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MODIFICATION OF THE MECHANICAL PROPERTIES OF PAPER BY THE ADDITION OF SYNTHETIC POLYMERS

A. A. ROBERTSON, Pulp & Paper Research Institute of Canada, Montreal, Canada

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Synopsis Polymers have been incorporated into paper by (*a*) solution impregnation, (*b*) latex impregnation and (*c*) latex beater addition.

Their effects on the strength properties of the sheet were measured by conventional tests and interpreted in terms of the separate effects of the polymers on bonds and fibres and the distribution of polymer in the sheet. It is noted, however, that the introduction of polymer resulted in time-dependent behaviour that deserves special consideration. Stress relaxation properties were therefore examined and analysed for a variety of polymers and conditions.

A procedure is described in which experimental data relating to relaxation and creep are conveniently obtained and can provide the basis for evaluation and analysis.

Introduction

THE concern felt by the papermaker about the competition between polymers and paper for future markets is evident in several recent surveys,(1–3) yet among the encouraging possibilities is the continued development of products based on combinations of polymer and paper. Such combinations are not new and many paper products incorporating rubbers or plastics are in wide use.

Incorporation of polymer into the sheet may be effected by additions before, during or after the papermaking process and it may be added as solution or latex or as synthetic fibres. Whatever the method of introduction and whatever the purpose of the addition, the mechanical properties of the sheet are altered and reflect the properties, distribution and interactions of the polymer. It is the purpose of this paper to make some observations about how paper properties change when polymer is added.

It cannot be expected that any detailed understanding of the mechanical

Under the chairmanship of Prof. V. T. Stannett behaviour will be readily found, considering the complexity of the system. Studies of the mechanical properties of paper have been in progress for some time(4–6) and non-woven, polymer-bonded fabrics have received a good deal of attention.(6–10) These studies can contribute to an understanding of the impregnated paper sheet, though the latter may be more complex, because the cellulose fibre, the cellulose interfibre bond and the polymeric binder and reinforcement are all involved.

The experimental work that we will introduce into a more general discussion involves the incorporation of a variety of polymers into paper. They are introduced into the sheet in one of three ways—

1. Solution impregnation of a bulky saturated paper with polymer in an organic solvent.
2. Emulsion or latex impregnation of a similarly formed sheet.
3. Addition of latex to stock before sheet formation.

These three methods of addition are intended to produce different effects. The addition of polymer by *non-aqueous solution* does not reduce the cellulose-cellulose bonding in the sheet, but the polymer is adsorbed or deposited to reinforce the existing bonding, to stiffen the fibre by encapsulation and, if there is enough, to fill pores. The impregnation of a sheet by *aqueous latex* has all the effects of solution impregnation, except that some of the original bonds are broken by water and replaced by polymeric interfibre bonds. The *wet end addition* of latex goes much further than impregnation in the substitution of polymeric interfibre bonds for direct fibre bonding.

Strength properties

THE effects of the polymer additions may be examined first by load/elongation curves and other conventional testing. Several generalisations can be made concerning the role of polymer properties and the method and level of addition based both on current and past work.

All the polymers added by organic solution increased the strength properties as expected. The original sheet strength is preserved and the polymer augments it. Fig. 1 shows the tensile strength of a saturating paper impregnated with several different polymers from the same solvent, dichloroëthane.

The effect of the polymer on strength is greater as one goes from an amorphous rubber polyisobutylene (1), to a viscoelastic polymer, polyethylene-polyvinyl acetate copolymer (2), to the brittle polymers polystyrene (3) and polymethylmethacrylate (4). Polyvinyl acetate (5), which at the testing temperature is near its glass transition point, shows a curve shape like the softer polymers, but, because of its adhesion to the cellulose and the speed of testing, it is as effective as harder polymers.

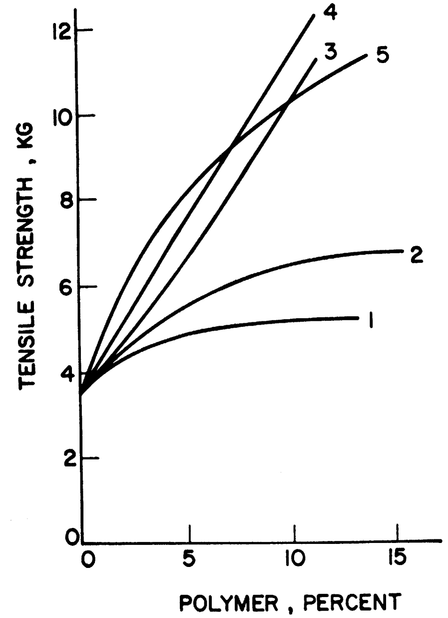

Fig. 1—Tensile strength of paper containing various amounts of polymer introduced by solution impregnation—(1) PIB; (2) PE/PVAc; (3) PS; (4) PMMA; (5) PVAc strip width 15 mm; paper grammage 220 g/m²

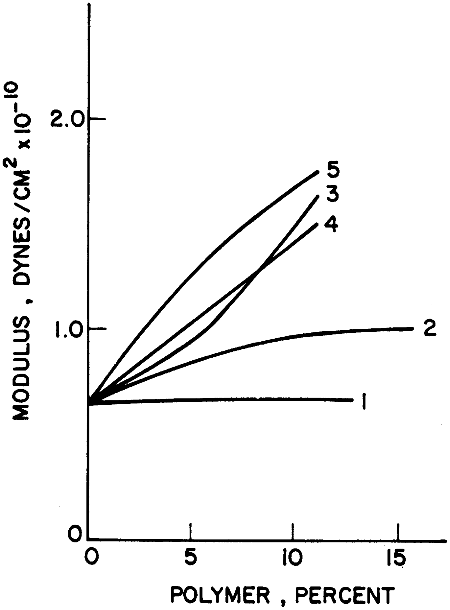

Fig. 2—Modulus of impregnated paper: additions and polymers as in Fig. 1

The modulus shows a similar pattern, although different in detail (Fig. 2), though the stretch increases as in Fig. 3.

