led to a quick failure of the fibres. The analysis of Fig. 13 shows that the energy seems to increase slowly with the peeling velocity, though the range covered is limited. This can also be observed in peeling of uncross-linked adhesives at small velocities [22]. A systematic analysis using SEM of the surfaces resulting from different rates was not possible but a global observation confirmed the presence of similar ribs and the absence of fibrils. The same non fibrillable fibres

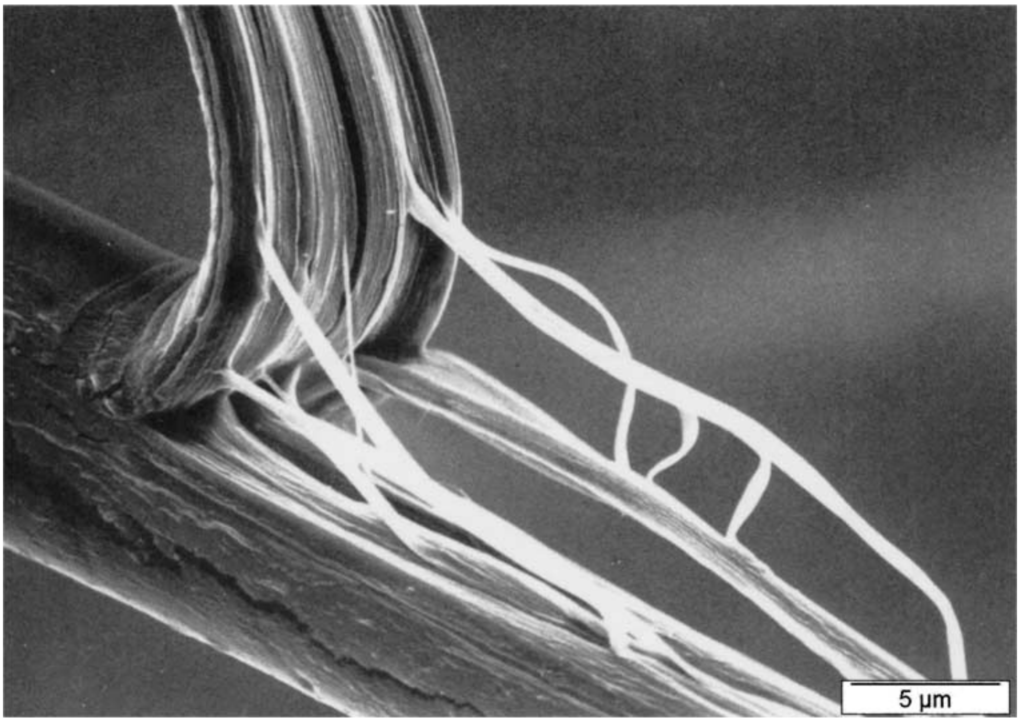

Figure 10 Peeling of a **fibrillable freeze-dried** fibre.

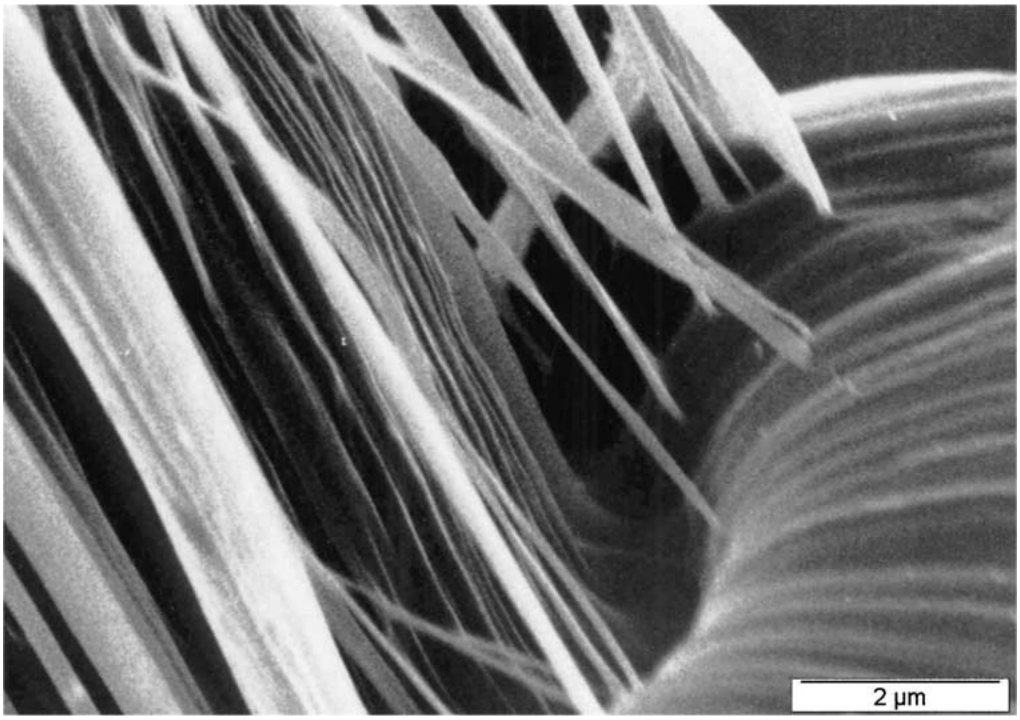

Figure 11 Formation of fibrils during peeling of a **fibrillable freeze-dried** fibre.

