Interfacial Properties of Regenerated Cellulose Fiber and Thermoplastic Systems

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Synopsis

In dry-formed polymer-bonded networks of cellulose fibers and in other types of nonwovens, the fiber–polymer joint is considered to be the primary factor determining the ultimate properties of the network structure. In an attempt to develop a model describing the joint failure, the well-known fiber pullout test has been applied to a system consisting of regenerated cellulose fibers and three different polymer matrices: a styrene–acrylate copolymer, poly(vinyl alcohol), and high density polyethylene. For each system, the interfacial bond strength was evaluated. The results are, to some extent, discussed in relation to the mechanical behavior of dry-formed networks bonded with similar polymeric materials. It is suggested that both the interfacial properties and the cohesive strength of the polymer binder are of importance for the mechanical strength of the bonded network.

INTRODUCTION

Structures such as nonwovens and dry-formed networks of cellulose fibers normally have rather poor mechanical properties, and polymeric binding materials are needed to obtain a product with an acceptable performance.[1-4] The polymeric binder can be added to the network either as an aqueous latex dispersion or as a solution. In either case, the polymer should form a film and join adjacent fibers together and thus improve the stress transfer characteristics of the fibrous network. Provided that the proper film forming conditions are available, the property profile of the bonded network is to a significant degree determined by the properties of the polymeric binder at the temperature of use.[2,3] For example, if a softer type of product is desired, a binder with a relatively low glass transition temperature (T_g) is often chosen.

It is obvious that the ultimate properties of the bonded network will, to a large extent, be influenced by the properties of the polymer–fiber joint, and in particular whether the joint fails due to cohesive rupture of the binder or whether the failure is of the adhesive type (along the interface). The effects of surface treatment of the fibers or of chemical modification of the polymeric binder are also important when an attempt is made to improve the joint strength. The present communication reports an attempt to study the failure of the polymer–fiber joint using a simple fiber pullout technique. In principle, the method consists of embedding a known fraction of the fiber length in a polymeric matrix and then pulling out the fiber from the matrix while monitoring the applied force. The fracture region is studied with both scanning electron and optical microscope. An attempt is also made to estimate the interfacial shear strength of the

CCC 0021-8995/84/010175-11$04.00

joint. The fiber material was viscose rayon and three types of polymer matrices (binders) were used: a styrene–acrylate copolymer with T_g below room temperature, poly(vinyl alcohol), and high density polyethylene. These three binders were expected to exhibit different types of joint failure.[2]

It should be pointed out that the fiber pullout test is a fairly well-known technique for characterizing interfacial properties of fiber-reinforced materials.[5–10] Many of these studies have been limited to glass fibers or high modulus fibers such as carbon or Kevlar fibers, which are pulled out from a brittle matrix of polyester or epoxy.[5–9] The effect of surface treatment of the fibers on the adhesion between fiber and matrix is important in these works. Only in very few cases has a ductile matrix been used for embedding the fibers. One example is the investigation in which Eagles et al.[10] studied the interfacial properties of Kevlar fiber–thermoplastic matrix systems. As thermoplastics, they used polyethylene, polyamide 12, polycarbonate, poly(methyl methacrylate), and an ethylene-based ionomer. They observed that the failure mode was fairly complex at the interface, but were able to estimate the interfacial bond strength.

Values of the interfacial bond strength for a number of fiber systems have been reported by Morley and Chappell.[11]

