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THE INFLUENCE OF MATRIX COMPOSITION AND SOFTENING ON THE MECHANICAL BEHAVIOUR OF CELLULOSIC FIBRES

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Synopsis Fibres from a bleached kraft pulp grafted with polystyrene by means of radiation initiation were studied. The purpose of grafting was to incorporate a polymer with a defined rheological behaviour, thereby changing the composition of the cell wall. The grafts had a polystyrene content ranging from 6 to 35 per cent by weight.

In order to decrease the crystallinity of the cellulose, the fibres were treated with aqueous zinc solutions of 65 and 70 per cent concentration. In addition to decrystallisation effects these treatments caused chemical degradation and dissolution of the cellulose.

Mechanical spectroscopy of the grafted fibres revealed an intense interaction between the polystyrene and the carbohydrate macromolecules. Apparently the treatment with zinc chloride causes degradation and structural breakdown of the grafted fibre which results in a less intense interaction between the cellulose and polystyrene phases.

The results of creep measurements in water and toluene indicate that the polystyrene can control the properties of the matrix while the amorphous cellulose still governs the stress transfer between the reinforcing microfibrils.

Introduction

A CLOSE examination of the cell wall of tracheids reveals a structural design that resembles fibre-reinforced composites. The basic reinforcing element is the cellulose microfibril which is surrounded by a stress-transferring matrix of amorphous wood polymers. The cell wall consists of several layers, which are mainly distinguished by a difference in the orientation of the cellulose microfibrils.(1) In this way nature has provided the fibre with an excellent ability to take up both longitudinal and transverse stresses.(2)

Under the chairmanship of Dr N. K. Bridge

Recent advances in composite material theory have provided theoretical tools to analyse the mechanical properties of the single fibre under both uniaxial and biaxial loading conditions.(3) However, the verification of the theoretical calls for extremely sophisticated experimental techniques to solve the practical problems of single fibre testing.(4–6) Theoretical calculations by Mark(7) have demonstrated that the parameters governing the elastic properties are the degree of crystallinity, the orientation of the microfibrils and the mechanical properties of the matrix polymers.

The properties of the matrix wood polymers change from a glassy to a rubbery behaviour with changes in the surrounding temperature and humidity. It is well established that lignin and hemicellulose are essentially thermoplastic polymers.(8, 9) It is thus recognised that isolated dry lignin and dry hemicellulose become rubbery in the temperature interval between 180–220° C. In water the transition temperature for lignin is lowered to 80–90° C and hemicellulose is highly swollen already at room temperature. The great effect of moisture on the mechanical properties of hemicellulose may be expected to be responsible for the change in elastic properties of the fibre with humidity. At increasing temperature the softening of lignin will also contribute to the change in mechanical properties. According to the theoretical predictions, the softening of the fibre matrix should lead to a reduction in elastic properties which may range from 50–90 per cent.

Viscoelastic behaviour and strength properties are much more difficult to predict due to the complex nature of the flow mechanism and the poor understanding of the viscoelastic character of amorphous polymers in composite systems such as in semi-crystalline polymers.

In this paper an attempt is made to quantify the effect of softening of the fibre matrix on the mechanical properties of single fibres.

The composition of the matrix has been altered by grafting different amounts of polystyrene into the fibre and by increasing the amorphous fraction in the cellulose by zinc chloride treatment. Decrystallisation with zinc chloride is accompanied by chemical degradation of the cellulose macromolecule. Special attention was therefore paid to the characterisation of the extent of these effects on the fibres at various temperatures.

The synthetic polymer has the advantage of exhibiting a well-defined glass transition temperature which may be detected by means of dynamic mechanical testing at different temperatures (mechanical spectroscopy). This type of test may also reveal whether the inclusion of the polystyrene in the cell wall distorts the relaxation characteristics of the chain. It is well established that relaxation spectra of polymers are shifted due to interfacial interactions between amorphous polymer and filler or crystalline phase. *Vice versa* a shift of the relaxation spectrum may serve as an indication of the intensity of the interaction in a multiphase material.(10) It is also possible to study the fibre system at different humidities. Since polystyrene may be considered inert to moisture, the dynamic mechanical testing in this case reveals the influence of the carbohydrates. In this study dynamic mechanical testing has been performed with a freely oscillating torsion pendulum.

To illustrate the effect of softening of the wood polymer on the flow properties of the systems, creep experiments were performed in toluene and water. The solvents were used to plasticise the polystyrene and the amorphous cellulose components, respectively.

Experimental

1—MATERIALS

ALL chemicals used were of analytical grade.

The aqueous zinc chloride solutions had densities of $1{\cdot}85 \cdot 10^3$ kg/m^3 and $1{\cdot}96 \cdot 10^3$ kg/m^3, which correspond to zinc chloride concentrations of 65·0 and 70·0 per cent respectively.(11) The zinc chloride contained an average amount of 1 per cent zinc oxide.

The pulp studied was a bleached kraft pulp of southern pine obtained from the Forestry Department at North Carolina State University. The pulp was grafted with polystyrene (PS) by means of mutual irradiation to polystyrene contents ranging from 6 to 35 per cent by weight (Table 1). The grafting was performed at Professor V. Stannett's laboratory at the North Carolina State University.

TABLE 1—RADIATION DOSES USED IN GRAFTING

Radiation dose (Mrad)	*PS content (%)*
0·2	6·4
1·7	13·2
3·8	21·9
6·8	30·5
12·0	35·1

2—APPARATUS AND TESTING PROCEDURES

2.1—*Torsion pendulums for single fibres*

The torsion pendulum systems used were described at the Fifth Fundamental Research Symposium.(12) Since then, the technique has been further developed and improved. An extensive description of the apparatus is under compilation and will be published.(13)

Fibres are glued between paper strips at a nominal span of 1 mm with a resorcinol glue. A thin disk is suspended from the fibre to provide a moment of inertia. The load on the fibre is approximately 4 mN. The influence of creep deformation induced by this load on the mechanical properties of ordinary pulp fibres is negligible. Free oscillations are induced magnetically and are recorded with a photo-electronic system. The logarithmic decrement (damping) and the square of the frequency are evaluated from the damping curves by means of a minicomputer. The relative torsional rigidity is calculated:

$$\text{Relative rigidity} = \frac{\text{square of the frequency}}{\text{square of the frequency in the dry state at } 25^\circ\text{ C}}.$$

Computer programs are used to plot the mechanical properties versus temperature or relative humidity (mechanical spectra) and to calculate the mean values for several fibres.

Two different conditioning systems have been used. In one system the fibre is kept in a nitrogen flow and the temperature is increased, normally at 2° C/minute, while the damping curves are recorded. The fibre is dried for twelve hours at 105° C prior to measurement. The other system is connected with a humidity generator which produces conditioned air in the range of 25–75° C and 5–95 per cent relative humidity. At 25° C the accuracy of this system is better than 0·5 per cent. The fibres are dried in nitrogen at 80° C for at least 36 hours prior to any measurements. The fibres are kept at least eight hours at each humidity to reach an equilibrium state. Two or three fibres of each kind were tested and mean values calculated.

