

The Effect of Chemical Composition of Interphase on Dispersion of Cellulose Fibers in Polymers.

I. PVC-Coated Cellulose in Polystyrene

P. GATENHOLM,^{1*} H. BERTILSSON,² and A. MATHIASSEN²

¹Department of Polymer Technology and ²Department of Polymeric Materials, Chalmers University of Technology, S-412 96 Göteborg, Sweden

SYNOPSIS

Cellulose fibers surface-coated with butyl benzyl phthalate (BBP)-plasticized PVC were evaluated as a reinforcement in thermoplastic matrices. Coated fibers were agglomerated during compounding with polypropylene (PP) and polyethylene (PE). However, an excellent dispersion and improved processability were achieved in polystyrene (PS). Melt rheology was also seen to be affected by fiber coating, and viscosity was lower for coated fibers. Fiber coatings seem to lubricate the blending process as well as to protect fiber from damage during processing. Fiber length was unaffected during treatment when coated fibers were used, as shown by microscopic investigation of extracted fibers, whereas the length of untreated fibers was reduced during processing. Introducing surface-coated fibers into PS resulted in an increased elongation at break and improved impact strength of composites. The pullout of the fibers is suggested to be responsible for both improvements. The interphase achieved in PS with PVC/BBP-coated fibers was simulated with PS/PVC/BBP blends. From DSC and DMTA, it was shown that BBP is a cosolvent for PS and PVC and that a single-phase material was achieved at the relevant concentrations, which also was confirmed by optical clarity. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Thermoplastic polymers with particulate filler or short-fiber reinforcement are enjoying a rapid growth in use because of their good processability and ability to be recycled. Filler is added to the polymer matrix with the aim of improving thermal and mechanical properties. There are, however, some adverse effects, i.e., toughness, and ultimate elongation of polymers often suffer on the addition of fillers.¹ A properly selected interface has a significant effect on the dispersion quality and adhesion between polymer and filler.²⁻⁴ It has been shown, e.g., that the ease with which fillers are dispersed in the polymer matrices is related to the acid-base interaction balance in the polymer-filler pair and varied

widely with the surface treatment given to the filler.⁵⁻⁸

Natural wood-cellulose fibers are gaining attention as a reinforcing phase in thermoplastic matrices.⁹⁻¹⁴ Low density, a highly reduced wear of the processing machinery, and a relatively reactive surface may be mentioned as attractive properties, together with their abundance and low price. Nevertheless, such fibers are used only to a limited extent in industrial practice, which may be explained by difficulties in achieving acceptable dispersion levels.¹⁵ The lack of fiber dispersion resulting in agglomeration is particularly pronounced when cellulose fibers are compounded with polyolefins, which is believed to be a result of strong hydrogen forces between fibers and a typically very low compatibility with most thermoplastics. Fibers have also been shown to agglomerate into knotty masses during mixing with elastomers. Although one can attempt to break down cellulose fiber agglomerates by shearing, this results in a breaking of the fibers. The deg-

* To whom correspondence should be addressed.

radation of the fiber aspect ratio from 30 to 5 is a common result of processing.¹⁶

Earlier investigations carried out in our laboratory have demonstrated the effect of various treatments applied onto the cellulose surface on the homogeneity and mechanical parameters of the corresponding composites. Dispersion aids, elastomeric additives, and adhesion-promoting agents were studied with polyolefinic matrices.¹⁷⁻¹⁹ Similar investigations have also been published by other authors using, among other methods, polymer encapsulation²⁰⁻²² and matrix materials modified with maleic anhydride.^{23,24} Improved dispersion and impact strength were the primary effects recorded. Problems associated with lack of dispersion and reduction of fiber length during the preparation of cellulose fiber/elastomer composites were overcome by pretreatment of cellulose fibers with polymer-coating materials. This facilitates the fiber dispersion and induces bond formation between fiber and elastomer.²⁵⁻²⁷ An example of this is the PVC/butylbenzyl phthalate (BBP)-coated fiber, commercially available under the name Santoweb W. Such fibers, however, have only been employed in elastomer-based composites.

Efforts are still needed to study and correct the agglomeration problem before the potential of cellulose fibers as a reinforcing material can be fully utilized. In this study, untreated cellulose fibers and surface-coated fibers with BBP-plasticized PVC (Santoweb W) were compounded with different polymers, and the rheology and the mechanical properties were investigated. The effect of compatibility at the interphase on dispersion was also studied in the model blend system.

EXPERIMENTAL

Materials

The following polymers were used as matrix materials:

Polystyrene (PS): Polystyrol 168N, BASF, density 1.05 g/cm³, MFI (200/5) 1.2 g/10 min.

Polypropylene (PP): Propathene GY 621M, ICI, density 0.905 g/cm³, melt flow index (MFI) (230/2.16) 13 g/10 min.

Low-density polyethylene (PE): Alkathene 017.040, Atochem, density 0.917 g/cm³, MFI (190/2.16) 7 g/10 min.

The cellulose was hardwood (60% beech, 40% birch) α -cellulose, Nymölla AB, Sweden, with an average

fiber length of about 1 mm. The coated cellulose fibers, Santoweb W, Monsanto, had the following composition: cellulose 77%, butylbenzyl phthalate (BBP) 15%, PVC 8%. The cellulose filling levels are given in the text as weight percentages.

