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The Mechanical Properties of Latex-Treated Papers

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The use of latex-treated papers has rapidly developed in the last few years, a considerable commercial outlet being found in such fields as gasketting paper, tape backings, imitation leather, and many others. The latex may be added to the slush stock before sheet formation or may be impregnated into the formed paper sheet. The former process is difficult to control, and the properties obtained may vary considerably according to the method of addition. On the other hand, it offers considerable economic advantage and may yield products with properties unobtainable by the impregnation procedure. The latter process is easier to control and, with care, yields very reproducible results. Studies of papers prepared by both methods of addition have been reported; however, no detailed investigation of the mechanical properties of latex-treated paper has been recorded. The present paper outlines some of the results obtained from such a study. To avoid the variables encountered in the slush stock-addition method, the impregnation technique has been used throughout the major part of this investigation. A comparison of impregnation with preliminary beater addition data will be included at the end of this report.

EXPERIMENTAL

The paper used throughout most of this investigation was machine-made from a wood pulp of high alpha content specifically intended for latex saturation. The basis weight was 34.5 lb. (25 × 40 × 500) and the caliper was 5 mils. Impregnation was accomplished by soaking strips of the paper for 2 min. in the latex (longer times of immersion gave the same polymer retention), and removing excess of latex by drawing the strips through two parallel bars. The strips were hung up to dry at room temperature. No difference in polymer content was found at one end of the strip as compared to the other. The strips were then conditioned for 24 hr. at 23°C. and 50% R.H.

The beater additions were made as follows. Bleached Kraft pulp was beaten to 500 cc. Canadian standard freeness. The pulp was then diluted to a 0.18% consistency, and varying amounts of latex were added slowly to the agitated stock. Alum was added slowly to a pH of 4.5, after which the stock was mixed for another half hour. Handsheets were then made, according to Tappi standards, with a thickness of 4.4 mils for the untreated paper, and conditioned for 24 hr. at 23°C. and 50% R.H. The stress–strain curves were obtained with an Instron Model TTB testing machine, on 15 mm. × 10 cm. test specimens. For convenience in this presentation, the normal paper technology tensile units have been converted to psi; Tappi standard tests were used wherever relevant.

RESULTS

Typical values are given in Table I at two levels of GR-S (#2001) addition for wet and dry tensile properties, bursting strength, tear and edge tear resistance. It can be seen that all properties are improved by the addition of latex, particularly at the higher addition level. Results of this kind, coupled with excellent ply adhesion, chemical resistance, and other properties, have led to the widespread use of latex-treated papers for many applications.

The addition of an elastomer to paper by impregnation introduces two important factors which can greatly affect the stress–strain properties of the paper: (*1*) the stress–strain and adhesive properties of the free film and (*2*) the film-forming temperature of the latex. Furthermore, treatment of the paper with latex serum, which may contain emulsifiers, catalyst fragments, salts and unreacted monomer, may permanently break some of the bonds in most papers, causing a small decrease in the modulus of elasticity. It should be pointed out that laboratory experiments of the type described involve soaking of paper samples in an aqueous medium and redrying in the free state.

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TABLE I
Properties of Paper Treated with GR-S Rubber by Saturation

	GR-S, parts/100 parts paper		
	0	8.4	110
Burst strength, psi	10.2	17.9	37.0
Tensile strength, psi[a,b]			
MD	1900	2380	3570
CD	1000	1350	2320
Elongation[a,b]			
MD	0.0178	0.0275	0.0537
CD	0.0368	0.0625	0.1230
Wet tensile strength, psi[a,b]			
MD	279	496	666
CD	204	295	540
Wet elongation[a,b]			
MD	0.0222	0.0360	0.1450
CD	0.0647	0.0875	0.2920
Edge tear, kg.			
MD	1.50	2.32	4.14
CD	1.36	2.50	6.24
Tear, g.[b]			
MD	70	104	76
CD	84	104	108

[a] Strain rate: 6 in./min. or 150%/min.
[b] MD denotes machine direction; CD denotes cross direction.