[20] with a hydration around 7% w/w corresponding to a relative humidity of 30% only allowed us to cover the lowest rates (Fig. 13). Indeed the peeling was stable at a rate of 0.05 mm/min. However, application of a 0.5 mm/min rate led to destabilisation producing a decrease in the area of rupture and consequently a reduction in the energy needed for the propagation. This phenomenon could be assumed to be similar to the transition from cohesive to adhesive mode as observed during peel tests [26]. As in the previous case, the energy is only mildly dependent on the rates but the values are higher. A global examination using SEM allowed us to observe the absence of fibrils and a reduced plastic deformation.

3.2.2. Fibrillable fibres

The third experiment was performed with fibrillable hydrated fibres. Values were determined for three rates but the peeling at 2 mm/min was unstable. As opposed to the results obtained during the transversal rupture of highly oriented polyethylene films [6], the energy required during the peeling of these fibrillable fibres leading to the appearance of fibrils was higher than the

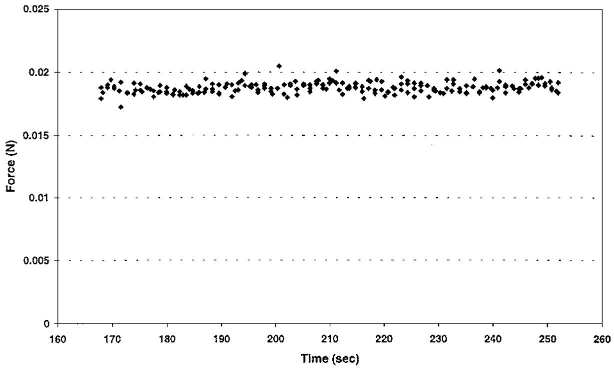

Figure 12 Force versus time during peeling of a **non fibrillable hydrated** fibre at 0.5 mm/min.

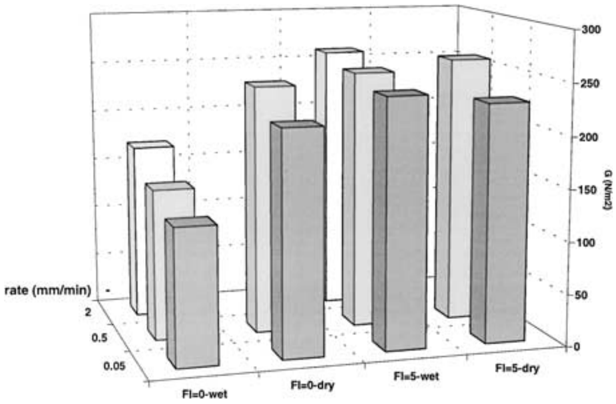

Figure 13 Energy release rate G for the different fibres as a function of peel rate.

one obtained with non fibrillable ones. This result can be explained by the presence of fibrils and can be compared to the reinforcing effect of copolymers at interfaces [27] but at a larger scale. Indeed such fibrils act in the direction of force and create a reinforcement effect; their diameter appears to be larger (between 0.1 μm and 0.5 μm) compared to the cases with copolymers (diameter around 0.01 μm or less). The corresponding added surface, which is not measurable, should be taken into account when trying to predict the global peel force.

As in the case of non fibrillable fibres, the drying from 30% to 7% w/w prevents the study using a rate equal to 2 mm/min. The corresponding energy in both states is similar (Fig. 13).

The average value of the energy release rate (around 200 J/m^2) is low. It would correspond to the energy measured for linear polyethylene with a molar weight around 10^3 g/mol [24]. This value is of course temperature dependent, but is still small at room temperature far from Tg. It could be also compared to the levels obtained in peeling of uncross-linked adhesives [22], in the range of about 10 J/m^2 where similar mechanisms have already been discussed. Such values of the peeling energy would require the use of cross-linked adhesives to reach levels of about 100 J/m^2. Due to the fact that most of the energy comes from the deformations involved at the peeling front, we may conclude that the levels obtained are small due to the formation of small ribs, induced by the high orientation of cellulose molecules. These energy values are enhanced in the case of fibrillable fibres, due to the reinforcement effect involved in the formation of fibrils.

4. Conclusion

From a textile point of view, this work showed that the SEM analysis of the surfaces resulting from the peelback of fibres is an interesting way to study the fibrillar structure. The correlation between the cohesion of the fibrils and their fibrillability was pointed out. Other aspects of peeling of adhesives were compared. Furthermore this technique also allowed the original observation of regular ribs resulting from peeling of a highly oriented material. The study of their shape as a function of the degree of orientation and of the peeling speed on well characterised systems could be very promising.

The measurements of the energy release rate showed that it is possible to obtain a very stable tearing in the centre of the fibre. These values allow fibres to be differentiated. Model samples should allow the study of the energy release rate in more detail, as a function of draw ratio and orientation for example.

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