BACKGROUND TO THE FIBER PULLOUT TEST

For short fiber-reinforced polymer composites, the properties of the fiber–polymer interface and the aspect ratio of the fiber, i.e., the ratio of length to diameter, are important factors which control the mechanical properties of the composite. For a fiber of given diameter, it is known that if the fiber length is less than a critical value, the stress transfer from the matrix to the fiber will be insufficient.[10] The simplest estimate of the critical fiber length l_c is[10]

$$l_c = \sigma_{uf} d / 2\tau_B \qquad (1)$$

where d is the fiber diameter, σ_{uf} is the ultimate strength of the fiber, and τ_B is the interfacial bond (shear) strength. In short-fiber-reinforced polymers, three failure modes can be visualized: matrix failure, interfacial failure (fiber pullout), and fiber rupture. If the fiber length is less than l_c, the fibers are normally pulled out from the matrix, whereas if the fibers are longer, fiber failure is the dominant mode of composite failure. It also follows from eq. (1) that if the fiber length exceeds l_c further improvement in the interfacial bond strength will have little effect on the composite strength.[10]

Both the interfacial shear strength τ_B and the critical length l_c can be estimated using eq. (1) and the single fiber pullout test by embedding different lengths of the fiber and subsequently measuring the force required to pull the fiber out of the matrix. There has been some discussion in the literature as to whether this type of test can actually model the debonding mechanism and the failure of composites, but the test can in any case, in our opinion, provide valuable information concerning the properties of the interface. Furthermore, the fiber pullout test has been analyzed in great detail, and more accurate and rigorous treatments than that given in eq. (1) have been presented, see, e.g., Ref. 8.

In this work, we are not primarily interested in the deformation behavior of short-fiber-reinforced composites, but rather in the strength properties of dry-formed cellulose networks containing not more than 10–15% by weight of poly-

mer. In this context, it is reasonable to assume that the fiber pullout test can be used to provide information concerning the failure behavior of the cellulose fiber–polymer joint. It is not our aim to give any detailed analysis of the stress field around the embedded fiber, and we have thus chosen to adhere to the simple eq. (1) in order to obtain some knowledge of the interfacial properties of bonded cellulose networks.

EXPERIMENTAL

Materials. The fiber material used was a semimodal viscose rayon fiber produced in the Pulp Technology Department of the Swedish Forest Products Research Laboratory. During manufacture it was stretched 90% at 96°C (in the stretch bath). The diameter of the rayon fiber was 23 μm and its tensile strength ca. 32 MPa. After spinning and stretching, the fibers were washed in order to eliminate chemical residues. In some cases the fibers were also washed a second time in ethanol.

Three kinds of thermoplastic were used in this investigation, a dispersion of a styrene–acrylate copolymer, poly(vinyl alcohol), and polyethylene. The styrene–acrylate copolymer was a soft binder with a glass transition temperature of ca. 15°C, determined with a torsional pendulum working at ca. 1 Hz, and a density of ca. 1.1 g/cm^3. The poly(vinyl alcohol) was a fully hydrolyzed grade (98.4%) with a density of ca. 1.3 g/cm^3. The high density polyethylene had a density of 0.95 g/cm^3 and a melt flow index of 0.5 g/10 min (MFI 190/5).

Preparation of Fiber Pullout Specimens. Two different techniques were used to prepare the fiber pullout specimens depending on the type of polymeric matrix: one for the styrene–acrylate copolymer (SAC) and the poly(vinyl alcohol) (PVOH) and the other for the high density polyethylene (HDPE). In the first case, the rayon fiber was threaded through a hole with diameter of 0.5 mm in a steel plate with thickness of 0.15 mm. The fiber was centered in the hole using a specially designed fixture. At this stage the fiber was fixed in both ends. A small quantity of either the SAC dispersion (25% dry content) or an aqueous solution of PVOH (ca. 7%) was placed on the hole. Prior to the application, both the polymeric systems had been colored. When the assembly dried, a polymer "button" developed around the fiber. With this method, which is rather similar to that described by Favre and Merienne,[5] the thickness of the polymer button (the embedded length of the fiber) can, with some experience, be controlled with reasonable accuracy. In this case, the thickness of the button ranged from ca. 80 μm to 550 μm. One end of the fiber was then carefully cut very close to the polymeric film using a razor blade. The other end of the fiber was glued with an epoxy resin to a brass plate. The distance between the polymer button and the brass plate, i.e., the free length of the fiber, was always 5 mm. The whole assembly was then placed in the tensile tester, equipped with specially designed clamps, and the force required to pull the rayon fiber out of the matrix (polymer button) was recorded. Ten assemblies of this type were produced at the same time. Figure 1 shows a schematic drawing of the fiber pullout specimen when mounted in the tensile tester and also a photograph of a sample.