Latex impregnation of the sheet produced a wider difference in behaviour. Eight different acrylic latices (Table 1) were tested and are arranged numerically in increasing order of hardness (cf. McLaughlin(11)).

The tensile strength was increased by all the latices, except the softest and in approximate order of their hardness in conformity with previous reports.(12)

TABLE 1—ACRYLIC EMULSIONS USED FOR IMPREGNATION

Code	1	2	3	4	5	6	7	8
Designation	P497	K3	K14	K87	HA8	E32	HA12	HA16
T_{300}	−17	−32	−47	−18	−14	−2	+17	+33

Note that T_{300} is the temperature (°C) at which the modulus is 300 kg/cm²
The designations are those of the manufacturer Rohm and Haas

Some of the results are given in Fig. 4. Initial modulus is plotted as a function of tensile strength and all curves originate with the values for the control

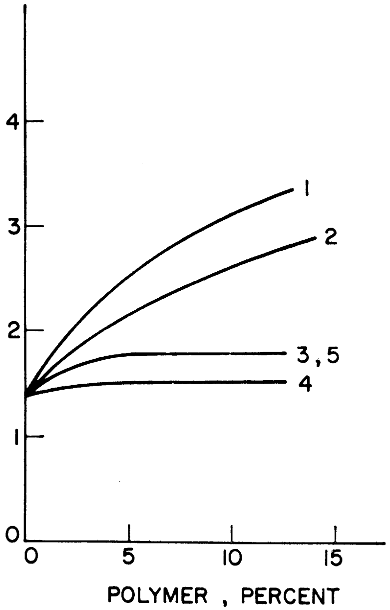

Fig. 3—Stretch of impregnated paper: additions and polymers as in Fig. 1

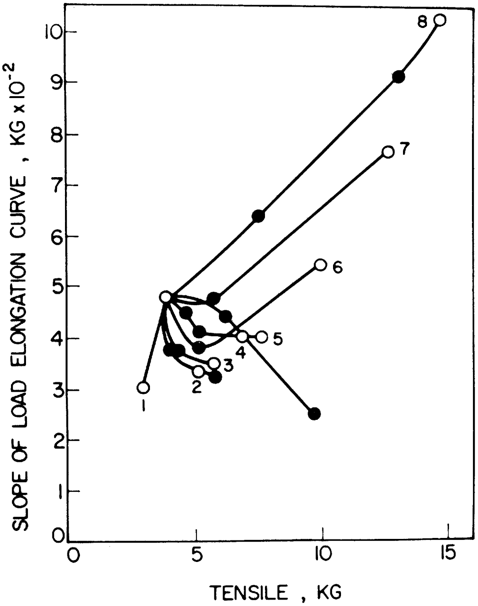

Fig. 4—Initial modulus plotted as a function of tensile strength: each curve represents increasing additions of a given polymer (Table 1), the untreated sheet and the 30 per cent addition levels are represented by open points

paper. The curves are drawn for increasing addition; open points represent a level of 30 per cent polymer added to the sheet. The corresponding stretch data appear in Fig. 5.

The modulus decreases at low additions with the soft polymers and is presumably due to deformable polymeric bonds replacing direct interfibre bonding. The modulus can subsequently increase as more polymer is added (curve 6) and as fibres are thereby stiffened or the interspaces filled. Polymer 8, which increases the modulus at all levels of addition, is the hardest polymer with a glass transition near room temperature.

The stretch exhibited by both solution-impregnated and latex-treated sheets is consistent with the independent variation of strength and modulus. If the strength increase can be attributed to strengthening of bonds and the increase of modulus to the stiffening of fibres, it is logical that the stretch should increase if the bonding is enhanced more than the fibre stiffness. This is shown in Fig. 3 & 5, in which the stretch tends to be greatest when the tensile/modulus ratio is high.

The addition of latex to the stock before sheetforming produces effects that are more difficult to assess in a systematic way. The mechanical properties depend more on the polymer presence because of the greater participation of polymer in the interfibre bonding.