Compounding

Selected polymer/cellulose combinations (see Table I) were compounded in a Buss-Kneader compounding extruder (Model PR 46, screw diameter 46 mm, L/D 11, exit die 6 mm) at 190°C. The residence time in the extruder was about 3 min. The compounded material was passed through a granulator, Rapid GK 20, then subjected to a further homogenizing step in a drum mixer. The model system of the interface was obtained by mixing the PVC, PS, and BBP plasticizer combinations at 190°C for 10 min in a Brabender Kneader at 70 rpm.

Injection Molding

After homogenization, the samples were injection-molded in a conventional injection-molding machine, Arburg 221E/170 R. The molding compositions were as follows: injection time 1.1 s, holding time 15 s, cooling time 29 s, and temperature along the three zones of the barrel varying as 180, 190, and 190°C. The injection pressure, specified in Figure 5, increased with the fiber content. The holding pressure was about 15% lower. At the highest contents of untreated cellulose, difficulties were experienced in filling the mold at the pressures used.

Fiber-length Distribution

The length distribution was determined on both the as-received fiber material and fibers Soxhlet-extracted from the injection-molded composites, using tetrahydrofuran as the solvent. An optical device (Kajaani FS-100) was used to record the length of

Table I Sample Composition

Sample	Reinforcement	Fiber Content [w %]
PS	none	0
20 cell/PS	α -cellulose	20
30 cell/PS	α -cellulose	30
40 cell/PS	α -cellulose	40
27,4 SW/PS	Santoweb W	20
41,1 SW/PS	Santoweb W	30
54.8 SW/PS	Santoweb W	40

the fibers in dilute suspension while flowing through a 0.4 mm capillary. The results given below are presented as weighted length distributions.

Rheometry

The rheology measurements were carried out in a Weissenberg Rheogonimeter R-20 with a cone and plate geometry.

Mechanical Testing

The injection-molded test bars (DIN 53455), having a cross section of 10×3.5 mm and an effective length of 75 mm, were conditioned at 23°C and 50% RH for 24 h before testing. The initial modulus, E , the stress at yield, σ_y , and the corresponding elongation, ϵ_y , were determined from the stress-strain curves (Instron Model 1193, extensometer G51-15MA, deformation rate $4.5 \times 10^{-3} \text{ s}^{-1}$). The Charpy impact strength, IS , was measured on notched and unnotched samples (Frank, Model 565 K, DIN 53455). The mechanical parameters were evaluated from data using at least 10 test bars for each composition.

Dynamic Mechanical Properties

The dynamic mechanical properties were evaluated in the bending mode using a Rheometrics RSA II Dynamic Mechanical Analyzer. The frequency of the forced oscillations was kept at 1 Hz.

Differential Scanning Calorimetry

Differential scanning calorimetry (Mettler TA 3000) was used to determine the glass transitions of selected blends. The heating rate was 10°C/min.

Scanning Electron Microscopy (SEM)

The cellulose fibers and tensile fracture surfaces of the composite samples were studied with a Jeol JSM-350SM scanning electron microscope operated at 10 kV.

RESULTS AND DISCUSSION

Untreated and Coated Cellulose Fibers

Untreated and coated cellulose fibers, hardwood α -cellulose and Santoweb W, were investigated by SEM prior to compounding with polymers. Figure 1 (a) and (b) shows SEM photomicrographs of typical bundles of the virgin and coated fibers, respec-

tively. There is apparently not a great difference between the two fiber types: both are ribbon-shaped and have a relatively high aspect ratio. However, the coated fibers are better separated from each other. Figure 2 (a) and (b) shows the two fiber types at higher magnification. Whereas the surface of untreated fibers is rough and uneven owing to the presence of fibrils, the coated variety has a rather smooth surface, with the coating layer evenly distributed.

Dispersion Behavior

Untreated and surface-coated cellulose fibers were compounded with PP, PE, and PS. Untreated fibers were not dispersed in any matrix, but formed bundles. Further agglomeration possibly took place during injection molding. Figure 3 shows a typical agglomerate extracted from an injection-molded sample of 40% untreated cellulose and PS. The introduction of polymer coating onto fiber surfaces separated fibers from each other, eliminating the hydrogen bonding that holds fibers together. When the coated fibers were compounded with PP and PE, a level of agglomeration similar to that of untreated fibers was observed. However, significantly better results regarding the degree of dispersion were achieved when PS was used as a matrix. The molded samples exhibited a high degree of homogeneity within the entire range of fiber concentration covered by the experiments. This difference in dispersion behavior was investigated further.

Processing and Rheology of Fiber Suspensions

As a rule, the incorporation of particles or fibers into a polymer results in an increased viscosity of the corresponding melt. In addition to the filler content, the viscosity is also influenced by the nature of the interface between the two phases.^{28,29} Results related to the systems used in the present study are shown in Figure 4 as complex viscosity vs. frequency diagrams. The influence of fiber concentration and surface modification is evident, especially in the low-frequency range. At a 20% filling level, the coated fibers show a significantly lower viscosity than that of untreated cellulose. At the highest fiber content, 40%, this effect is less pronounced, as could be expected for a system with a high degree of fiber interaction. At higher frequencies, the differences dependent on fiber concentration and surface treatment tend to disappear.