The torsion pendulum equipment is also used for measurements on very small polymer samples. In this case a small glass braid is impregnated with a polymer solution and the damping and the rigidity of the braid are measured.

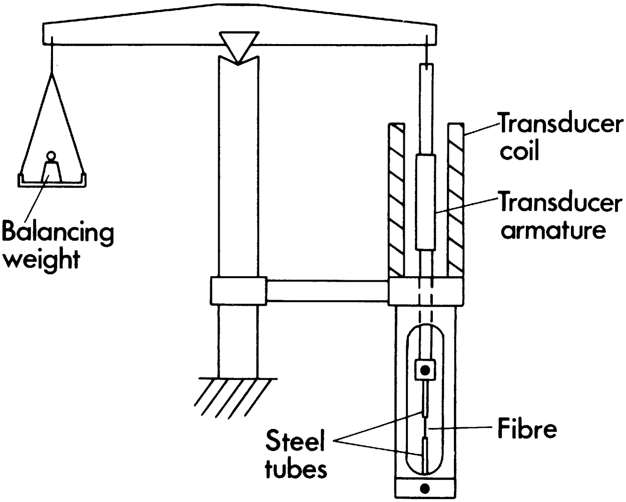

Fig. 1—A schematic drawing of the creep measurement apparatus

2.2—*Creep measurement apparatus and testing procedures*

A schematic drawing of the apparatus used to determine the creep response of single fibres is shown in Fig. 1. The fibre is glued between stainless steel tubes (tips of hypodermic needles) at a nominal span of 1 mm with a commercial epoxy adhesive (Araldite Rapid).

The fibres were subsequently mounted in a rack and immersed in water for 1 hour. The fibres were allowed to dry for at least 12 hours at 23° C and 50 per cent relative humidity, the drying load being that of the steel tube (0·3 mN). This conditioning was carried out in order to reduce the differences in the strains built into the fibres during pulping and grafting processes.

The steel tubes holding the fibre were inserted into a fixed clamp and a movable clamp which was suspended from an ordinary beam balance. The deformation of the fibre was measured with a linear variable differential transducer, its core being a part of the connection between the movable clamp and the beam. The coupling between the clamp and the core consists of a glass tube which minimises temperature effects on LVDT signals. A minimum load of 1 mN (0·1 g) was used to balance the system and straighten the fibre. A travelling microscope was used to calibrate the signal from the LVDT and to measure the absolute fibre length. The temperature was measured with a thermocouple kept close to the fibre. The experiments were carried out in a room kept at 23 ± 1° C and 50 ± 5 per cent relative humidity.

The fibre was loaded in air with 15 mN for 90 minutes and was allowed to recover for 180 minutes with 1 mN load. After the first loading and recovery the fibre was immersed in water or toluene by raising a beaker containing the solvent to a position where the fibre was just immersed. After 60 minutes the load was increased to 15 mN and the fibre was allowed to creep for 90 minutes and then to recover under a load of 1 mN for about 12 hours. Creep measurements in air were performed in the same way, naturally omitting the soaking stage. The complete procedure is shown schematically in Fig. 2. Logarithmic creep curves for fibres in air and in water are shown in Figs. 3 and 4. The results for all fibres tested are shown in Table 5.

Three characteristic values were obtained from the creep curves: The first elastic recovery after creep in air, $\mathrm{ER_I}$, the creep deformation in the solvent, CD, and the elastic recovery in the solvent, $\mathrm{ER_{II}}$. The relation between the stress level in the fibres and the creep deformation in the solvents has not been established. However, an approximate correction has been made by dividing the creep deformation by the elastic recovery in air. The creep deformation thus corrected is henceforth called normalised creep deformation:

$$\mathrm{CD}' = \frac{\mathrm{CD}}{\mathrm{ER_I}}$$

The relative tensile rigidity of the fibres in the solvent is defined as the ratio of the elastic recovery in air and the elastic recovery in the solvent:

$$\text{relative tensile rigidity} = \frac{\mathrm{ER_I}}{\mathrm{ER_{II}}}.$$

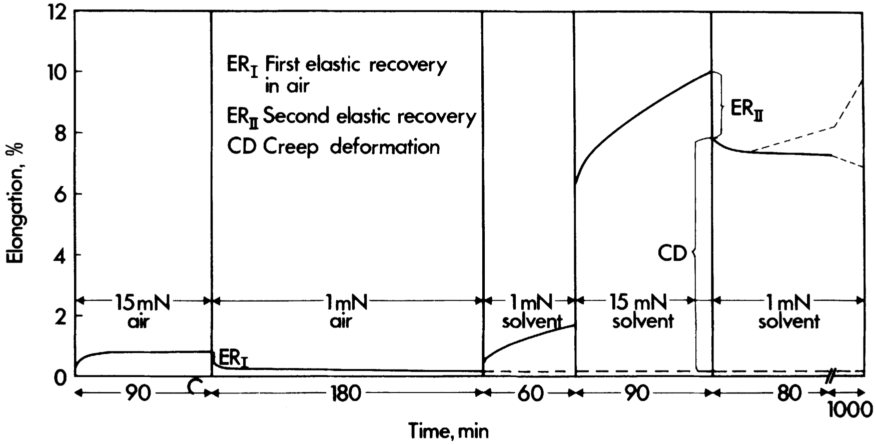

Fig. 2—Treatment conditions and concepts used in evaluation of creep measurements

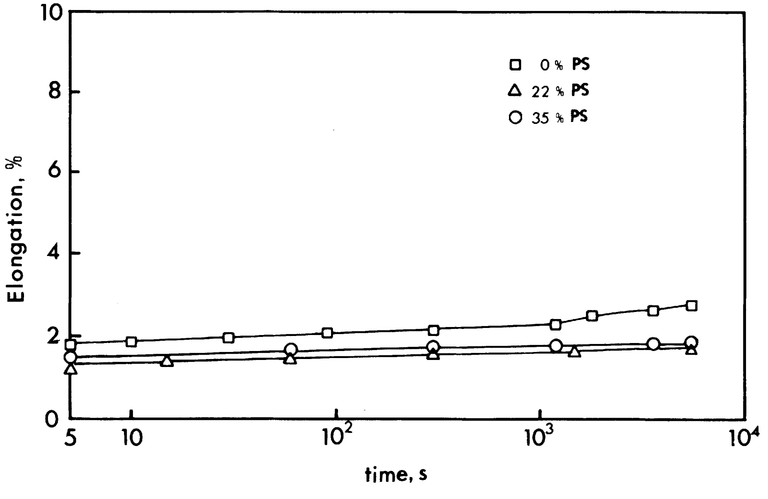

Fig. 3—Creep elongation *versus* time for fibres in air under 15 mN load

2.3—*Measurement of moisture sorption*

The moisture sorption was measured by suspending about 30 mg of the fibre sample from a quartz spring and measuring the change in length of the spring by