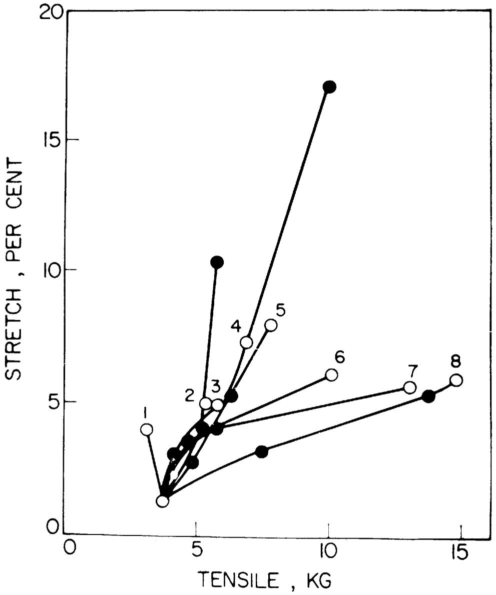

Fig. 5—Stretch as a function of tensile strength for latex-impregnated papers: additions and polymers as in Fig. 4

Even so, considerable variability is introduced by factors controlling the retention of the polymer in the sheet, the distribution of the polymer on the fibres and the formation and structure of the sheet. These are controlled or influenced primarily by colloidal properties so that effects caused by particle size, dispersion, concentration, stabilisers, electrotyte concentration, pH value and the timing and sequence of addition are added to all the polymer variables and papermaking variables that determine the final properties of the sheet.

The latex that is added to the stock can be deposited to form a uniform fibre coating; or coagulated and deposited as aggregates; or it may be lost from the sheet in the whitewater as a stable latex or as coagulum. The choice of appropriate conditions to produce optimum retention and distribution appears to be based as much on art as science, although de Mendoza & Bobalek(13) have clarified many of the observed phenomena.

The variability that we have emphasised has so far discouraged us, as it has discouraged others,(14) from attempting a quantitative study of beater addition, yet some general comment can be made about wet end latex additives and their effect.

The majority of reports seem to suggest that beater addition of latices reduces dry tensile strength relative to the saturation impregnation treatment and sometimes even to the untreated controls.(11, 13, 15) Rahman(16) compared solution impregnation, latex impregnation and wet end latex addition using the same polyvinyl acetate. The wet end addition was considerably less effective in enhancing strength properties than the other two. Heyse(14) found a contrary result in another system.

Our results obtained with the addition of acrylic latices to the stock were quite variable in both retention and effect, but they suggested that addition to the stock improved the strength of weak alpha-cellulose fibre sheets and impaired the strength of a strong kraft. The result confirms a similar finding of Usuda *et al.*,(17) who found (similarly with polyvinyl acetate) that the interfibre bond produced by polymer may be greater or less in extent or quality than the cellulose bond that would otherwise form, depending on the type of fibre and polymer.

It must be noted that, although tensile strength is often decreased, beater latices can improve other important properties,(17–21) including elongation, wet tensile, edge tear, fold and ply adhesion.

A general principle becomes clear from this cursory examination of load/elongation testing. The observed effects and their relation to the method of addition are primarily due to the extent of cellulose-cellulose bonding and the degree to which it is supplemented or supplanted by polymer bonds.(18)

Thus, the strength is improved by solution impregnation and may be improved or impaired by latex addition. The modulus is related to the rigidity of the bonds and of the fibre and may be modified by the degree of encapsulation and reinforcement. The modulus and strength may be somewhat independent as we have shown. A similar independence of strength and modulus has been demonstrated when paper is immersed in various liquids.(22)

Polymer-fibre interactions

THE importance of the modulus and cohesive strength of the polymer is obvious, but there are of course additional important considerations. The adhesion of the polymer to the cellulose plays an important role,(23) particularly for soft polymers and for low levels of addition. The role of functional groups in improving the adhesion of latex polymers has been noted.(11, 12, 24, 25) The effectiveness of polymers of similar modulus at low levels of solution impregnation or latex addition(23) are in order of their interaction forces with cellulose as determined from adsorption and desorption studies.(26)

The polymer-cellulose interface is also affected by the presence of plasticisers and emulsifiers, which can adsorb preferentially to form weak boundary layers.(23) When anionic latices are added in the beater or as saturants, the precipitation on the fibre may be induced by deposition aids,(15, 25, 27) often cationic polyelectrolytes, that then may play a role in the mechanical properties of the interface.

Although it may be of less importance, it is of interest that the polymer structure and properties may be modified close to the interface. The interaction forces affect the molecular orientation and Mizumachi,(28) for example, has demonstrated a change in glass transition temperature of SBR and NBR rubbers adsorbed on wood. The extraordinary properties of thin polymeric films(29) may also come into play. Rahman(16) has noted higher tensile, but lower stretch in latex films in solvent-cast films with polyvinyl acetate.

The ability to form a film is essential with latex additions and the effectiveness of a polymer is related to its minimum film-forming temperature (MFT),(31) its tack temperature,(30) its inflection temperature T_i or similar characteristic softening point.(14, 17, 24, 32) Since film-forming ability and the modulus of the binder are more or less inversely related, an optimum effectiveness in relation to strength is often found with intermediate 'hardness'.(31, 32) The effectiveness of harder latices can be improved by fusing or curing at higher temperatures.(11, 23)

The distribution of polymer in the sheet is rarely uniform. Migration to the evaporating surface is commonly observed and less commonly controlled. This occurs with both latices(33) and solution impregnation.

With latices, particularly in beater addition, the uniformity of deposition is a function of the coagulation or aggregation occurring before deposition and its control is the basis of the art of wet end addition. To complicate matters, it is not always clear whether uniform distribution is desirable. A continuous film can prevent cellulose bonding and it is likely that the distribution should be such that both natural and reinforcing bonds can develop.(34)

Another note should be made concerning the change of sheet properties as more polymer is added. It might be expected that, as with other additives, property changes are proportionately greater at low additions and more modest as more polymer is added. This is not always true and results from various sources suggest that there are two points of interest in the relation between properties and level of addition.