The other technique, which was used for HDPE, differs in the way of producing the polymer button. In this case, HDPE was used in the form of a film with a thickness of 80 μm. After centering the rayon fiber in the hole in the steel plate
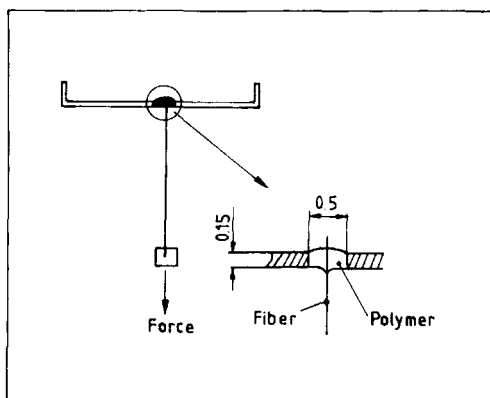
(a)
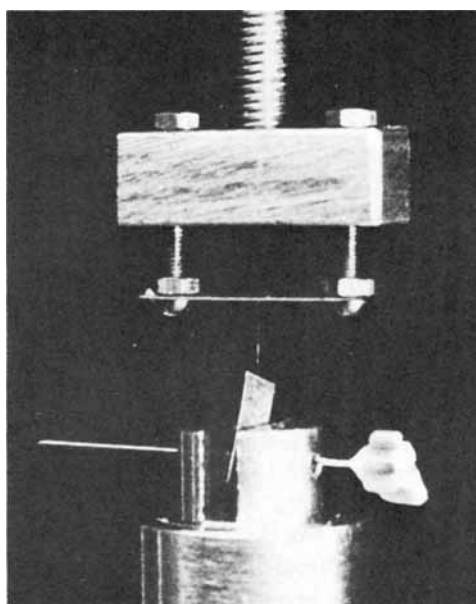
(b)

Fig. 1. Schematic drawing (a) of the fiber pullout sample and a photograph of the assembly mounted in the tensile tester (b).

as described above, the fiber was threaded through a very fine hole in a small piece of the HDPE film. The pullout test assembly was then placed in a preheated oven (ca. 150°C) for a few minutes. The film then softened and closed around the fine hole in the HDPE film to give a polyethylene button. Using several layers of HDPE film, the embedded length of the fiber could be varied from ca. 100 μm to 2000 μm. This technique has been described by Eagles et al.[10]

Tensile Tests. The fibers were pulled out of the polymeric matrix using an Instron tensile testing machine. The experiments were performed at 23°C and 50% relative humidity. The speed of the moving clamp of the machine was 10 mm/min.

Determination of the Embedded Fiber Length. The embedded fiber length was determined in two ways. In the preceding section it was mentioned that a coloring agent was added to the SAC dispersions and the PVOH solutions.
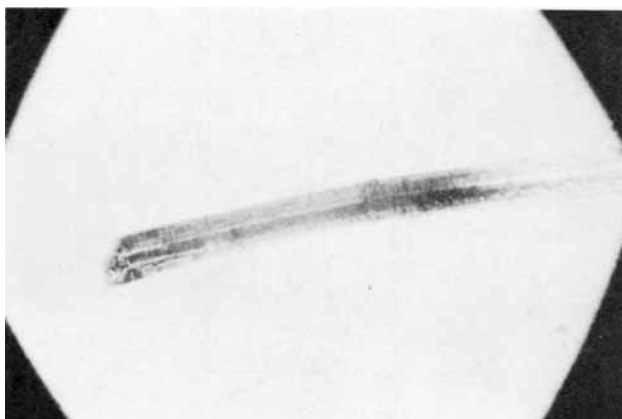
Fig. 2. Optical micrograph of a rayon fiber which has been pulled out of the PVOH matrix. The colored part of the fiber is a measure of the embedded length.