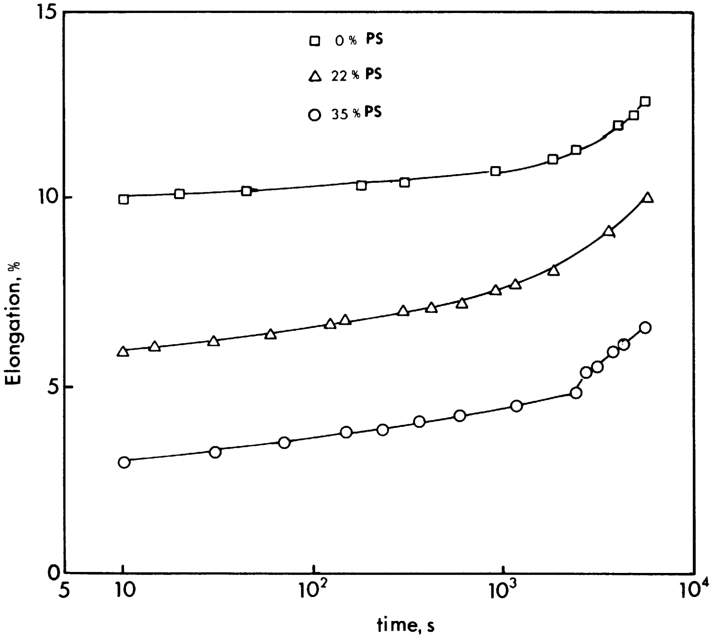

Fig. 4—Creep elongation *versus* time for fibres in water under 15 mN load

means of a travelling microscope. Eight springs were mounted in a small aluminium box furnished with a glass window. Different relative humidities were obtained by circulating the air in the box over saturated salt solutions to give 11·3, 22·4, 32·8, 54·2, 75·1, 84·5, 90·5 per cent relative humidity, respectively.

To reach the dry state the box was flushed with nitrogen for at least 36 hours. The complete system was placed in a conditioned room held at 23 ± 0·5° C. The overall accuracy of the isotherms is primarily dependent on temperature fluctuations but also on the accuracy of calibration weights, microscope readings, etc. The relative humidities have not been measured, but are usually considered to be within 2 per cent of the nominal values.(14) The accuracy of the weight determinations has experimentally been shown to be within 0·3 per cent.

Moisture sorption data were plotted by a computer and a polynomial of the sixth degree was fitted to the points to give a smooth curve. Moisture sorption isotherms before and after zinc chloride treatment for the ungrafted fibres and for the fibres containing 35 per cent polystyrene are shown in Fig. 5. The equilibrium moisture content (EMC) at 60 per cent relative humidity was calculated from the fitted polynomial. The deviation in equilibrium moisture content at 60 per cent relative humidity of samples tested twice was found to be less than 3 per cent.

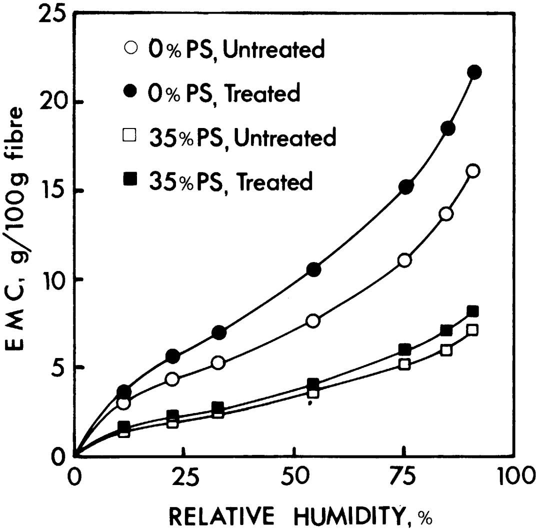

Fig. 5—Moisture sorption isotherms (23° C) for zinc chloride treated (70 per cent) and untreated grafted (35 per cent polystyrene) and ungrafted fibres

3—ZINC CHLORIDE TREATMENT

3.1—*Treatment of single fibres*

The fibres were glued to steel tubes and inserted into the creep apparatus following the same procedure as for the creep measurements. The fibre was unloaded and immersed in the zinc chloride solution in the slack condition. Elevated temperatures could be reached by heating the solution electrically. The fibre was loaded for 15 seconds with a 4·6 mN load at given intervals until failure of the fibre.

3.2—*Bulk treatment*

Preliminary treatment of rayon showed that aqueous zinc chloride solutions of 65 to 70 per cent concentration not only caused swelling of the fibres but also dissolved some of the cellulose. When a 70 per cent aqueous zinc chloride solution containing 0·05 per cent rayon was diluted with 0·05 M hydrochloric acid, precipitation of the cellulose occurred at about 25 per cent zinc chloride concentration. The critical concentration below which no significant influence of zinc chloride on cellulose other than swelling can be detected is about 60 per cent.(15, 16)

The zinc chloride treatment was carried out by adding 45 cm^3 of 65 or 70 per cent aqueous zinc chloride solution to 0·5 g of air-dry fibre. The reaction mixture was kept at a constant temperature and agitated by means of a magnetic stirrer. After a given treatment time the reaction was quenched by adding a 20 per cent zinc chloride solution to the fibre slurry to give a final zinc chloride concentration of 50 per cent. As mentioned above, the dissolved cellulose does not precipitate at 50 per cent salt concentration and the fibres retain a sufficient degree of swelling to allow the dissolved cellulose to be washed out. After the solution had been filtered on a glass filter, the fibres were washed once with an aqueous 50 per cent zinc chloride solution at the reaction temperature. After two subsequent washing steps with 20 per cent zinc chloride the fibres were washed with 0·05 M hydrochloric acid in order to remove any precipitated zinc oxide. The fibres were washed with distilled water until no traces of chloride ions could be detected in the filtrate. The fibres were finally freeze-dried and the yield was determined gravimetrically.

Results and discussion

1—*Zinc chloride treatment*

FIG. 6 shows that the load bearing capacity of single fibres was reduced on immersion in zinc chloride solutions, and that the reduction increased with increasing temperature and decreasing polystyrene content. The ungrafted fibre was very susceptible to the zinc chloride treatment.

Table 2 shows the effect of zinc chloride treatment on the yield, equilibrium moisture content and DP of ungrafted and grafted fibres. The yield decreased

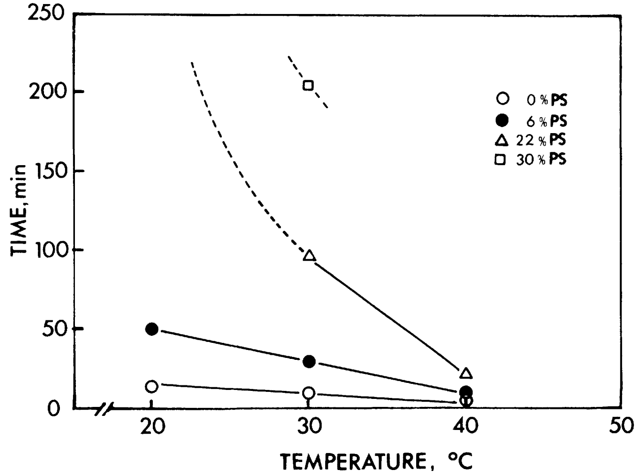

Fig. 6—Time in 70 per cent zinc chloride to reduce load bearing capacity of single fibres below 4·6 mN (0·5 g) *versus* temperature