Differences were also noted in the viscosity of the melts containing coated and untreated fibers, as re-



a



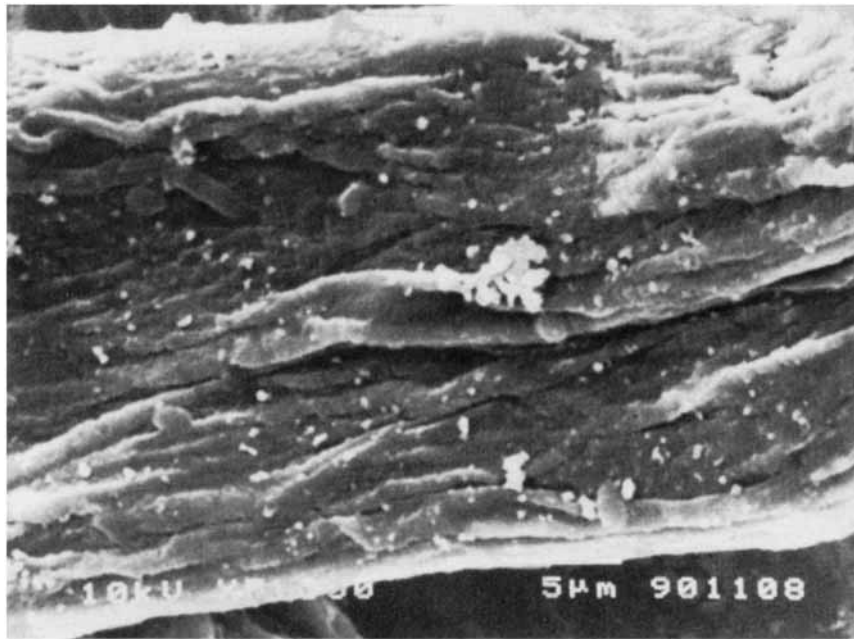
b

Figure 1 SEM photomicrographs of (a) untreated cellulose fibers and (b) Santoweb fibers.

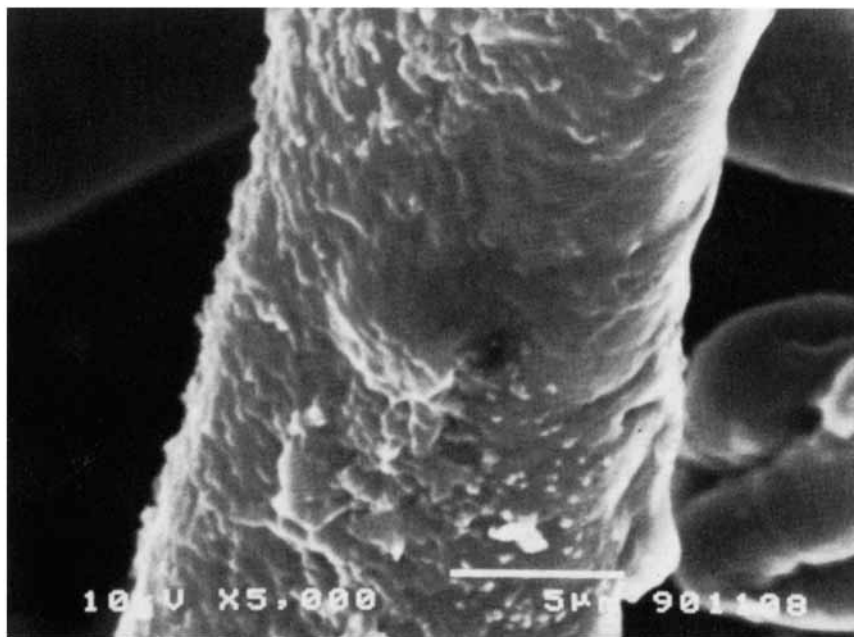
flected in the data in Figure 4, when recording the injection pressures required to completely fill the mold during injection molding of the samples. These data, reproduced in Figure 5, show clearly that the composites containing treated fibers can be processed at significantly lower pressures. This is especially pronounced at high filling levels.

Fiber-length Distribution

Figure 6(a) shows the weighted fiber-length distributions of as-received untreated fibers and fibers extracted from an injection-molded sample filled to 40%. As evident from the shift of the distribution curves, a severe fiber length degradation took place



a



b

Figure 2 SEM photomicrographs of (a) untreated cellulose fibers and (b) Santoweb fibers.

during the compounding and molding stages. In contrast, the level of degradation exhibited by the surface-treated fibers is negligible (Fig. 6(b)), a highly significant effect from a technical point of view.

Processing of fiber-reinforced thermoplastics by extrusion or injection molding commonly results in a substantial decrease in the original fiber length.

Such degradation effects have been amply documented for glass fibers¹⁵ and cellulose.¹⁶ Although the exact value of the underlying mechanisms is not known,³⁰ it is safe to assume that the fiber/melt interlayer will also play a role in this context. The results presented in Figure 6(a) and (b) show that this indeed is the case.