One of these is the level at which the fibres become completely coated wtih polymer. With latices, this may be at 5–8 per cent(13) and properties may change abruptly at this point. Another point is at higher additions, perhaps

50–100 per cent, depending on sheet structure when the pores or interfibre spaces become significantly filled with polymer,(12, 35, 36) reducing the deformability of the sample and initiating the transition from polymer-reinforced paper to paper-reinforced polymer composites. This is frequently suggested by stretch going through a maximum and decreasing as the modulus increases faster than the strength. Other properties have been shown to have optimum values in this range as well.(12, 14, 35, 36)

Another general observation is that, when properties are improved by polymer addition, the anisotropy of sheet properties is usually reduced, since the polymer effects are non-directional.

Time-dependent effects

THE stress/strain curves that are obtained for polymer-treated sheets are similar in shape to those for paper, but it would be wrong to conclude that the mechanisms of deformation and failure remain the same. As direct fibre bonds are replaced and as stresses are shared by viscoelastic polymers, ideas of elastic deformation, brittle failure, stress concentrations and sequential loading must be modified.

The change from elastic to viscoelastic behaviour is gradual and cannot be readily followed by examining stress/strain curves, so other approaches are required. The rate of elongation now becomes important in the testing of samples. This is evident in the load/elongation curves in Fig. 6 at different rates. The deformation and failure properties are little changed for paper by a 20-fold change in rate (cf. other authors (5, 37–41)), but a polymer-treated sheet shows increasing tensile, stretch and modulus with increasing rate of strain.(14, 18) In other cases, the initial modulus and stretch may be less affected than the post-yield properties and tensile strength.(11)

Recently, Guthrie & Fulmer(42) have shown dramatic evidence of time-dependent behaviour in this field. They determined the time to rupture the sheet as a function of the load applied. At short times, corresponding to conditions of conventional testing, a typical latex-impregnated sheet required a much higher load to rupture it than did the untreated sheet. On the other hand, under a sustained low load—really, a creep experiment—the untreated sheet was found to outlast the impregnated sheet by perhaps thousands of times. Thus, time dependence is a factor of some significance in the general testing of polymer-treated paper.

In addition, the time-dependent properties are often of specific importance to the products in which polymer-treated papers are used. Packaging, sack papers, textile substitutes, gaskets and tapes are examples in which response to creep and cyclic loading are important.

Creep and stress relaxation experiments have become conventional approaches to the study of the mechanical properties of polymers and other materials over extended time periods, whereas dynamic (vibrational) testing methods are appropriate for studying deformation on a shorter time scale. All have been applied to studies of the mechanical properties of paper—creep by Brezinski,(43) stress relaxation by Kubát(44, 45) and dynamic methods by Kurath(46) and Craver.(47) Limited measurements of time-dependent properties of polymer-paper composites have been reported using techniques of recoverable creep(14) and resilience.(11) Although these studies have been illuminating, their interpretation is hampered by the complexity of the structure being studied.

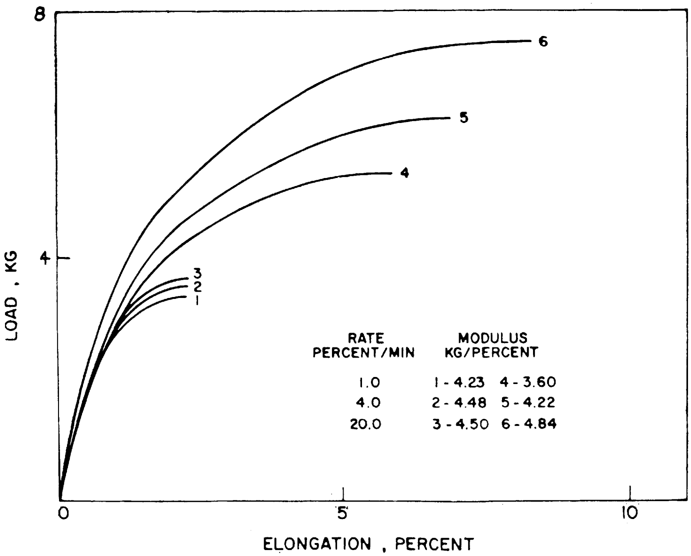

Fig. 6—Load/elongation curves for paper (curves 1, 2 and 3) and for latex-impregnated paper (20 per cent latex 7) at different rates of extension

Our understanding of the mechanical properties of polymers has grown from studies of ideally amorphous polymers that show brittle, viscoelastic, rubbery or viscous behaviour depending on the temperature or the time scale of the experiment; thus, a systematic description of behaviour in deformation and failure has been built up on the basis of theory and experiment using such materials. This concept of mechanical behaviour based on idealised molecular processes requires modification when it is extended to partially crystalline polymers, copolymer or composites. The description cannot be expected to apply to *paper* without even greater modification. The structure is not a continuum, the cellulose is primarily crystalline and deformation appears to occur by sequential bond failure, as well as by molecular processes.

To this bonded network system, whose time-dependent mechanisms are not at all well understood, we are now adding a viscoelastic polymer that provides deformable bonds and reinforcement.