TABLE 2—EFFECT OF ZINC CHLORIDE TREATMENT ON THE YIELD, EQUILIBRIUM MOISTURE CONTENT AND DP OF FIBRES

	Zinc chloride treatment			*Recovered material*		*EMC at 23°, 60% RH*	
PS (%)	[$ZnCl_2$] (%)	*Temp.* (°C)	*Time* (*min*)	*Yield* (%)	*DP*	g H_2O/100 g *fibre*	g H_2O/100 g *cellulose*
0	0	—	—	100·0	1 040	8·5	8·5
0	65·0	21	120	86·0	806	11·1	11·1
0	70·0	21	120	73·9	495	11·8	11·8
22	0	—	—	100·0	—	5·7	7·4
22	65·0	21	120	98·1	—	6·4	8·2
22	65·0	21	1 140	89·0	—	9·4	12·5
22	70·0	21	120	96·2	—	6·2	8·0
22	70·0	21	1 140	86·7	—	7·8	10·4
22	70·0	30	60	96·6	—	6·8	8·8
22	70·0	30	120	90·9	—	6·7	8·8
22	70·0	30	1 140	73·6	—	8·8	12·6
22	70·0	40	120	84·5	—	8·0	10·8
22	70·0	40	1 140	72·7	—	9·0	12·8
35	0	—	—	100·0	—	4·1	6·2
35	70·0	30	120	96·7	—	4·5	7·1

with increasing time and temperature of the zinc chloride treatment. Moreover, when ungrafted fibres were treated with 70 per cent zinc chloride solution, 26 per cent of the cellulose was dissolved and the remaining material had lost its fibrous character and its DP was reduced by 50 per cent.

A single experiment with a bleached kraft pulp further showed that a 120 min treatment with 65 per cent zinc chloride solution at 21° C dissolved 15 per cent of low molecular cellulose without decreasing the DP of the residual fibrous material.

It has been shown(17, 18) that the swelling of regenerated cellulose with zinc chloride is accompanied by simultaneous temperature dependent dissolution and hydrolytical breakdown. Moreover, when hydrochloric acid is added to the swollen cellulose the rate of breakdown is drastically increased, leading to a complete hydrolysis of the cellulose macromolecule.

It is therefore reasonable to suggest that a simultaneous dissolution and degradation of cellulose occurs in the grafted fibres on treatment with zinc chloride solutions. The non-degrading dissolution affects the low molecular and preferentially amorphous parts of the cellulose, whereas the dissolution of the crystalline parts involves chemical degradation. Obviously the grafted polystyrene delays but does not prevent the chemical degradation of the fibres.

Table 2 shows that at 60 per cent humidity the equilibrium moisture content of untreated fibres based on both total material and cellulose decreased with increasing polystyrene content.

The equilibrium moisture content of cellulosic fibres has been shown(19) to decrease with increasing polystyrene content. It has been suggested that this effect reflects the even distribution of polystyrene in the cellulose material. It has also been reported(20) that a radiation dose of 4·5 Mrads on wood pulp cellulose causes a decrease in equilibrium moisture content at 65 per cent relative humidity of the cellulose from 8·7 to 7·7 g water per 100 g of cellulose. This effect was believed to be caused by the cross-linking of cellulose.

Table 2 shows the influence of zinc chloride treatment under different conditions on the equilibrium moisture content at 60 per cent relative humidity of ungrafted and grafted fibres. Fig. 7 shows the effect of treatment conditions on a grafted fibre at a given polystyrene content. It can be seen that the equilibrium moisture content increased with increasing time and temperature of treatment with zinc chloride with a simultaneous decrease in yield.

Jeffries(21) has suggested a linear relation between the moisture sorption

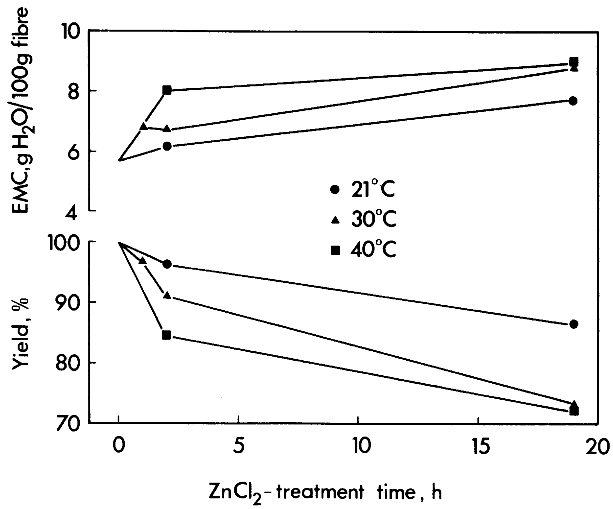

Fig. 7—Yield and equilibrium moisture content (60 per cent RH) of grafted fibres (22 per cent polystyrene) *versus* time of treatment with zinc chloride (70 per cent)

and the amorphous fraction of cellulose. Due to the effect of polystyrene on the equilibrium moisture content of untreated fibres, this relation cannot be used. The relative change in moisture regain of the cellulose in fibres as a result of zinc chloride treatment may, however, serve as a measure of the extent of decrystallisation.

Table 3 shows the relative increase in equilibrium moisture content of ungrafted fibres after zinc chloride treatment. It can be seen that the change in cellulose crystallinity measured as change in moisture absorption is most pronounced for ungrafted cellulose and that the polystyrene has a retarding effect on the process.

TABLE 3—THE RELATIVE INCREASE IN EQUILIBRIUM MOISTURE CONTENT ON ZINC CHLORIDE TREATMENT OF FIBRES

	Relative increase in equilibrium moisture content (%)		
	$ZnCl_2$ treatment, 70%, 120 min		
PS (%)	*21° C*	*30° C*	*40° C*
0	39	—	—
22	8	19	46
35	—	15	—

It has been suggested(22, 23) that on treating polyethylacrylate-rayon grafts with a 70 per cent chloride solution, the cellulose is decrystallised and that the recrystallisation of cellulose on washing out the swelling agent is hindered by the presence of the polymer.

Apparently, the presence of polystyrene has hindered the decrystallisation, which is contrary to the situation found for polyethylacrylate-rayon grafts. This can be explained by the fact that the polystyrene is in its glassy state and the polyethylacrylate in its rubbery state under the swelling conditions used. Thus the glassy polystyrene may prevent the diffusion and penetration of the bulky zinc chloride hydrate molecules into the cellulose structure which, according to many studies,(15, 16, 24, 25) is an important and essential part of the decrystallisation mechanism.

2—*Torsion pendulum measurements*

The torsion pendulum measurements were carried out on the fibres tabulated in Table 4.