Although the average fiber length may play only

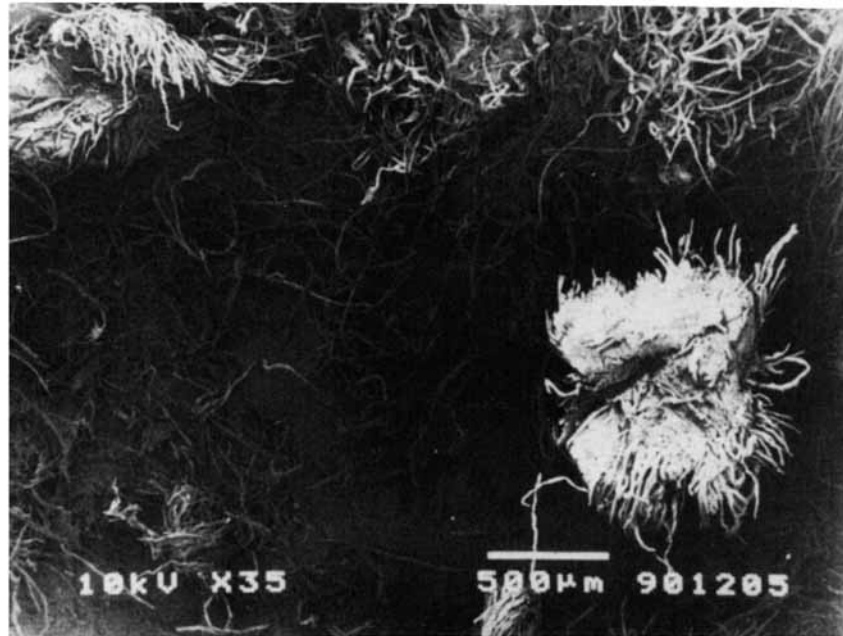


Figure 3 SEM photomicrograph of a fiber bundle extracted from an injection-molded composite sample of 40% untreated cellulose and PS matrix.

a minor role in determining the modulus of a composite, it has a decisive influence on its mechanical behavior at higher strains. This will be demonstrated in greater detail in the next section.

Mechanical Properties

The primary mechanical parameters of the injection-molded samples included in this study are summa-

rized in Table II. As is evident, the approximately linear increase in initial modulus with the fiber content is almost identical for both fiber types. As regards the surface-coated fibers, one must consider the negative effect of the plasticizer on the rigidity of the matrix. However, available data did not allow for a separation of the latter effect and the contribution of an improved fiber dispersion.

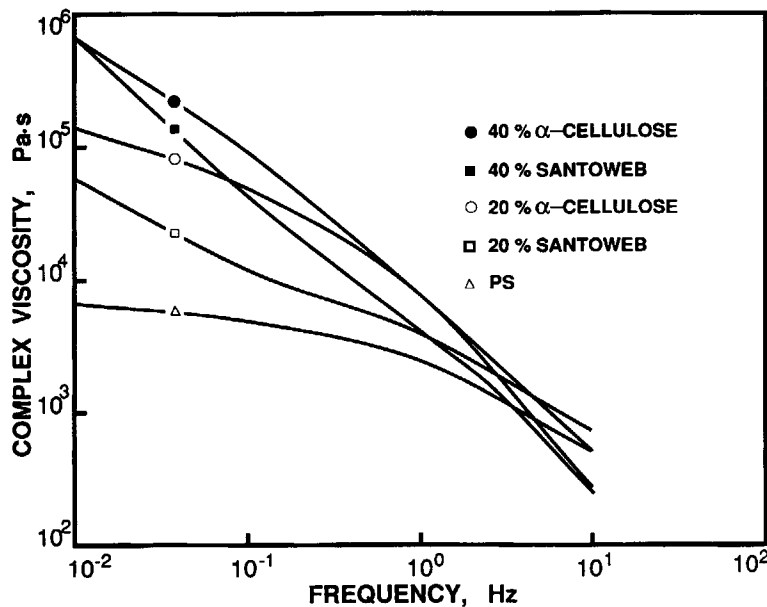


Figure 4 Complex viscosity vs. frequency for PS, 20% α-cellulose, 40% α-cellulose, 20% Santoweb, and 40% Santoweb.

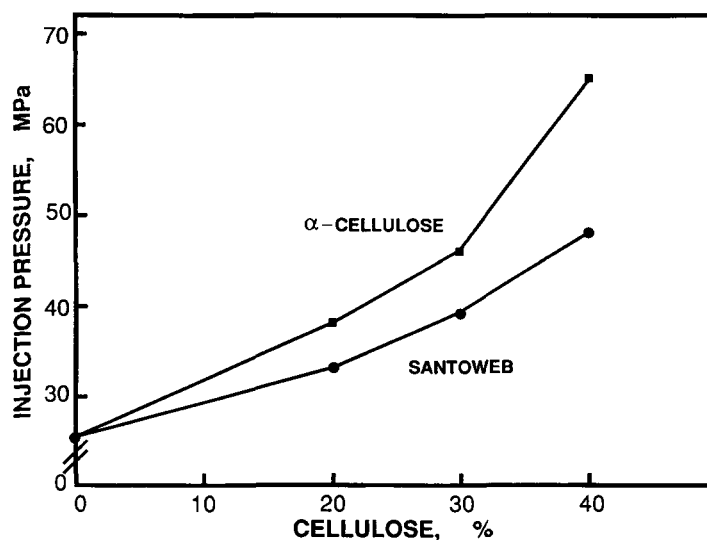


Figure 5 Required injection pressure for PS filled with untreated and treated cellulose fibers.