Such a treatment with water itself can also cause a small drop in elastic modulus due to the relief of frozen-in stresses introduced during the drying under tension.

The film-forming temperature of the latex is of prime importance in choosing a latex for impregnation. To illustrate this property, a number of copolymers of styrene and 2-ethylhexyl acrylate were prepared. At room temperature all the copolymers except the 75% styrene–25% acrylate and 100% styrene were film-forming. A plot of the tensile strength of paper containing 50 parts elastomer per 100 parts paper versus the styrene content in the copolymer shows an increase in tensile strength with increasing styrene content in the region where the latex is film-forming (see Fig. 1). At the point where the latex was no longer film-forming, the strength curve was abruptly discontinuous, and the strength values coincided closely with the strength of the untreated paper. Similar curves were obtained for burst and elongation versus styrene content.

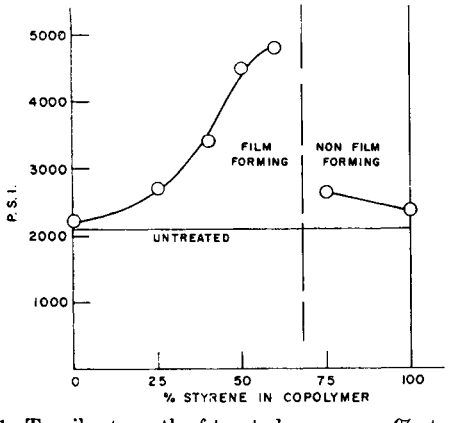

Fig. 1. Tensile strength of treated papers vs. % styrene in copolymer for film-forming and nonfilm-forming latices (strain rate: 50%/min.).

To further illustrate this point, the 75% styrene–25% acrylate latex is film-forming at about 100°C., whereas polystyrene is not. Samples impregnated with five of the latices were cured in an oven at 115°C. for 2 min. Table II shows a comparison of the tensile and elongation values at yield of the cured and uncured samples. The 75% styrene–25% acrylate values changed dramatically upon curing, the tensile strength increasing by more than 100% and the elongation increasing 45%. The polystyrene-treated papers, however, were unaffected, as were the previously film-forming latices.

TABLE II
Effect of Cure on Tensile Strength and Elongation[a]

	Tensile strength, psi		Elongation	
Polymer[b]	Uncured	Cured	Uncured	Cured
100A	2210	2180	0.0222	0.0221
75A–25S	2720	2720	0.0291	0.0261
50A–50S	4500	4100	0.0457	0.0468
25A–75S	2650	5050	0.0237	0.0342
100S	2420	2540	0.0194	0.0221
None	2100	2100	0.02	

[a] Strain rate: 2 in./min.; cure: 2 min. at 115°C.
[b] A denotes acrylate; S denotes styrene.

From these data it could be assumed that small microfilms were being superimposed on the wood fiber matrix, and photomicrographs of latex-treated papers (made by Mr. H. Yasuda in our laboratories) gave direct proof of this theory. A study of the stress–strain curves of the latex-treated papers shows little variation in the modulus of elasticity. With few exceptions, the addition of an elastomer to paper mainly improves the post-yield extensibility of the paper. A comparison of the stress–strain curve of untreated paper with the same paper treated with 50 parts 60% styrene–40% acrylate is given in Figure 2. The curve of the treated paper consists of two straight lines connected by a

small curved yield region. This type of curve is similar to the stress-strain curve of cellophane, as reported by Gibbon.[1] The untreated paper starts on the same modulus and then rapidly falls off on a smooth curve to the break value.

Essentially, the addition of an elastomer reinforces the paper matrix, producing additional bonds and thus delaying the fracture of the test sample. The ability of the small plastic films to hold the fibers in position is directly dependent upon the elastic film properties of the polymer. An extensible film which will flow will give virtually no support to the paper matrix, as can be seen by comparing Figure 1 with the properties of the free film.