The relative rigidity and the damping are shown *versus* temperature for untreated fibres in Figs. 8a and 8b. For comparison the corresponding curve for

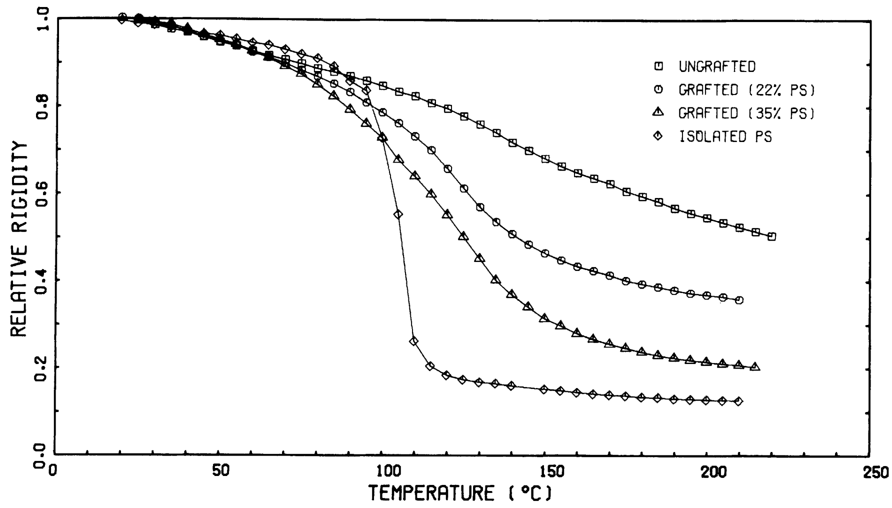

Fig. 8a—Relative rigidity *versus* temperature for single fibres of different polystyrene content and for polystyrene isolated from grafted fibres

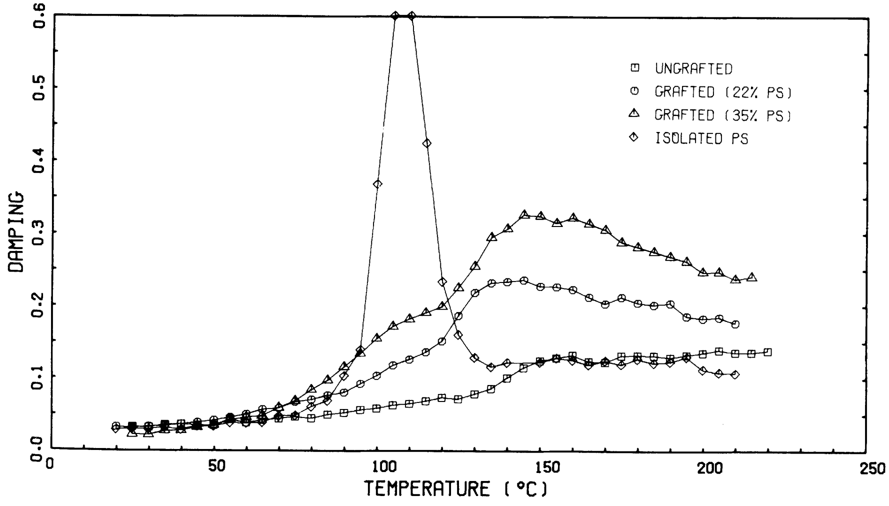

Fig. 8b—Damping *versus* temperature for single fibres of different polystyrene content and for polystyrene isolated from grafted fibres

TABLE 4—FIBRES USED IN MECHANICAL TESTING

PS (%)	*Treatment conditions* [$ZnCl_2$] (%)	 *Temp.* (°*C*)	 *Time* (*min*)
0	—	—	—
0	65	21	120
22	—	—	—
22	70	21	120
22	70	30	120
22	70	40	120
35	—	—	—
35	70	30	120

polystyrene isolated from one of the grafts is included. It is evident from the graphs that the damping peak accompanying the glass transition of polystyrene around 105° C does not show for the fibre containing 22 per cent polystyrene and is only just discernible at 35 per cent polystyrene content. Apparently, the relaxation spectrum of polystyrene in grafted fibres is broadened and spread over a wide temperature range. This is probably due to a strong interaction between the synthetic polymer and the cell wall material. Similar observations have been made for filled polymer systems. The nature of the interaction is believed to emanate from the interfacial phenomena in a multiphase system.(26) According to the diffusion theory of adhesion,(27) it is necessary that the polymer molecules mix in order to achieve a good bonding. In the case of polystyrene and cellulose, however, it is difficult to envisage an intensive exchange of chain segments due to the large differences in polarity and in the solubility parameters.

It is therefore more reasonable to assume that the relaxation spectrum is a reflection of the heterogeneous stress field which must be present in the dry fibres. Differences in thermal expansivity and hygroexpansivity of the two polymers lead to substantial local stresses during the drying of the grafted fibre. It has been reported(28) that the glass transition temperature of polystyrene is shifted to 150° C under a hydrostatic pressure of 200 MPa (2 000 kg/cm^2). Both thermal and hygrostresses may reach this level in a heterogeneous composite such as the grafted fibre. It is suggested that the hygrostresses in the polystyrene grafts are of primary importance, since no drastic shift in the relaxation spectrum of polyacrylamide has been found.(29) In polyacrylamide grafts, the synthetic polymer has the same swelling capacity in water as the amorphous cellulose and shrinkage stresses are consequently not likely to be of the same magnitude as when the non-swelling polystyrene is incorporated in a swollen cellulose matrix.

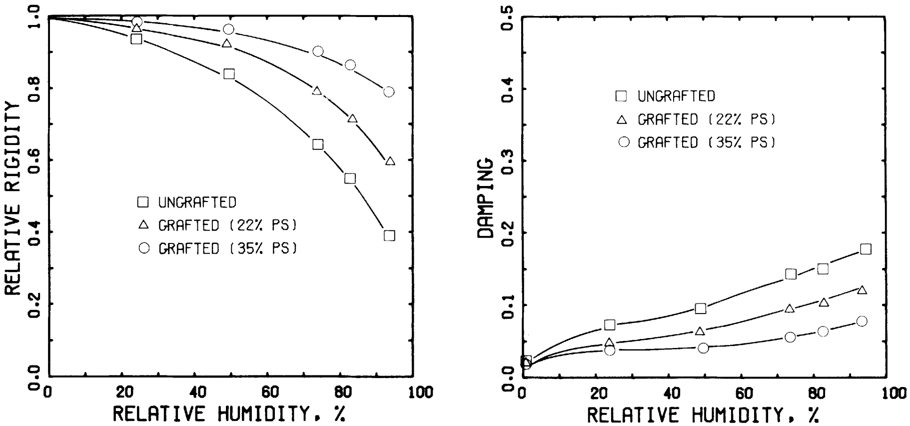

Fig. 9—Relative rigidity and damping *versus* relative humidity at 25° C for single fibres of different polystyrene content

In Fig. 9 the rigidity and damping are shown *versus* relative humidity at 25° C for untreated fibres. It is evident that the grafted fibres are less sensitive to humidity than the ungrafted fibres. This behaviour is expected owing to the pronounced hydrophobic character of polystyrene.