The influence of the plasticizer, which amounts to 15% of the weight of the fiber, may also be added when explaining the 10–20% decrease in tensile strength of the samples containing 20–40% treated fibers as compared with the strength of the matrix. Slightly higher strength values are observed for samples filled with untreated cellulose.

With regard to the elongation at break, the surface treatment produces a fair degree of improvement, especially at intermediate loading levels. On the other hand, samples loaded with untreated fibers show ϵ_b values below those obtained with the matrix material.

The unnotched impact strength values are only slightly higher for the composites with surface-treated fibers. There is a slight increase in these values with the loading level for both fiber types. It may be noted that the unnotched impact strength of the matrix is substantially higher than the values measured on the composite samples.

The notched samples exhibit a different behavior. Here, the matrix and the composites show a similar impact strength level. Untreated fibers produce only a slight decrease, whereas a moderate increase of about 30% is noted with the surface-treated material.

Figure 7 shows SEM photomicrographs of the tensile fracture surface of 40% cellulose–PS composites. Whereas a rather smooth fracture surface is seen in virgin cellulose–PS composites, fiber pull-out is observed for coated fibers. Normally, such pullout is observed when the adhesion between fiber and matrix is not sufficient. Fiber pullout contributes to an improvement in both impact strength and elongation at break.

Simulation of Interphase Phenomena

Interfacial phenomena in the system composed of coated cellulose/PS were studied more closely in a model system. When the PVC-coated fibers are incorporated into the PS matrix, an interphase consisting of a mixture of PS and PVC is likely to be formed as a result of molecular interdiffusion of the two components. Such an effect is to be expected in view of the high content of the plasticizer, BBP, in the PVC coating, which acts as a solvent for both PVC and PS.

To corroborate this supposition, a series of PVC/PS blends with various amounts of BBP (0, 10, 20, 40, and 50%) were prepared in the Brabender mixer, after which their miscibilities were studied using DSC and DMTA. The optical clarity of these blends was also taken into account.

Figure 8 shows thermographs of the PVC/PS 50/50 blend and blends with additions of various amounts of BBP plasticizer. Two distinct transitions are seen, one at 87°C and another at 100°C, which are characteristic of glass transitions of PVC and PS, respectively. Upon the addition of 30% BBP, based on total amount of polymer, only one transition is seen at 10°C. The addition of 50% BBP shifts the transition to –40°C. Although PVC and PS are immiscible, each is soluble in BBP. Exceeding a critical BBP concentration is therefore expected to result in a single-phase ternary blend.

The dynamic mechanical properties of a PVC/PS 50/50 blend containing varying amounts of BBP were studied over a wide temperature range (–100 to 150°C). Figure 9 shows the mechanical loss factor