Stress relaxation

We have attempted to follow the changes that are produced by addition of polymers to the sheet, by following the stress relaxation behaviour of paper with and without polymer addition. Typical stress relaxation curves are shown in Fig. 7. Polymer additions are 10 per cent and strain is 0·5 per cent. Addition is by solution impregnation.

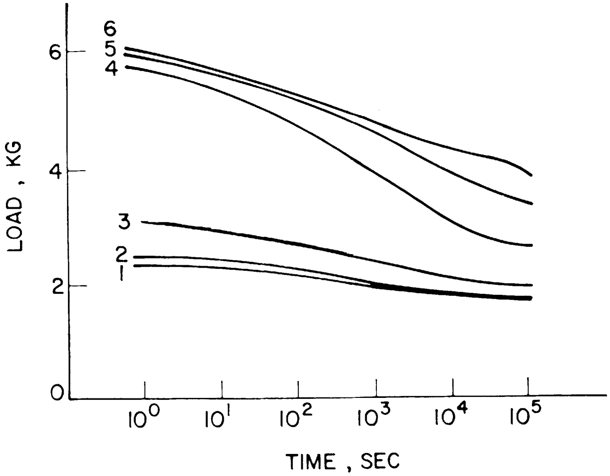

Fig. 7—Stress relaxation curves for paper containing polymer introduced by solution impregnation—(1) Control; (2) PIB; (3) PE/PVAc; (4) PVac 30° C; (5) PBAc 23° C; (6) PS

Although the modulus is changed and therefore the initial stress, the shapes of the curves are not greatly altered. Soft rubbery polymers added to the paper do not sustain stress and the curve for polyisobutylene (PIB) addition (curve 2) is close to that of paper alone (1).

The brittle polymer bears much of the stress in a paper-polystyrene (PS) composite, but the relaxation rate is *proportionately* not greatly different than for paper itself (cf. curves 6 and 1).

A viscoelastic polymer polyvinylacetate (PVAc) at 30° C (above its glass transition point) bears stress at short times like PS and exhibits high modulus and high tensile strength by conventional testing, but the stress borne by the polymer relaxes more quickly and the curve (4) is steeper than for paper (1) or paper plus PS (6).

One basis for comparing stress relaxation properties is, following Kubát,(44, 45) to evaluate the maximum stress relaxation rate $(d\sigma/d \log t)_{max}$, a quantity given the symbol *F*. We had anticipated that the position of the maximum slope relative to the time axis would show significant variation. This has proved to be a rather insensitive and unreliable criterion of behaviour.

The maximum slope *F* is significant in two ways and is related to the possible stress relaxation by—

$$F = 0{\cdot}23\ (\sigma_0 - \sigma_p) \text{ or } F/\sigma_0 = 0{\cdot}23\ (1 - \sigma_p/\sigma_0) \quad . \quad . \quad (1)$$

where σ_0 is the initial stress and σ_p is the apparent plateau value at extended times. Kubát(48) has shown that this has a wide range of validity for polymers, paper, metals, crystals, composites and other materials. The validity has been verified in the current work and the constant appears to fall within the limits 0·18–0·24.

The quantity $(F/0{\cdot}23\sigma_0)$ can thus be regarded as a measure of the fraction of the initial stress σ_0 capable of relaxation, the remainder representing the elastic component of σ_0.

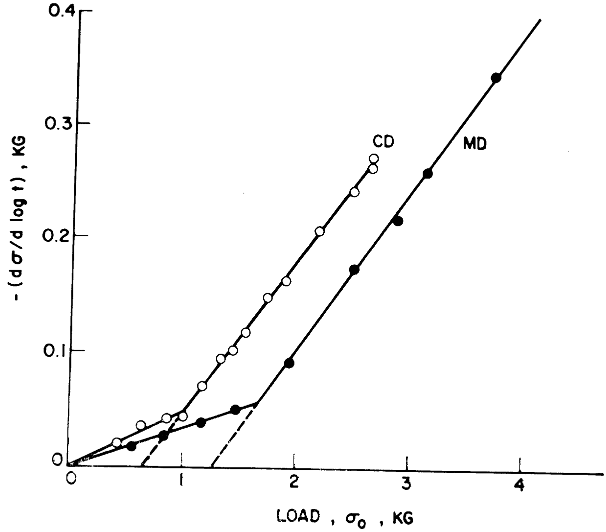

Fig. 8—Maximum slope of stress relaxation curves plotted against initial load for cross-direction and machine-direction

The slope *F*, plotted as a function of the initial stress, provides some description of the stress relaxation properties of the sheet.(44, 45, 49) Two such graphs for paper are shown in Fig. 8. The lower rates of relaxation at lower stresses are correlated with the initial part of the load/elongation curve, in which, because of tensions during drying, the initial stress is borne by elastic elements. The graph for a freely dried sheet passes through the origin at the steeper slope.

A variety of behaviour is shown in similar graphs for sheets impregnated by acrylic latices at the 30 per cent level and by 10 per cent PVAc solution (Fig. 9). The attainable stresses and the stress relaxation rates are increased substantially by all the polymers. The low relaxation rates corresponding to the initial 'elastic' part of the load/elongation curve are present with the PVAc, but are absent for the acrylics, owing to relatively stress-free drying after impregnation.