The response to temperature and humidity of zinc chloride-treated fibres containing 22 per cent polystyrene are shown in Figs. 10 and 11, respectively. The untreated fibres are represented by heavy solid lines. Zinc chloride-treatments of the fibres at 21° C and 30° C do not affect the properties to any great extent. Only at a very high humidity do the fibres treated at 30° C differ from the untreated fibres. The fibres treated at 40° C, however, show an increased sensitivity to both temperature and humidity. There is also an indication at about 105° C of the damping peak of free polystyrene. Apparently the treatment with zinc chloride causes degradation and structural breakdown of the grafted fibre which results in a less intense interaction between the cellulose and the polystyrene phases.

The effect of zinc chloride-treatment on the ungrafted fibre and on the fibre containing 35 per cent polystyrene is shown in Figs. 12 and 13. Owing to the fact that ungrafted fibres do not retain their fibre structure after treatment with 70 per cent zinc chloride, a milder treatment with 65 per cent zinc chloride was chosen. The untreated fibres are represented by heavy solid lines. Obviously, even the relatively mild treatment of the ungrafted fibre causes an increased sensitivity to both temperature and humidity.

This corresponds to the increase in amorphous material on decrystallisation.

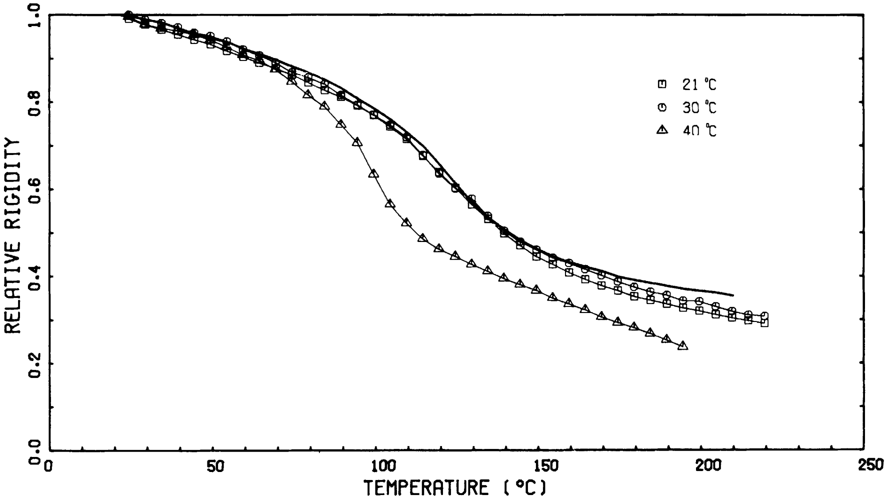

Fig. 10a—Relative rigidity *versus* temperature for zinc chloride-treated grafted (22 per cent polystyrene) fibres. The heavy solid line represents the untreated fibre

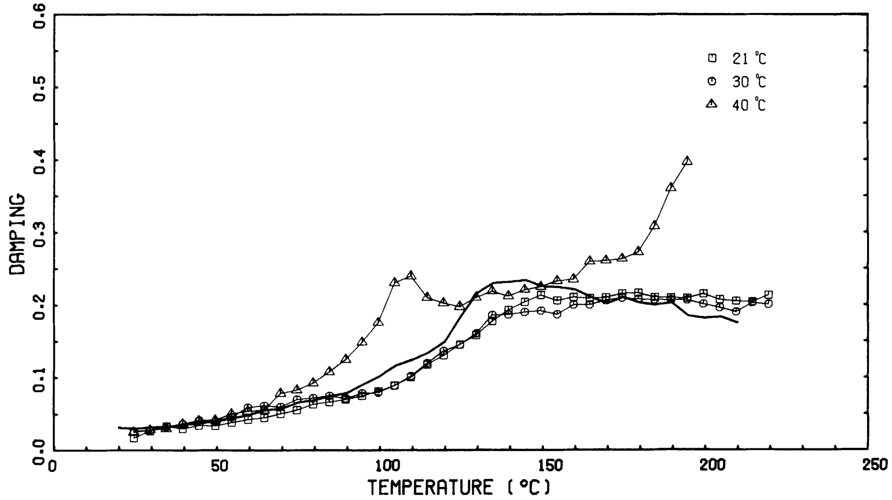

Fig. 10b—Damping *versus* temperature for zinc chloride-treated grafted (22 per cent polystyrene) fibres. The heavy solid line represents the untreated fibre

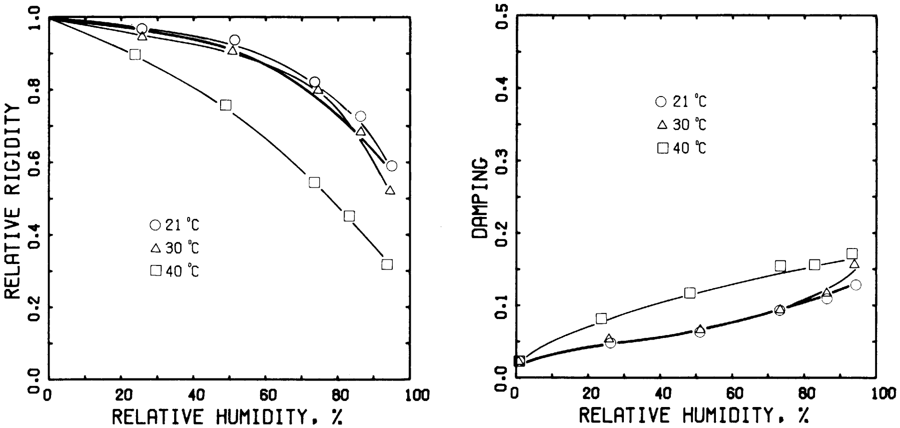

Fig. 11—Relative rigidity and damping *versus* relative humidity at 25° C for zinc chloride-treated grafted (22 per cent polystyrene) fibres. The heavy solid line represents the untreated fibre

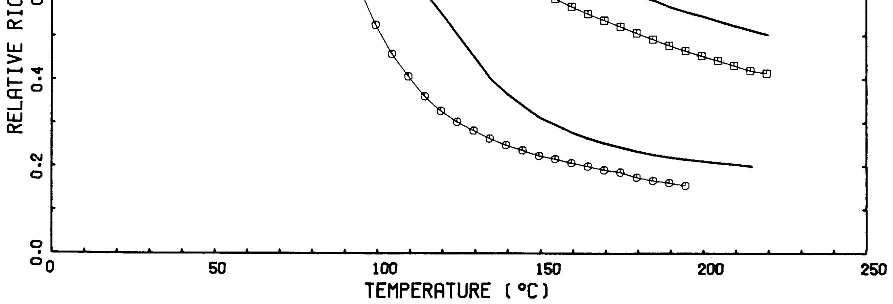

Fig. 12a—Relative rigidity *versus* temperature for zinc chloride-treated ungrafted and grafted (35 per cent polystyrene) fibres. The heavy solid lines represent untreated fibres