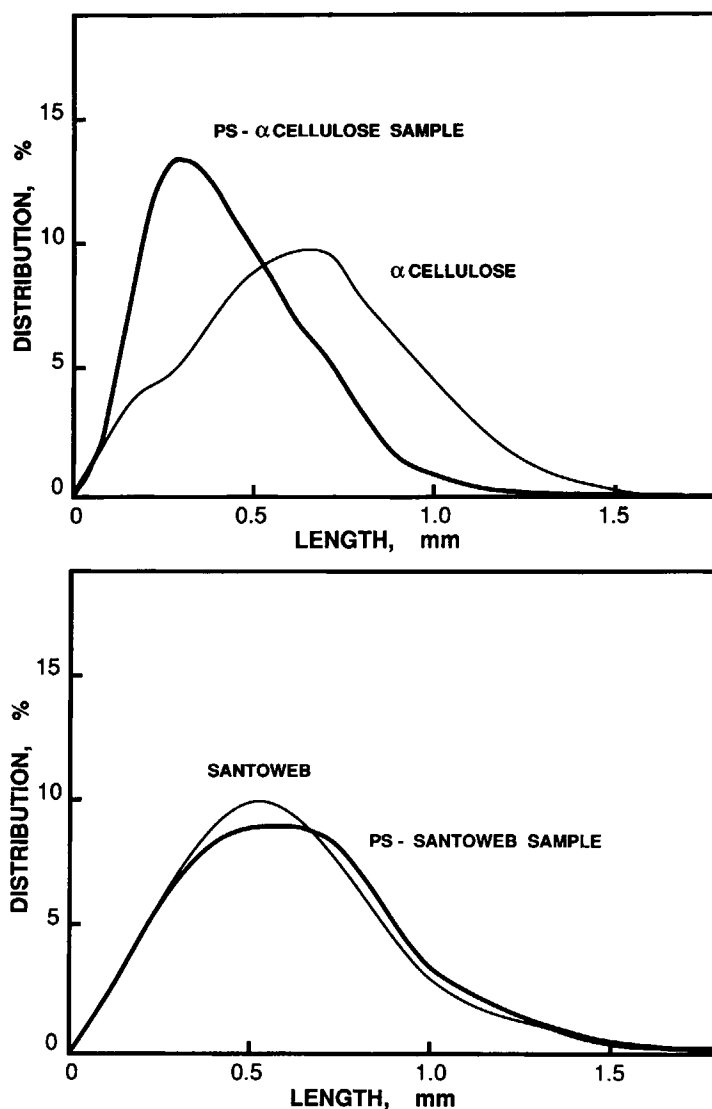


Figure 6 Distribution of fiber length: (a) virgin fibers and fibers extracted from 40% PS composite; (b) Santoweb fibers and fibers extracted from 40% PS composite.

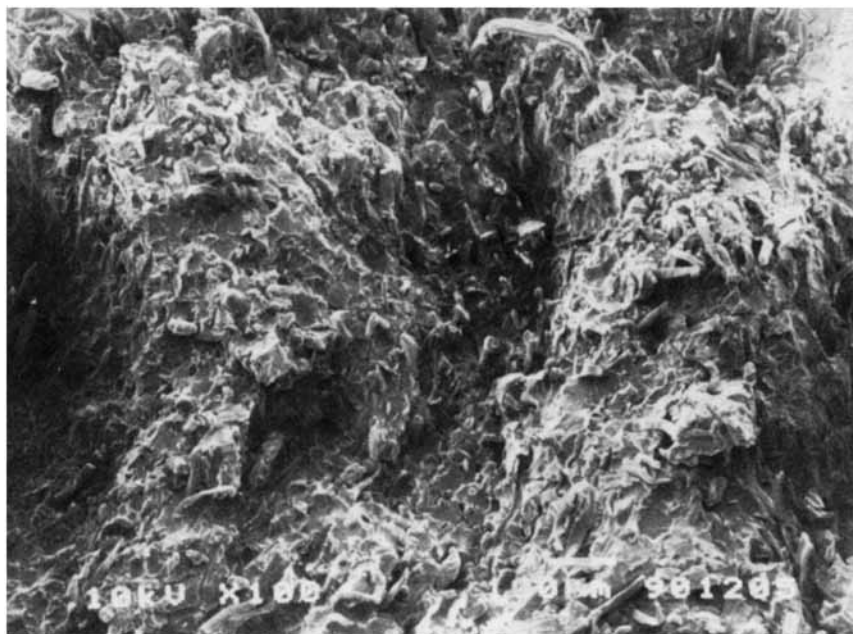
$\tan \delta$ for the different samples. Two distinct maxima are seen for all compositions below 50% BBP. The distance between the maxima becomes smaller as more BBP is added. The damping peak of PS is

shifted to a greater extent than that of PVC, indicating that the plasticizer used is a slightly better solvent for PS. With samples containing 50% BBP, only one damping peak is recorded. The fact that at

Table II Mechanical Properties

Sample	E-modulus [GPa]	σ_b [MPa]	ϵ_b [%]	IS un_1 [kJ/m ²]	IS n_2 [kJ/m ²]
PS	3,3	40,1	2,2	41,5	11,5
20 cell	4,6	40,8	1,9	13,9	10,9
30 cell	5,4	42,5	1,9	13,5	9,5
40 cell	6,2	43,6	1,7	14,6	10,0
27,4 SW	4,5	34,3	3,4	14,6	14,7
41,1 SW	5,3	36,7	3,3	15,3	13,2
54,8 SW	6,0	32,9	2,6	18,0	14,3

¹ Unnotched; ² notched samples.



a



b

Figure 7 SEM micrographs of fracture surface: (a) 40% α -cellulose/PS composite; (b) 40% Santoweb/PS composite.

this plasticizer content the samples also exhibit optical clarity may be considered a strong indication that the system in question represents a single-phase ternary blend.

The damping data reproduced in Figure 9 are supplemented in Figure 10 by the corresponding modulus-temperature curves. The rubbery properties of interphase in Santoweb W/PS composites may explain why the modulus of such composites

was not higher than for untreated fibers, despite the higher aspect ratio and good dispersion of fibers.

CONCLUSIONS

The agglomeration of virgin cellulose fibers that occurred in PP, PE, and PS is believed to be a result of extensive fiber-fiber hydrogen bonding. The sep-

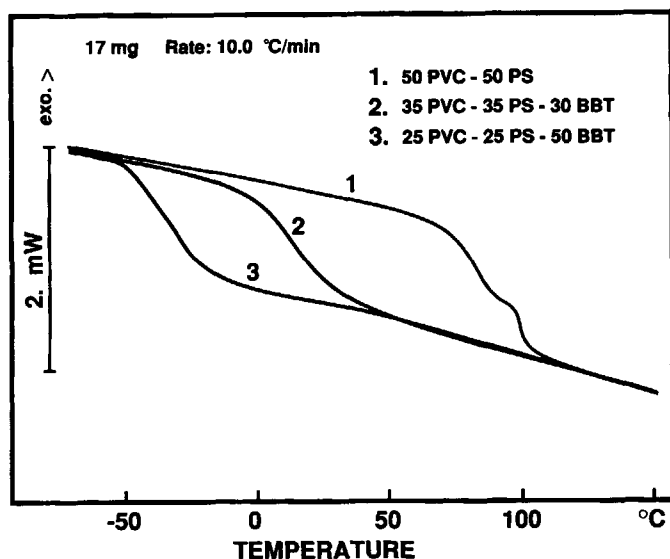


Figure 8 DSC data from PVC/PS 50/50 blends with addition of various amounts of BBP plasticizer.