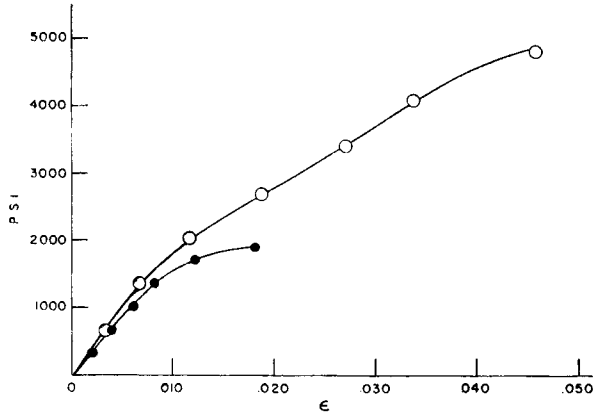

Fig. 2. Effect of addition of 60% styrene–40% acrylate to a weak saturating paper (stress vs. strain at strain rate 50%/min.): (●) untreated; (○) treated with 50 parts 60% styrene–40% acrylate.

For example, the pure poly-2-ethylhexyl acrylate films had virtually no strength, even at very high rates of straining, and, even with 25% of copolymerized styrene, the films began to flow at low stresses.

The stress–strain curves of the treated papers gradually changed in shape from the smooth curve of the untreated paper to the typical cellophane curve with increasing content of styrene in the styrene–acrylate copolymer to 60%. Therefore, a moderately strong, highly extensible elastic polymer will increase the amount of post-yield extensibility of an impregnated paper. It is interesting to note that, whereas only one break is apparent in the untreated papers, several "breaks" are visible in ruptured latex-treated papers. It is possible that the latex preferentially reinforces the weaker regions of the paper, since such microregions may have a locally higher void content and absorb more latex. There is a sharp decrease, for example,

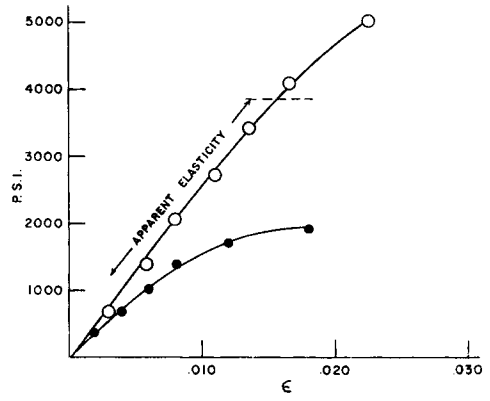

Fig. 3. Effect of addition of polyvinyl acetate to a weak saturating paper (stress vs. strain at strain rate 50%/min.): (●) untreated; (○) treated with 35 parts polyvinylacetate.

in the amount of latex absorbed by paper as beating proceeds.

A strong, inextensible polymer, such as polyvinyl acetate, will add considerable strength while not markedly increasing the elongation. In this case, a very stiff, brittle polymer is reinforcing the paper matrix, rigidly holding the paper's bonds in place with the polymer, absorbing some of the increased stress per unit elongation. The polyvinyl acetate-treated paper showed high elasticity on examination of the stress–strain curve (Fig. 3), but information obtained from load–deload cycles proved that most of the elasticity was only apparent and that permanent set began to occur at about the same point as it occurred in the untreated paper. The stress–strain curve of cured 75% styrene–25% acrylate-treated paper lies midway between the 60% styrene—40% acrylate curve (Fig. 2) and the polyvinyl acetate curve (Fig. 3).

It should be pointed out that even in the most extensible latex-treated papers studied, the instantaneously recoverable elasticity amounted to only 1.5% at yield and that all the rest was permanent set. The load–deload cycles also showed the instantaneously recoverable elasticity stress–strain curve was in the form of a straight line with a slope equal to the apparent initial modulus of elasticity for the normal whole stress–strain curve.