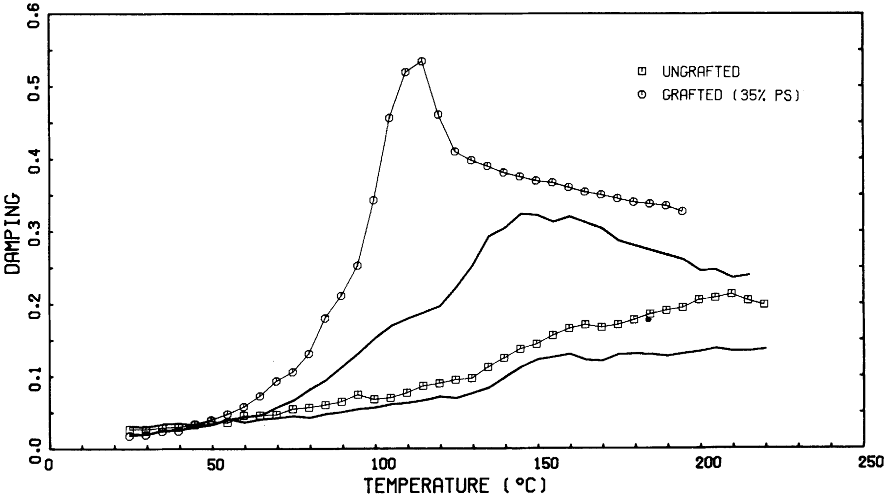

Fig. 12b—Damping *versus* temperature for zinc chloride-treated ungrafted and grafted (35 per cent polystyrene) fibres. The heavy solid lines represent untreated fibres

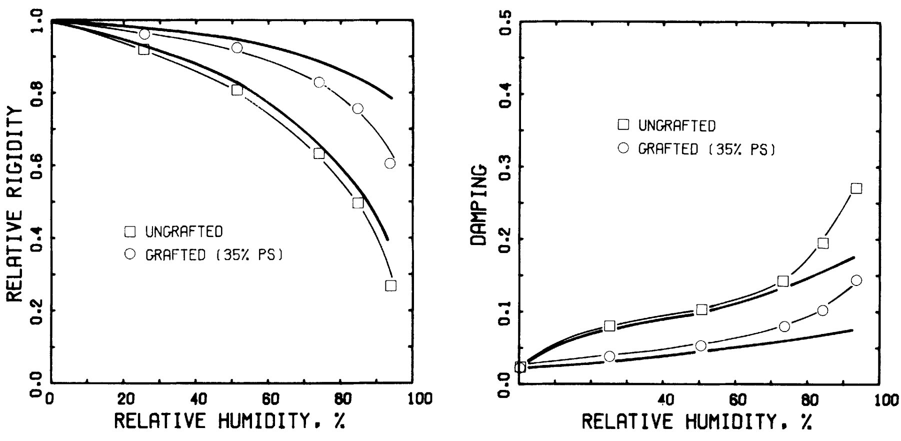

Fig. 13—Relative rigidity and damping *versus* relative humidity at 25° C for zinc chloride-treated ungrafted and grafted (35 per cent polystyrene) fibres. The heavy solid lines represent untreated fibres

At 95 per cent relative humidity the fibre exhibited a slow continuous twist, probably due to creep deformation, a behaviour not normally found for pulp fibres.

The damping peak of free polystyrene is exhibited at about 105° C for the zinc chloride-treated graft containing 35 per cent polystyrene. The level of damping in the vicinity of the peak is probably increased by a simultaneous twist at a rate comparable to the frequency of the oscillations.

Evidently at the higher graft level the relaxation behaviour of polystyrene is more sensitive to the treatment with zinc chloride than at lower graft levels. This may be interpreted as meaning that a smaller extent of degradation of the carbohydrated matrix is necessary to 'free' the polystyrene chain.

3—*Creep measurements in air and solvents*

The influence of polystyrene and zinc chloride treatment on the normalised creep deformation and relative rigidity was studied for the fibres tabulated in Table 4.

The results in Table 5 show that the creep behaviour of the ungrafted fibre is the same in both toluene and air. This is expected as toluene plasticises only the polystyrene in the grafted fibre.

Fig. 14 shows that the tensile rigidity is decreased when the polystyrene component is plasticised with toluene. In comparison, softening the carbohydrate component with water seems to be a much more effective means of reducing the rigidity in tension. This indicates that the stress transfer to the

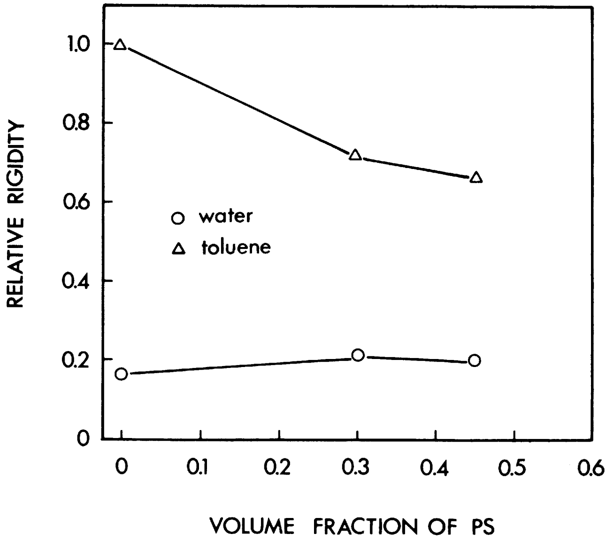

Fig. 14—Relative tensile rigidity in water and toluene *versus* polystyrene content

TABLE 5—CREEP MEASUREMENTS OF FIBRES IN AIR, WATER AND TOLUENE

Weight (%)	PS volume fraction	$ZnCl_2$ treatment			Solvent	Elastic recovery in air (ER_I) (%)	Elastic recovery in solvent (ER_{II}) (%)	Relative tensile rigidity	Creep deformation (CD)	Normalised creep deformation (CD′)
		[$ZnCl_2$] (%)	Temp. (°C)	Time (min)						
0	0	—	—	—	air	1·58	1·58	1·00	1·58	1·00
0	0	—	—	—	air	1·36	1·26	1·08	1·10	0·81
22	0·30	—	—	—	air	1·10	0·86	1·28	0·95	0·86
35	0·45	—	—	—	air	1·02	1·05	0·97	0·86	0·84
0	0	—	—	—	water	0·38	2·38	0·16	10·58	27·84
0	0	65	21	120	water	0·60	8·83	0·07	13·56	22·60
22	0·30	—	—	—	water	0·43	2·04	0·21	7·87	18·30
22	0·30	70	21	120	water	0·96	5·10	0·19	21·10	21·98
22	0·30	70	30	120	water	1·24	5·17	0·24	14·14	11·40
35	0·45	—	—	—	water	0·38	1·90	0·20	4·81	12·66
35	0·45	70	30	120	water	1·20	5·85	0·21	18·14	15·12
35	0·45	70	30	120	water	0·85	8·50	0·10	23·05	27·10
0	0	—	—	—	toluene	1·36	1·36	1·10	0·73	0·54
22	0·30	—	—	—	toluene	1·07	1·49	0·72	3·82	3·57
22	0·30	70	21	120	toluene	0·79	1·68	0·47	3·70	4·68
22	0·30	70	30	120	toluene	0·68	1·26	0·54	0·87	1·28
35	0·45	—	—	—	toluene	0·36	0·54	0·67	3·27	9·08
35	0·45	70	30	120	toluene	0·66	2·42	0·27	3·96	6·00