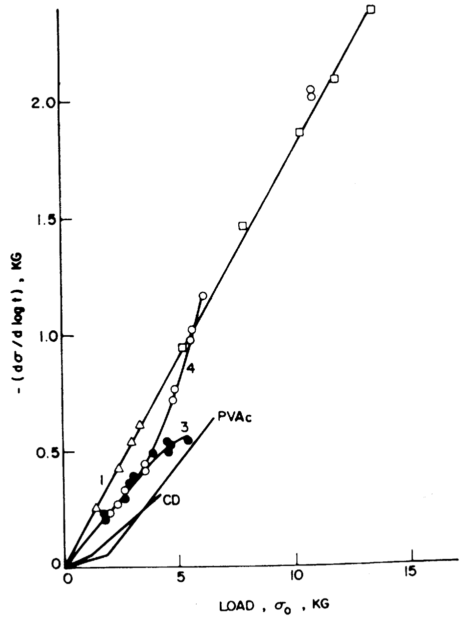

Fig. 9—Maximum slopes of relaxation curves plotted against initial load—CD paper; PVAc solution-impregnated 10 per cent; 1, 3, 4, 8 acrylic latices (Table 1) at 30 per cent level

The $(F - \sigma_0)$ relationship is similar for the weakest (1) and the strongest (8) polymers, although over a different range. Here, the common slope is 0·18 and equation (*1*) suggests that approximately 80 per cent of the initial stress is capable of stress relaxation compared with only 25 per cent in the corresponding untreated paper at low stresses and no more than 50 per cent at high stresses.

The graph indicated by polymer 4 shows an increasing slope. A similar curvature has been noted with other softer polymers. It is suggested without further evidence that the proportion of stress borne by the polymer increases as the sample is strained. The opposite curvature of sample 3 is unexplained, except by the possibility of some sort of strain hardening, which may be characteristic of the one polymer (K14) that we have found to show the behaviour.

Whether or not these tentative explanations are true, it is evident that the observed properties of the sheet can depend not only on the properties of the fibre, the polymer and the interface, but also on the extent to which the strain is taken up by the two components and the proportion of the stress that is borne by each. Furthermore, it is possible that the distributions of stress and strain change with deformation and time.

The effects produced by polymers introduced by non-aqueous solution impregnation on time-dependent properties are considerably less than those produced by aqueous latex impregnation. The restrictions imposed by the inextensibility and the limited relaxation of the intact fibre network are evident in the results. It is apparent in Fig. 7 that the base sheet largely determines the course and limit of stress relaxation.

Temperature and humidity

SOLUTION impregnation of PVAc has been shown (Fig. 7) to produce substantial changes in stress relaxation. These have been examined further by varying the temperature and humidity and observing the effect on $(F - \sigma_o)$ curves similar to the PVAc curve in Fig. 9. The intercepts produced by extension of the steeper slope to the load axis persist, because the drying stresses in the base stock remain after impregnation. These intercepts are also responsive to temperature and humidity.

The slope increases and the intercept decreases with increasing temperatures at constant humidity and with increasing humidity at constant temperature (Table 2). The same qualitative effects can be observed in similar tests on the base sheet, though it is evident that the untreated paper sheet is relatively insensitive to temperature and is more sensitive to humidity, whereas the polymer sheet is sensitive to both humidity and temperature.

The intercepts that relate to the existence and effect of elastic processes show decreases with humidity both for the treated and untreated sheets, presumably as dried-in stresses are relieved. The behaviour with temperature is rather more erratic, but it may be noted that the intercepts become small for impregnated sheets above the glass transition temperature for PVAc (27° C).

TABLE 2—EFFECT OF TEMPERATURE AND HUMIDITY ON THE PROPERTIES OF PVAc COMPOSITES

	11° C		*23° C*		*35° C*	
Conditions	*Paper*	*Composite*	*Paper*	*Composite*	*Paper*	*Composite*
50 per cent r h						
Slope	0·085	0·105	0·090	0·13	0·10	0·16
Intercept	0·50	1·2	0·65	1·6	0·70	0·3
Modulus	4·9	10·7	4·5	10·6	3·7	6·6
70 per cent r h						
Slope	0·095	0·110	0·095	0·14	0·10	0·16
Intercept	0·35	0·9	0·25	0·5	0·35	0·3
Modulus	3·7	8·2	3·5	8·4	3·0	5·1
85 per cent r h						
Slope	0·105	0·125	0·100	0·145	0·115	0·16
Intercept	0·20	0·8	0·10	0·0	0·10	0·3
Modulus	3·3	7·2	3·3	5·6	2·5	3·2

Slopes of the (F—σ_o) curves are dimensionless; intercepts on the load axis are expressed in kg; moduli in kg/per cent

The modulus is also included in Table 2 and shows the decreasing trend in strength properties with temperature and humidity. A large effect is again noted for a temperature increase above the glass transition of the polymer.

Stress relaxation measurements have not yet been attempted with samples formed by beater addition of polymer latices, but it is sufficiently clear from the results described so far that the introduction of synthetic polymers into paper can profoundly affect the time-dependent properties of the resulting material and that these are varied systematically and can be compared.

Evaluation methods

The determination of stress relaxation or creep curves provides a graphical record, but appropriate means for extracting numerical data to facilitate practical evaluation or to permit meaningful comparisons of samples is required. The evaluation of the maximum slope F has been shown to provide a means of demonstrating systematic variations, but the procedure is not particularly facile or adaptable.