The above discussion assumes that the polymer properties, i.e., strength, are governing the situation and not the strength of the polymer-fiber bond, i.e., the cohesive strength and not the adhesive. This we believe to be true for the various polymers studied, although there are undoubtedly systems where adhesive failure is predominant. A good example of this is to be found with polyethylene

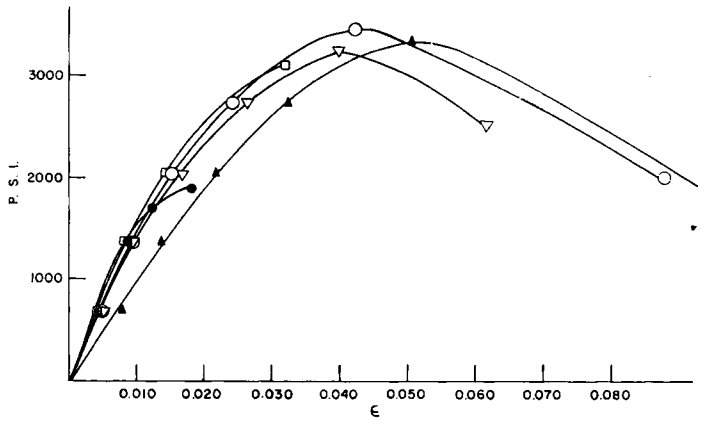

Fig. 4. Comparison of GR-S-impregnated papers at different levels of elastomer addition (stress vs. strain at strain rate 25%/min.): (●) untreated; (□) 28 parts GR-S; (▽) 59 parts GR-S; (○) 85 parts GR-S; (▲) 165 parts GR-S.

latex-treated papers where, in spite of the good cohesive strength, no additional strength is found to be imparted to the paper.[2]

Characteristic stress–strain curves at a number of levels of elastomer addition are shown in Figure 4. The elongation at final yield increases with increasing latex content, but the tensile strength at final yield remains fairly constant. After the final yield point, there is a steady decay in the load until the break point occurs. This decay of stress, characteristic of papers saturated with highly elastic latices, is a function of the latex content and leads to artificially high elongation values if only the stretch at break is reported.

Early in the investigation it was noticed that in the case of GR-S the properties changed markedly with aging, even at room temperature. Such changes are characteristically associated with the vulcanization of rubber, and results obtained with latex, with and without antioxidant, showed that the presence of the antioxidant considerably retarded the change in properties with aging.

It appears from the results that latex, when added to paper by normal impregnation procedure, does not produce substantial numbers of polymer-fiber bonds in place of any of the previously existing fiber-fiber bonds, but rather superimposes a series of polymer films on the original paper matrix. If the polymer were to replace any large proportion of the fiber bonds, a marked change in modulus would result. Probably the latex, i.e., the serum, penetrates between and solvates some of the fiber-fiber bonds; this, together with stress relief on wetting and drying, causes the observed small decreases in the modulus. The decline of stress after a certain elongation is probably due to the pulling apart of the loose polymer structure after the main body of the paper has been ruptured.

If extremely strong, tough, and extensible latex-treated papers are desired, a way must be found to enable the paper itself to have stretch to go along with the saturant as it extends. One way to accomplish this is to use the new stretchable papers pioneered and developed by Cluett-Peabody and the West Virginia Pulp and Paper Company.[3] Some preliminary results have been obtained by us on this remarkable new paper and also with the