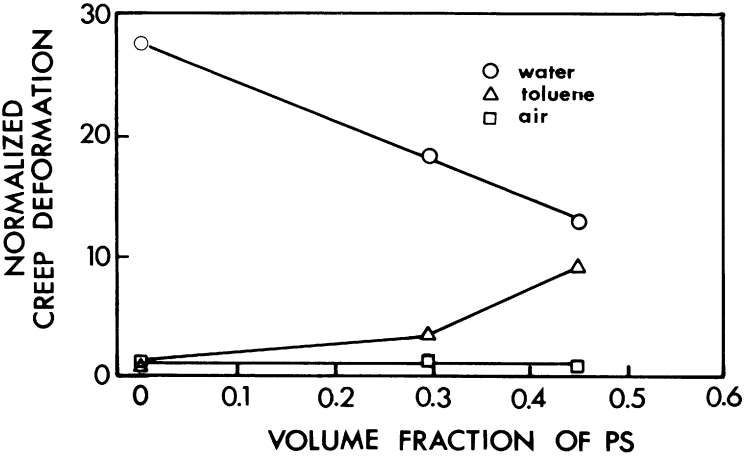

Fig. 15—Normalised creep deformation in water and toluene *versus* polystyrene content

microfibril is mainly dependent on the properties of the carbohydrate component of the matrix. A small increase in relative rigidity is, however, observed when the polystyrene content is increased. This may suggest that polystyrene can control the properties of the matrix while the amorphous cellulose still governs the stress transfer between the reinforcing microfibrils.

The creep behaviour exhibits the same general pattern as the rigidity. Fig. 15 shows that the normalised creep in water is decreased with increasing polystyrene content. The opposite is true when toluene is the plasticised agent. However, the total creep in water is higher than the creep reached in toluene for grafted fibres. This is in line with the interpretation of the relative function of the amorphous components in the matrix.

The effect of zinc chloride treatment on the relative tensile rigidity and normalised creep deformation may be derived from Table 5.

The decrease in tensile rigidity of the grafted fibres in toluene after zinc chloride treatment indicates an increased influence of polystyrene on the stress transfer of the fibre. This is in accordance with the dynamic mechanical study in which the polystyrene was softened by increased temperature. The treatment with zinc chloride leads to a more pronounced decrease in relative rigidity and the appearance of a sharper relaxation peak indicating the presence of 'free' polystyrene.

While the tensile rigidity of ungrafted cellulose in water decreases with zinc chloride treatment, no significant change is seen for the grafted fibres. The relative decrease in crystallinity on zinc chloride treatment would thus be greater for the ungrafted than the grafted fibres. This is in accordance with the interpretation of the equilibrium moisture content in Table 3.

Final remarks

THE selective softening of the matrix polymers has demonstrated the extent to which the elastic properties are dependent on the changes in the properties of the matrix. The relative decrease in rigidity ranges from 30–80 per cent depending on which component is plasticised. This is in agreement with the analysis of Mark(7) in which the influence of matrix properties on the elastic properties of the cell wall is predicted. In this analysis, it is assumed that the matrix properties change by a factor of 1 000, which corresponds to a transition from a glassy to a rubbery state. It may be noted that the relative change in modulus is dependent on the orientation of the microfibrils. This effect is more pronounced in tension than for the shear mode.

An alternative analysis of the contributions of the components to the stress transfer in a semicrystalline system has been suggested by Smith *et al.*(30) In this approach, the system is treated as a combination of a series and a parallel coupling of elastic moduli for the components. The relatively small change in the fibre modulus on softening indicates that the microfibrils and the matrix components must be considered to act mainly in parallel. In order to allow the polystyrene to take a more active part in the stress transfer it is evidently necessary to break down the cellulose, as shown by the experiments with zinc chloride treated fibres.

The creep tests performed in this study indicate that plastic flow of the fibre is more enhanced when the carbohydrates are softened with water than when the polystyrene is softened with toluene. It is suggested that the carbohydrate is the stress-transferring medium surrounding the microfibril. Obviously this implies consequences with regard to the localisation of the components which will need further verification by suitable microscopic techniques.

An interesting aspect in the pendulum measurements is the broadening of the relaxation spectrum of the polystyrene. The drastic shift in fibre modulus corresponding to a conventional transition from glassy to rubbery state does not take place. Instead, a more gradual decrease in the elastic properties is observed. It is not unlikely that the amorphous wood polymers are subjected to the same kind of shifts of the relaxation characteristics. This undoubtedly corresponds to the gradual decrease in elastic properties of wood fibres on increasing the humidity or the temperature.(12)

To make comparisons between the performance of lignin in high-yield fibres and the behaviour of polystyrene as described in this study is inescapable. In many respects lignin-rich fibres display the same characteristic changes in elastic properties with changes in humidity and temperature. However, it still remains to make a close examination of this kind of fibre with the techniques described in this study.

Finally, it is obvious that information concerning the stress transfer situation and morphology of the matrix polymers in high-yield fibres is needed to permit an intelligent approach to designing process techniques for the improvement of high-yield fibres.

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Transcription of Discussion

Discussion

Prof. R. H. Marchessault In what form do you see the amorphous cellulose? Would it be amorphous oriented at the surface of the microfibrils such as the Frey-Wyssling model which Dr Scallan showed on Monday?

de Ruvo The configuration of amorphous cellulose is difficult to envisage but our results indicate to some extent that the amorphous cellulose which is important for the stress transfer must be coupled in series with the crystalline cellulose. Thus it is the coupling agent between crystalline regions. At least that is one suggestion. The degree of order has been a long-term question for a crystalline cellulose and all other forms of cellulose have been discussed, so I won't go into more detail than that.

Dr A. A. Robertson Have you given any consideration to the possibility that some crystalline polystyrene might have been formed due to the structure and geometrical restraints of the microfibril system. One might imagine that the polymerising polystyrene chains could be aligned to such an extent that they form crystalline material. If so, the melting point would be very much higher than any of the temperatures that you have looked at. This might upset some of your conclusions. I ask this because there was a suggestion in one of your experiments in another grafting system, that crystalline polystyrene was being formed although we can't say so with certainty.

de Ruvo This question can be better answered by Prof. Stannett.

Prof. V. T. Stannett All the polystyrenes after isolation are easily soluble in cold benzene whereas crystalline polystryene isn't. So if there is any it is a very small amount.

Dr H. G. Higgins The moisture-induced transition at ambient temperatures in the vicinity of about 70 per cent RH, presumably in the hemicelluloses,

Under the chairmanship of Dr N. K. Bridge is interesting from a practical point of view. McKenzie and I drew attention to this in an unpublished paper we delivered at an Appita conference a few years ago. In Australia we test our paper at 65 per cent RH which seems inappropriate because it is near the transition point. In U.S.A. and in U.K. it is 50 per cent RH.