This also colors the rayon fiber to some extent. After it has been pulled out of the polymer matrix, the colored length of the fiber can thus be used as an estimate of the embedded length. The addition of the small amount of coloring agent was found to have no influence on the force required to pull the fiber out of the matrix. Figure 2 is a photograph of such a fiber which has been pulled out of the PVOH matrix, and, as can be seen, the embedded length is easy to estimate.

The embedded length can also be determined using scanning electron microscopy (Cambridge 600). When the fiber has been pulled out of the matrix, the steel plate with the remaining polymer button is immersed in liquid nitrogen for some time. The steel plate, being very cold, can then be broken into two pieces and normally the fracture proceeds through the hole with polymer matrix. The thickness of the polymer matrix can then be measured using the scanning electron microscope (SEM), and this value is then used as the embedded fiber length. In this case the coloring agent was not always added to the SAC dispersions or the PVOH solutions. Figure 3 shows an example of such a fracture surface. In this case SAC was the matrix.
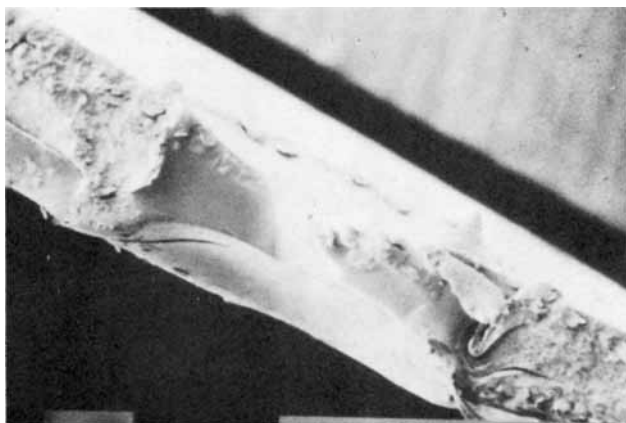

Fig. 3. Scanning electron micrograph of the fractured SAC matrix. The steel plate and the polymer matrix were fractured after being cooled with liquid nitrogen.
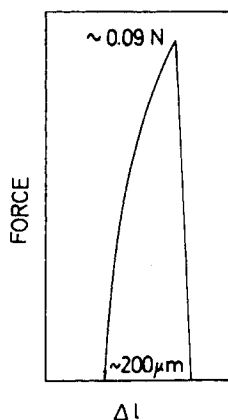
Fig. 4. Example of a force–crosshead movement curve when the rayon fiber is pulled out of the SAC matrix. The approximate values of the maximum force F_m and the crosshead displacement Δl are indicated.

RESULTS AND COMMENTS

Styrene–Acrylate Copolymer as the Matrix. Figure 4 shows a typical example of the force vs. clamp movement curve when the ethanol-washed rayon fiber is pulled out of the SAC matrix. The interfacial bond strength τ_B is calculated from the maximum value of the recorded force (F_m) using the expression:

$$\tau_B = F_m/\pi dl_e \tag{2}$$

where l_e is the embedded length of the fiber and d the fiber diameter. It should be noted that no friction stress level at which the fiber slips through the matrix after debonding is recorded with this fiber–polymer system (cf. Ref. 10).