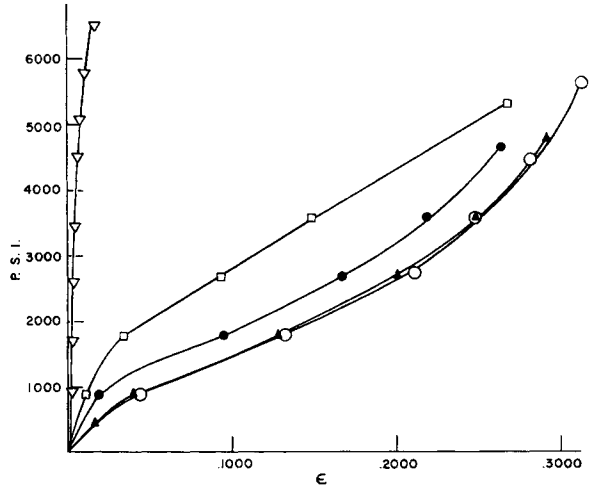

Fig. 5. Effect of latex impregnation on West Virginia stretchable paper (strain rate 50%/min.): (▽) unmodified base paper; (●) stretchable paper, untreated; (□) stretchable paper treated with 40 parts polyvinyl acetate; (▲) stretchable paper treated with 40 parts GR-S; (○) stretchable paper treated with 40 parts 50% styrene–50% acrylate.

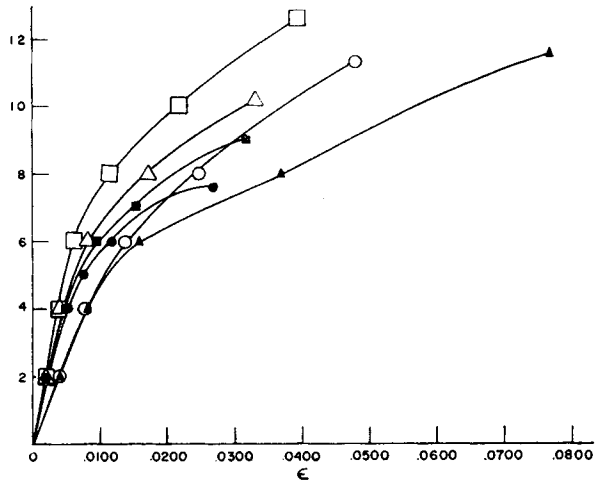

Fig. 6. Stress–strain (units of 500 lb./in.²) curves of handsheets containing various levels of 60% styrene–40% acrylate elastomer by beater addition and impregnation (strain rate: 50%/min.): (●) untreated handsheet; (■) treated with 13 parts 60:40 elastomer by beater addition; (△) treated with 29 parts 60:40 elastomer by beater addition; (□) treated with 69 parts 60:40 elastomer by beater addition; (▲) treated with 54 parts 60:40 elastomer by impregnation; (○) treated with 13 parts 60:40 elastomer by beater addition, then treated with 48 parts 60:40 elastomer by impregnation (total 61 parts).

unmodified base paper. The results are shown in Figure 5. It can be seen that tremendous increase in toughness are now possible, amounting to more than a 30-fold increase in many cases. The results are preliminary only and by no means represent the optimum possible.

Another method would be to replace some of the rigid, strong fiber-to-fiber bonds with extensible polymer-to-fiber bonds. This does not appear to be possible by simple impregnation techniques, judging from the results recorded above. However, it should be possible if the sheets are formed from fibers after the polymer has been deposited, i.e., by the so-called beater addition technique. To study this possibility, a number of beater additions of latex to pulp have been made and the results compared with a comparable impregnation procedure on similar untreated handsheets. Some preliminary results are shown in Figure 6. It can be seen that the modulus of the impregnated sheet has decreased. This may be due to the water solubles of the latex which would not be effective at the extreme dilutions of the beater addition work. The similarity between the moduli of the untreated and the beater-added sheets indicates that little or no polymer bonds were formed at the expense of regular bonds. In other words, with the method used, beater addition merely added polymer to a sheet of similar structure to the untreated paper. It can also be seen that impregnation gave much better extension than beater addition. This is probably due to the more efficient use of the polymer, since, as the impregnated sheet dries, a good proportion will be drawn down by surface tension into the fiber-fiber bonding areas and there leave films. The deposition of polymer, as in beater addition, is probably in the form of isolated small areas of coagulum, many of which do not contribute to fiber-to-fiber bonding. These results do not mean that it is impossible to produce as tough a sheet with beater addition as with impregnation, but merely that it will be more difficult to accomplish, and further work is obviously needed in this field.