A more pragmatic and flexible procedure can be based on the use of an Instron or equivalent test apparatus that is adaptable to cyclic loading and to the measurement of stress relaxation. In recent studies, these facilities have provided a technique for approximate assessment of the creep and stress relaxation properties of paper and polymer-paper composites. A typical procedure is that the normal load/elongation curve is interrupted at a specified load and the stress allowed to relax for a given time, say, 10 min; the load is then restored by elongation. The cycle may be repeated (Fig. 10) to give a series of stress decrements ($\Delta\sigma$) and strain increments ($\Delta\gamma$) that reflect the stress relaxation and creep properties at the selected load. The method has previously been used in studies of the mechanical properties of wood.(50)

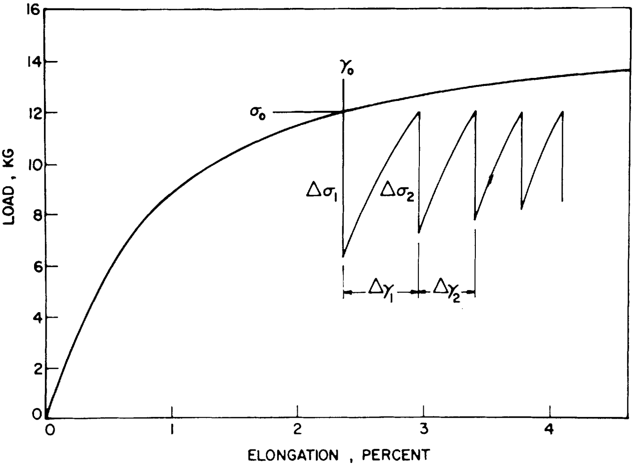

Fig. 10—Load/elongation programme incorporating cycles of stress relaxation: initial load (σ_0) and elongation (γ_0) are followed by stress decrements ($\Delta\sigma$) and strain increments ($\Delta\gamma$)—see text

The programme may be modified by varying the imposed load, the duration of the relaxation and the number of cycles, depending on the sample and the information required. Details of the individual stress relaxations or load elongations may be recorded.

TABLE 3—DATA OBTAINED BY REPEATED STRESS RELAXATION CYCLING

σ_0	γ_0	σ_f	γ_f	$\Delta\sigma_1$	$\Delta\gamma_1$	$\Delta\sigma_1/\sigma_0$	$\Delta\gamma_1/\gamma_0$	$\Delta\sigma_2/\Delta\sigma_1$	$\Delta\gamma_2/\Delta\gamma_1$	$\Delta\sigma_1/\Delta\gamma_1$
Untreated paper										
1	0·23	3·60	2·05	0·14	0·023	0·14	0·10	0·38	0·30	6·0
2	0·51	3·51	2·25	0·30	0·057	0·15	0·11	0·53	0·47	5·3
3	1·06	3·60	2·22	0·55	0·120	0·18	0·11	0·69	0·64	4·6
Polymer-impregnated paper										
1	0·24	4·30	4·90	0·23	0·040	0·23	0·16	0·47	0·50	5·8
2	0·55	4·27	4·83	0·54	0·113	0·27	0·20	0·67	0·62	4·7
3	1·17	4·25	4·97	0·94	0·233	0·31	0·20	0·80	0·72	4·0

Symbols as in Fig. 10; σ_f and γ_f are load and elongation at failure
Loads (σ_0, $\Delta\sigma$, etc.) are measured in kg
Extensions (γ_0, $\Delta\gamma$, etc.) are measured in per cent

The data shown in Table 3 are typical of the results obtained for paper and for paper impregnated with an acrylic latex to the level of 25 per cent. The initial modulus is somewhat reduced (initial slopes are 4·4 and 4·1 kg/per cent, respectively), but the load and elongation to failure are increased by polymer addition and are independent of intermediate cycling.

The increase in viscoelastic properties is indicated in the table for three different load levels by the initial stress decrement $\Delta\sigma_1$; the initial creep increment $\Delta\gamma_1$; the relative creep increment $\Delta\gamma_1/\gamma_0$; and the ratio of successive relaxation decrements $\Delta\sigma_2/\Delta\sigma_1$ and strain increments $\Delta\gamma_2/\Delta\gamma_1$.

All the quantities mentioned also reflect the increased time-dependent behaviour in paper alone when cross-direction samples are compared with those in the machine-direction, high humidity compared with low, polymer-impregnated sheets with untreated. It is noted, however, that the quantities and their interrelationships vary in a different way when viscoelastic response is changed by humidity or mechanical conditioning, compared with changes effected by varying the type or amount of polymer. Different deformation mechanisms are therefore suggested, but they remain to be characterised.

Further treatment of data obtained by the procedure described can provide more information. For example, a summation of the strain increments plotted as a function of time generates a creep curve that potentially provides the information available from a conventional curve.

It has also been noted that the first stress decrements $\Delta\sigma_1$, if plotted as a function of the initial stress, appear to show the same properties as the F versus σ_0 curves previously discussed (Fig. 8 & 9). The relations of the slopes, intercepts and curvature are similar and can be interpreted as before, although a quantitative relationship corresponding to equation (*1*) cannot necessarily be expected.