aration of fibers by coating each individual fiber with a layer of BBP-plasticized PVC eliminated fiber-fiber bonding. This was not a sufficient condition for achieving a good dispersion in polyolefinic matrices. An excellent dispersion was, however, achieved in a PS matrix.

A study of interphase phenomena by investigating the miscibility of PVC/PS as a function of BBP

concentration, using DMTA and DSC and studying optical properties, showed that BBP acted as a co-solvent for PVC and PS at concentrations prevailing in the interphase between PS and the BBP-plasticized PVC coating in the studied PS/Santoweb composite. The miscibility of the coating applied onto the cellulose surface with the matrix resulted, in addition to excellent dispersion, in improved pro-

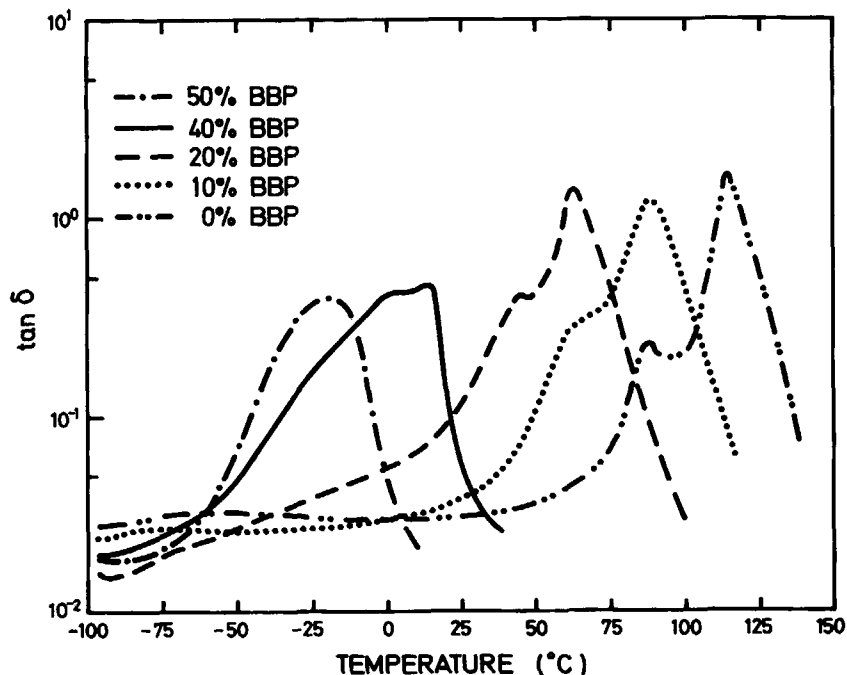


Figure 9 Tan δ vs. temperature at 1 Hz for PVC/PS 50/50 blends with various amounts of BBP.

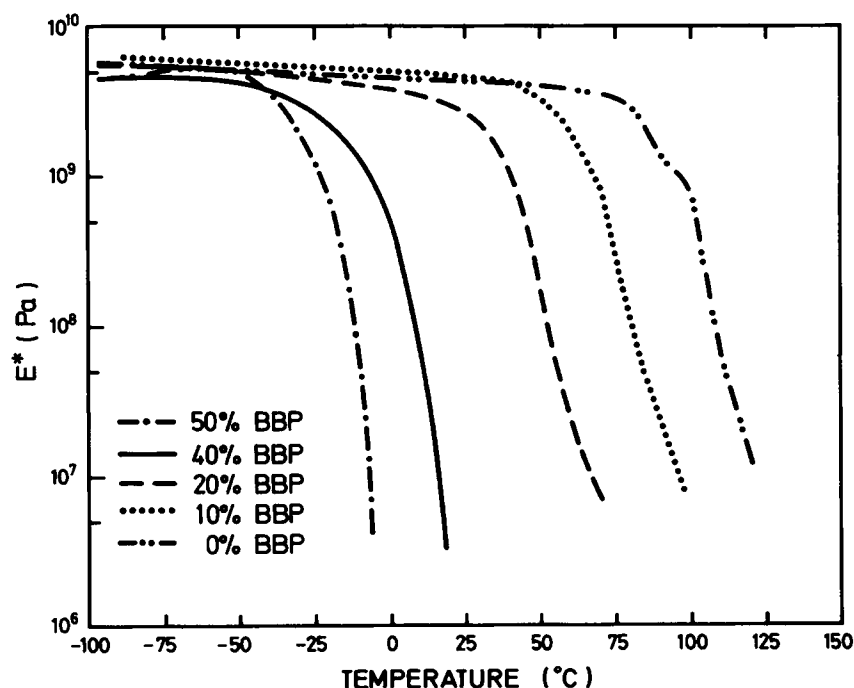


Figure 10 Complex modulus vs. temperature at 1 Hz for PVC/PS 50/50 blends with various amounts of BBP.

cessability and mechanical properties as well. Indeed, as a consequence of reduced melt viscosity, less energy was required for compounding. Fiber degradation was avoided during processing, a very important aspect from a technical point of view. The improvement of mechanical properties, such as an increase in elongation at break and an improvement of the impact strength, are typical results of an improved dispersion.