Nylon Paper

It was thought that a somewhat less rigidly bonded structure, such as nylon paper, might permit a greater elongation when treated with latex. Commercial samples of 100% nylon paper believed to be bonded by the fusible fiber technique were saturated by the same techniques as used with the other papers. The results obtained with GR-S rubber saturation are shown in Figure 7. It can be seen that considerable stretch is indeed imparted to the paper, but the tensile strength at break is still quite low. If the other properties of nylon paper, such as the tremendous fold and tear resistance, are necessary, then the substantial in-

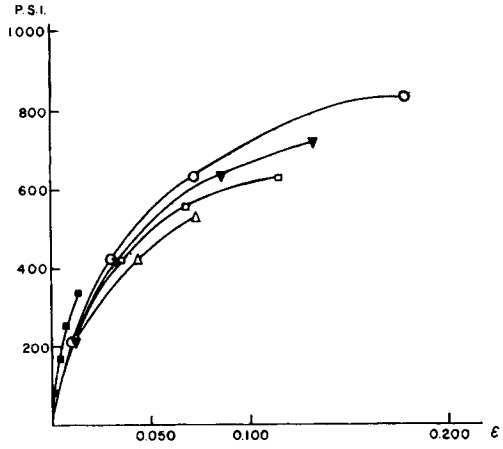

Fig. 7. The stress–strain curves of GR-S-treated 100% nylon paper (strain rate 5%/min.): (■) untreated nylon; (○) treated with 182 parts GR-S/100 parts nylon; (▼) treated with 82 parts GR-S/100 parts nylon; (□) treated with 52 parts GR-S/100 parts nylon; (△) treated with 32 parts GR-S/100 parts nylon.

creases in toughness imparted by the saturation are of great value. When mixtures of wood pulp and nylon fibers are used, the elongations were found to be much less, although again considerable improvements in toughness were brought about by rubber saturation. The high elongations found with the pure nylon paper will be shown below (see Fig. 13) to contain a considerable amount of elastic recovery, and such systems warrant further study for special applications.

Time-Dependent Behavior

The stress–strain curves were also measured at various rates of straining between the limits of 0.5 and 50%/min. Such measurements are important for predicting the behavior of papers under various conditions and also help our understanding of the mechanism of reinforcement by the latex. The untreated papers showed only small changes with a hundredfold change in straining rate, the tensile strength and modulus being somewhat higher and the elongation about the same for very high rates of straining in agreement with the results of Mason.[4] The latex-treated papers behaved somewhat differently.

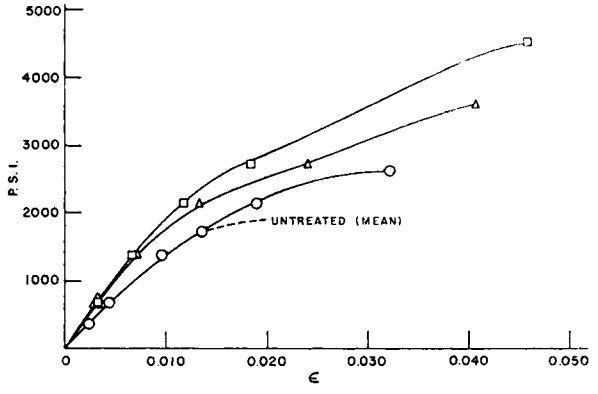

Fig. 8. Effect of strain rate on 50% styrene–50% acrylate-treated paper (stress vs. strain, 50 parts elastomer) at strain rates of (□) 50%/min.; (△) 5%/min.; (○) 0.5%/min.