The ratio of load and elongation increments measures an effective modulus that empirically relates stress relaxation and creep properties. The manner in which this changes with load or repeated cycling may provide some insight into the properties of deformation and failure. Various possibilities therefore exist and are being developed to relate these measured quantities to each other, to the processes involved and to evaluation for practical use.

Concluding remarks

THE introduction of viscoelastic polymers into a paper sheet affects the deformation and failure properties in degree and probably in kind. Time-dependent effects become more evident than in untreated paper and cannot be ignored in testing or in applications. The experiments and discussion provided here have not been related to evaluation of these materials for specific uses, although it is the purpose of the work to provide some basis for progress in that direction.

Even though the system is a complicated one and the analysis of the deformation behaviour in such a way as to identify and evaluate the processes involved—viscous, viscoelastic, elastic, slippage and failure—and their dependence on the nature and distribution of the components will not easily be achieved, the growing importance of polymer-paper composites suggests that further studies of structure/property effects could prove rewarding.

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Transcription of Discussion

Discussion

Dr K. Ebeling I would like to draw attention to two points—stress relaxation and change of modulus. I used dry paper in my study of moisture content (determined by Karl Fischer titration below 0·25 per cent). I did not observe the Kubát behaviour; there was no clear break point when plotting the relaxation speed against the unrelaxed load. The behaviour that I observed was similar to that in your Fig. 9 for the 4 per cent curve.

The other point is that the apparent initial straining modulus decreased after cycling that involved apparent plastic deformation. Only during cycling with relatively high average load did one observe that the slope of the load elongation curve was higher than the initial slope starting from zero load.

Mr A. A. Robertson We clearly have differences between us to resolve. We, too, have carried out these tests under completely dry conditions (at least as dry as anhydrous calcium sulphate can provide) and obtained the Kubát curves for a wide variety of papers. We have been able to relate the local modulus (which we measure after stress relaxation) to a local cycling modulus that also has been determined. We have found the local cycling modulus anywhere along the stress/strain curve to be higher than the initial modulus and very close numerically to that measured after stress relaxation. So our results are in direct contrast to your own.

Dr A. de Ruvo I think that Dr Robertson touched upon very important matters—what is the mechanical effectiveness of the latex in the paper structure and how do different ways of polymer deposition in the paper influence the mechanical effectiveness of the polymer? In our studies, we have worked with a torsional pendulum to measure the amount of polymer that is effective by following the damping curve with temperature. At the glass temperature, the polymer displays a damping peak, which is proportional to the amount of polymer present and mechanically active in the system. Of course, there are different ways in which the polymer can be deposited in the paper. One way is that it is between the fibres, where it constitutes the fibre bond; this is the

Under the chairmanship of Prof. V. T. Stannett most effective way if you want to use the polymer properties. The other way is on a free segment, where it is not taking any mechanical action at all; this is a very poor way of using the polymer. For Fig. G, where we have plotted the area of damping against the amount of binder, we used two different ways of putting the polymer into the system—spray bonding and beater addition. The curve shows that spray bonding is much more effective as indicated by the much higher increase in the area of the damping peak at specific loading levels.

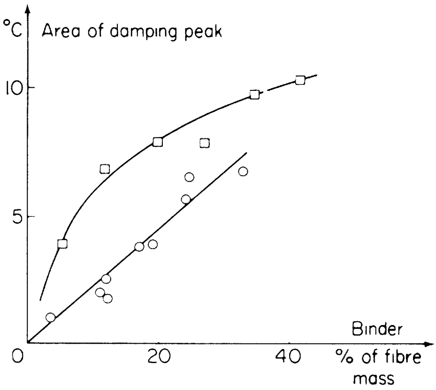

Fig. G

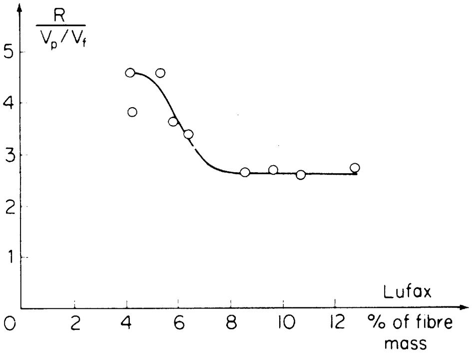

Fig. H

The same situation is shown for a more practical property—strain. Spray bonding is again the effective process for putting the polymers into the sheet.

A small comment about the colloidal system. Of course, when you are using better deposition, you have to have a colloidal system and use a retention agent. In Fig. H, we have plotted binder retention against the percentage of the retention agent (Lufax, in this case). As expected, if we overdose the system, the binder retention falls. What is important is that, exactly at the point where the retention falls, the mechanical effectiveness (that is, the damping area) also falls. This means that the mechanical effectiveness of the latex is reduced by changes in the colloidal system. Besides this, of course, the reduction of retention means that an excess of latex exists in the papermachine system, which can be rather difficult.

Discussion

Mr L. M. Lyne With the increasing limitation of petroleum in the world, do you see a limitation in the development of polymer papers over the next 25 years?

Prof. B. G. Rånby No, I don't see that, because it is a very small fraction of the petroleum that goes into the preparation of polymers. It is at present only about 5 per cent, but the burning of petroleum is 85–90 per cent, so it is in this that restrictions in petroleum usage must first apply.