The embedded fiber length l_e was determined using both the techniques described earlier. The embedded length could in many cases exceed the nominal thickness of the polymer matrix; the surface tension forces apparently produced a cone-shaped region around the embedded fiber, as shown in Figure 5. The force (F_m) required to pull out the fibers from the SAC matrix is shown vs. the
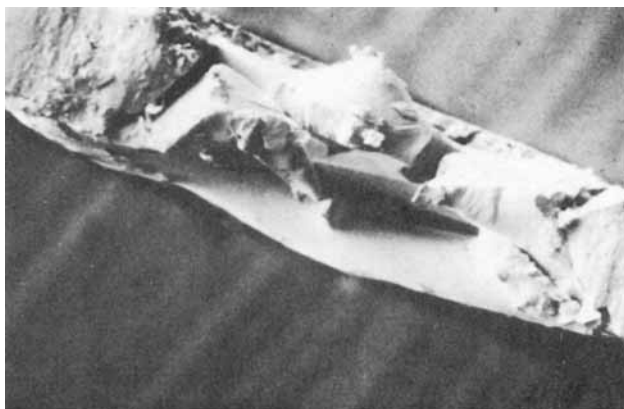

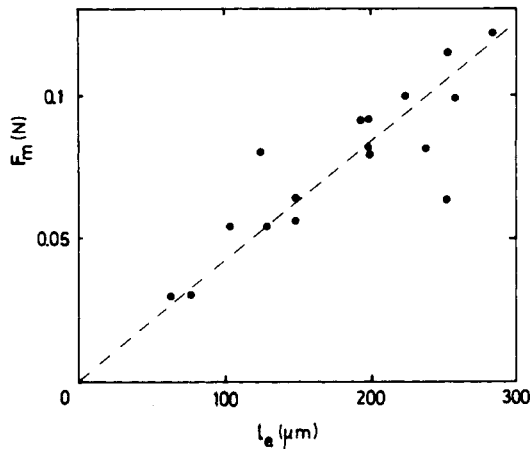Fig. 5. The cone-shaped region of the matrix close to the fiber.

Fig. 6. The force (F_m) required to pull out fibers from the SAC matrix vs. the embedded length l_e.

embedded length l_e in Figure 6. A linear relation holds approximately between F_m and l_e, and the corresponding straight line intersects the l_e axis very close to the origin. From eq. (2), the interfacial bond strength τ_B is estimated to be 6.1 ± 1.0 MPa provided that the rayon fibers have been washed in ethanol. If the fibers are used as received, i.e., without washing in ethanol, τ_B is only slightly lower, 5.8 MPa.

Further microscopic investigations showed that the failure was somewhat complicated. After being pulled out from the matrix, some parts of the polymeric binder still adhered to the fiber surface. This applies especially to the cone-shaped region of the matrix. Figure 7 is a photograph of a pulled-out fiber where the remaining polymer can be seen. This may indicate that, although the dominant fracture process occurs at or close to the interface, the cohesive strength of the SAC polymer is also be of importance, e.g., the debonding may start as a cohesive rupture of SAC and then proceed mainly along the interface. Tensile tests on films of SAC alone showed that the polymer itself had a tensile strength of ca 8.5 MPa, when the decrease in cross-sectional area was corrected for
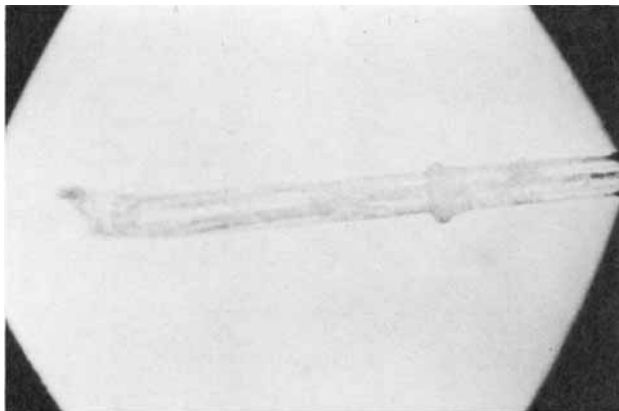

Fig. 7. A fiber which has been pulled out of the SAC matrix. Remaining parts of SAC can be seen on the fiber surface.