Papers treated with soft, extensible polymers were found to give increased tensile strength and elongation with increasing rates of strain, leading to considerably greater toughness at higher crosshead speeds. This behavior is exemplified by the case of the 50:50 styrene–2-ethylhexyl acrylate copolymer shown in Figure 8; GR-S and the higher acrylate copolymers all showed similar behavior. The stiffer copolymers and polyvinyl acetate behave like untreated paper, in that they show similar elongations at break but higher tensiles as the straining rate increases, as illustrated in Figure 9. The support of higher stresses at higher rates is probably due to the lack of time for stress relaxation and corresponds in a sense to the "freezing out" of viscous flow found with most high polymers. The simultaneous increase in stress and strain at break found with the softer polymers may be due to the hardening of such polymer at high rates of strain. Films of the 50:50 copolymer, for example, were found to have much less viscous flow at high straining rates, whereas at very low rates there was considerable viscous flow minimizing the reinforcing action in the paper sheet.

As mentioned earlier, a good deal of the elongation is irreversible in latex-treated papers, i.e.,

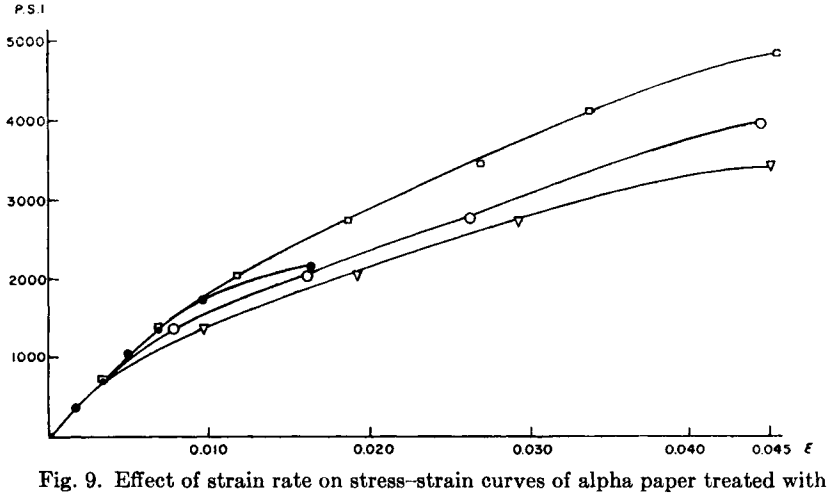

Fig. 9. Effect of strain rate on stress–strain curves of alpha paper treated with 60:40 styrene–2-ethylhexyl acrylate copolymer: (●) untreated paper (mean of all strain rates); treated paper at (□) 50%/min.; (○) 5%/min.; (▽) 0.5%/min.

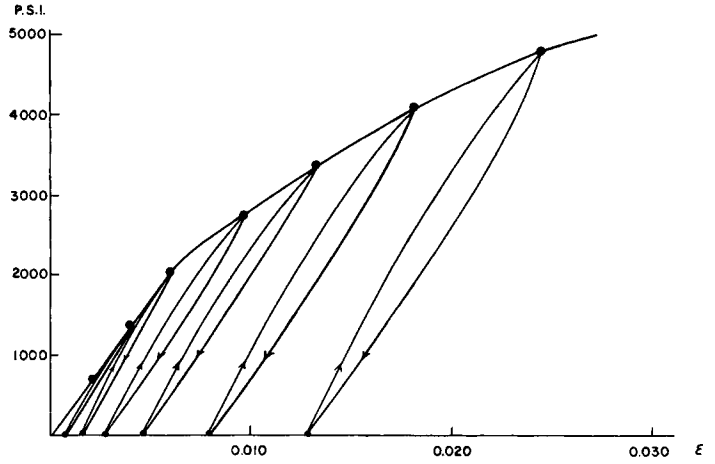

Fig. 10. Load–deload cycles of alpha paper treated with 35 parts polyvinyl acetate (Strain rate 2.5%/min.).