This work presently in progress in our laboratory aims toward investigating other miscible combinations of polymer coatings and matrices.

The authors wish to express their thanks to the National Swedish Board for Technical Development for financial support of this project. Thanks also go to Mrs. A. Josefsson and Mr. A. Persson for experimental assistance.

REFERENCES

1. L. E. Nielsen, *J. Appl. Polym. Sci.*, **10**, 97 (1966).
2. H. Ishida, *Polym. Compos.*, **5**, 101 (1984).
3. H. Ishida and J. L. Koenig, Eds., *Composite Interfaces*, Elsevier, New York, 1986.
4. M. Xanthos, *Polym. Eng. Sci.*, **28**, 1392 (1988).
5. M. Y. Boluk and M. P. Schreiber, *J. Appl. Polym. Sci.*, **40**, 1783 (1990).
6. M. Y. Boluk and M. P. Schreiber, *Polym. Compos.*, **7**, 295 (1986).
7. H. P. Schreiber, M. R. Wertheimer, and M. Lambla, *J. Appl. Polym. Sci.*, **27**, 2269 (1982).
8. M. J. Marmo, M. A. Mostafa, H. Jinnai, F. M. Fowkes, and J. A. Manson, *Ind. Eng. Chem. Prod. Res. Dev.*, **15**, 206 (1976).
9. C. Klason, J. Kubát, and H. E. Strömvall, *Int. J. Polym. Mater.*, **10**, 159 (1984).
10. C. Klason, J. Kubát, and P. Gatenholm, in *Cellulosics Utilization*, H. Inagaki and G. O. Phillips, Eds., Elsevier, London, 1989, p. 87.
11. P. Zadorecki and A. J. Michell, *Polym. Compos.*, **10**, 69 (1989).
12. A. J. Michell, J. E. Vaughan, and D. Willis, *J. Polym. Sci. Symp.*, **55**, 143 (1976).
13. D. Maldas, B. B. Kokta, and C. Daneault, *Int. J. Polym. Mater.*, **12**, 297 (1989).
14. R. G. Raj and B. V. Kokta, in *Wood Processing and Utilization*, J. F. Kennedy, G. O. Phillips, and P. A. Williams, Eds., Ellis Horwood, Chichester, 1989, p. 251.
15. L. Czarnecki and J. L. White, *J. Appl. Polym. Sci.*, **25**, 1217 (1980).
16. C. Klason, J. Kubát, and P. Gatenholm, in ASC Symposium Series, *Viscoelasticity of Biomaterials*, W. Glasser, Ed. American Chemical Society, Washington, DC, 1990.
17. H. Dalvåg, C. Klason, and H.-E. Strömvall, *Int. J. Polym. Mater.*, **11**, 9 (1985).
18. P. Gatenholm, J. Felix, C. Klason, and J. Kubát, *Cellulose-Polymer Composites with Improved Properties*, Contemporary Topics in Polymer Science, Vol. 7, J. C. Salamone, Ed., Plenum, New York, 1991.

19. J. Felix and P. Gatenholm, *J. Appl. Polym. Sci.*, **52**, 689 (1991).
20. D. Maldas and B. V. Kokta, *J. Appl. Polym. Sci.*, **40**, 917 (1990).
21. R. G. Raj and B. V. Kokta, *J. Appl. Polym. Sci.*, **38**, 1987 (1989).
22. B. V. Kokta, D. Maldas, C. Daneault, and P. Béland, *Polym. Compos.*, **11**, 84 (1990).
23. H. E. Strömvall, PhD Thesis, Chalmers University of Technology, Gothenburg, Sweden, 1984.
24. H. Kishi, M. Yoshioka, A. Yamanoi, and N. Shiraishi, *Mokuzai Gakkaishi*, **34**, 133 (1988).
25. J. E. O'Connor, *Rubber Chem. Technol.*, **50**, 445 (1977).
26. A. Y. Coran, P. Hamed, and L. A. Goetter, *Rubber Chem. Technol.*, **44**, 1167 (1976).
27. A. Y. Coran, K. Boustany, and P. Hamed, *Rubber Chem. Technol.*, **47**, 396 (1974).
28. I. D. Miller, H. Ishida, and F. H. J. Maurer, *Rheol. Acta*, **27**, 397 (1988).
29. C. D. Han, T. Van den Weghe, P. Shete, and J. R. Haw, *Polym. Eng. Sci.*, **21**, 196 (1981).
30. B. Franzén, C. Klason, J. Kubát, and T. Kitano, *Composites*, **20**, 65 (1989).

Received June 2, 1992

Accepted September 7, 1992