(nominal strength 1.1 MPa) and an elongation at rupture of 770%. This indicates that since the interfacial bond strength and the tensile strength are of the same order, cohesive fracture of the matrix may also occur with this type of polymer. This is important since, in practice, dry-formed networks of cellulose fibers are normally bonded with ductile and rubberlike polymer latices, and SAC is here used as a model system for such binders.

Poly(vinyl Alcohol) as the Matrix. Poly(vinyl alcohol) has been shown to be a very effective binder for dry-formed networks of cellulose fibers, especially with regard to strength characteristics.[2] If ca. 10% by weight of PVOH is added to a dry-formed sheet, the specific strength of the network may increase 20–30 times. Fiber pullout experiments on ethanol-washed fibers, performed as described above for the SAC matrix, gave the F_m–l_e curve shown in Figure 8. It may be noted that in this case the straight line does not intersect the l_e axis close to the origin. Such a behavior has also been noted by others,[5,12] and it has been suggested that this phenomenon is related to the shape and size of the cone-shaped region of the matrix close to the embedded fiber.

The interfacial bond strength was in this case estimated to be 6.7 ± 1.8 MPa using eq. (2). This is of the same order as that obtained with SAC. The tensile strength of PVOH is of the order of 50 MPa, which is significantly higher than the observed interfacial bond strength. In this case no remaining polymer can be found on the surface of the pulled-out fibers. The failure mode thus appears to be of the interfacial type.

In this case the washing in ethanol had a strong influence on the interfacial bond strength τ_B. If no washing was done prior to the fiber embeddment, the interfacial strength was much lower being 1.4 ± 0.3 MPa. This behavior is in contrast to that observed with the SAC system and implies that, for certain systems, the state of the fiber surface is very important for obtaining a sufficiently high interfacial bond strength. Similar phenomena relating to the surface characteristics have also been studied in the case of high modulus fibers and brittle matrices (see, e. g., Ref. 6).

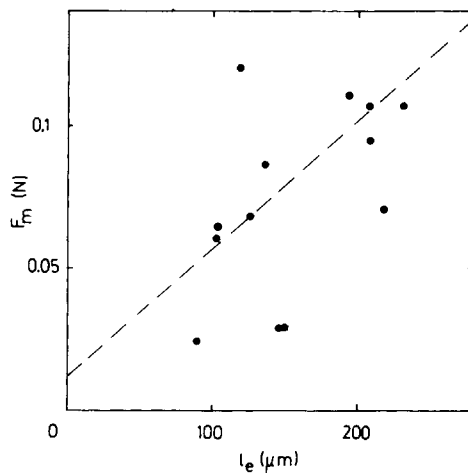**Polyethylene as the Matrix Material.** The possibility of using polyole-

Fig. 8. The force F_m required to pull the fibers out of the PVOH matrix vs. the embedded length l_e.

fin-based synthetic wood pulp (SWP) as a binder in dry-formed networks of cellulose fibers[13] motivates a closer study of the properties of the cellulose–HDPE interface using the fiber pullout test.   In addition to the microscopic techniques for determining the embedded length l_e, another method proposed by Favre and Merienne[5] can be used for measuring l_e when the adhesion between the phases is rather low.   Figure 9 shows a typical force–displacement curve when pulling out the fiber from the HDPE matrix (schematic figure).   This is here a completely controlled process and the displacement Δl shown in the figure gives the embedded length of the fiber.[5]   This value is in good agreement with the corresponding microscopic measurements of l_e.   In the following, both methods for determining l_e have been used.   When the elastic energy stored in the fiber prior to debonding is larger, i.e., sufficient for complete pullout without noticeable friction, force–displacement curves of the type found for the SAC system (Fig. 4) are obtained.

Using the fiber pullout test, the interfacial bond strength for the HDPE system was estimated to be 1.3 ± 0.2 MPa.   This is significantly lower than the values obtained with SAC or PVOH, indicating that the adhesion between HDPE and regenerated cellulose is rather low.   As with PVOH, washing the fibers in ethanol has a strong influence on the interfacial strength.   If the fibers are embedded as received, the τ_B value is significantly lower, 0.5 ± 0.2 MPa.   The tensile strength of HDPE itself was of the order of 50 MPa which is substantially higher than the observed value of τ_B.   This suggests that cohesive failure of the matrix is not the major failure mode, but that interfacial fracture is dominant in these pullout experiments.

DISCUSSION

In this work, the fiber pullout test has been used as a model to study the failure in polymer-bonded dry-formed networks of cellulose fibers.   Due to the limited length of native cellulose fibers, fibers of regenerated cellulose have here been used instead.   It is thus not possible to relate the results of this study directly to the mechanical behavior of the dry-formed networks.   Furthermore, the stress fields in a network and in the fiber pullout test are obviously not similar, and this also complicates any comparison.   Experiments of the fiber pullout type can,
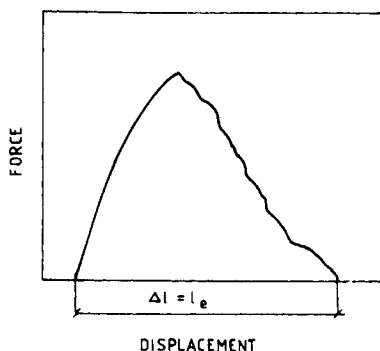

Fig. 9. A schematic drawing of the force–displacement curve during a fiber pullout test when HDPE is the matrix material.   The displacement Δl is here taken as a measure of the embedded fiber length l_e.

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TABLE I
Mechanical Properties of Polymer Matrices and Interfacial Bond Strength (τ_B) between
Polymer and Rayon Fiber (Washed in Ethanol)

Polymer	Tensile strength (MPa)	Elongation at rupture (%)	τ_B (MPa)
SAC	8.5	770	6.1 ± 1.0
PVOH	50	120	6.7 ± 1.8
HDPE	50	500	1.3 ± 0.2

nevertheless, cast some light upon the failure mechanisms in bonded networks. This applies especially to the evaluation of the interfacial bond strength. Work is in progress to develop the method further in order to enable native cellulose fibers to be studied.

In Table I the interfacial bond strengths τ_B for the different fiber–matrix systems are summarized as well as the ultimate properties of the matrices. Here it is of interest to note that for SAC the interfacial bond strength τ_B and the tensile strength σ_B are of the same order. This indicates that cohesive failure of the polymer plays an important role when fibers are pulled from the matrix. It is tempting to speculate as to whether the failure mode in the corresponding bonded networks may also be partially of a cohesive nature. However, more experimental work is required to substantiate this point.

The data given in Table I and the microscopic examination of the pulled-out fibers suggest that the debonding of the fibers is of a more adhesive nature when PVOH or HDPE are used than when SAC is used. In such a case, any improvement in adhesion, e.g., by a surface treatment of the fibers, will be expected to have a significant influence on the interfacial shear strength τ_B. According to the pullout experiments reported here, the degree of adhesion between regenerated cellulose and polyethylene is low compared with the values for the other two polymers. In terms of eq. (1) it means that the critical aspect ratio of the rayon fibers is four to five times larger when polyethylene is used as matrix. Adhesion-promoting agents, surface treatment, etc. would certainly be of value to improve the performance of this grade of HDPE.

The well-known pullout test used in the composite field may be a valuable technique for analyzing or modeling the behavior of fiber–polymers joints in bonded networks of cellulosic or synthetic fibers. Problems relating to the proportions of adhesive and cohesive failure for a given fiber–matrix system can be dealt with in fairly straightforward manner. This can be of especially important when a soft type of matrix (binder) is used, which is normally the case for bonded networks of cellulose fibers.

The fiber pullout test, as described here, can also be useful for the interpretation and evaluation of the performance of polymeric binders which are of the same basic type, but which contain fractions of different pendant groups. With such polymers, different degrees of adhesion to cellulose can be expected, and their efficiency can be evaluated in terms of the interfacial bond strength.

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