there is a large amount of permanent set. This effect is best illustrated by the load–deload cycles and is shown for paper treated with polyvinyl acetate in Figure 10. Similar curves were obtained for all the other polymers investigated. The recoverable creep could be divided up into instantaneous recoverable (measured by immediately releasing the stress) and the total primary (recoverable) creep (measured after 1 hr. at the given loading before allowing the stress to return to zero). The elastic primary creep for both GR-S and polyvinyl acetate is shown in Figure 11. The genuine increase in elasticity imparted by the stiffer polymer is quite evident. It is possible that much more elasticity could be conferred on the GR-S-treated papers by vulcanization of the rubber. The case of nylon paper, referred to previously, is of interest and is illustrated by the instantaneous creep–load curve presented in Figure 12. The instantaneous reversible stretch and the total (after 1 hr. at zero stress) are shown for paper saturated with the toughest saturant (60:40 styrene–2-ethylhexyl acrylate copolymer) in Figure 13. Although the actual elongations involved are less than 2%, they are undoubtedly of considerable effect in many applications. The total recoverable stretch is plotted as a function of applied strain and is shown in Figure 14. It can be seen that this polymer appears to add smoothly to the amount of recoverable stretch of the untreated paper.

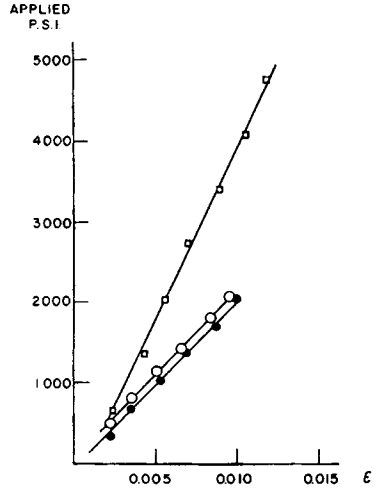

Fig. 11. Elastic primary creep at zero stress (ϵ) (instantaneously recoverable) vs. applied stress of alpha paper (strain rate 2.5%/min.): (●) untreated paper; (○) treated with 60 parts GR-S rubber; (□) treated with 35 parts polyvinyl acetate.

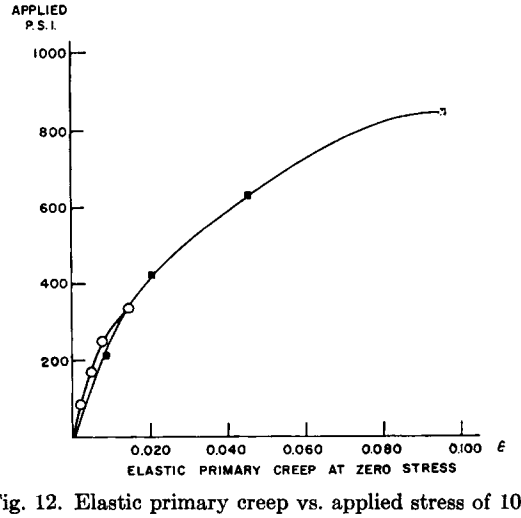

Fig. 12. Elastic primary creep vs. applied stress of 100% nylon paper (strain rate 2.5%/min.): (○) untreated paper; (■) treated with 82 parts GR-S rubber/100 paper.

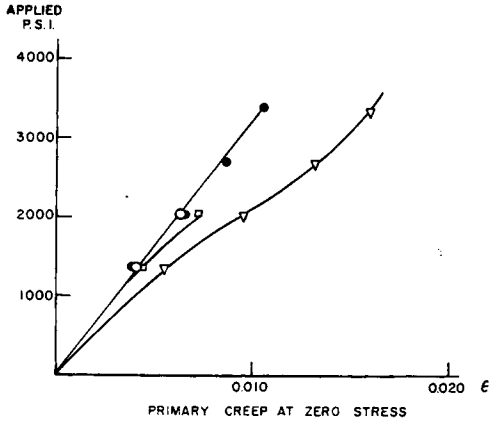

Fig. 13. Elastic and total (1 hr. relaxation) primary creep of alpha paper vs. applied stress (strain rate 2.5%/min.): (○) untreated alpha paper, instantaneous; (□) untreated alpha paper, total; (●) treated with 50 parts 60:40 styrene–2-ethylhexyl acrylate copolymer, instantaneous; (△) treated with 50 parts 60:40 styrene–2-ethylhexyl acrylate copolymer, total.

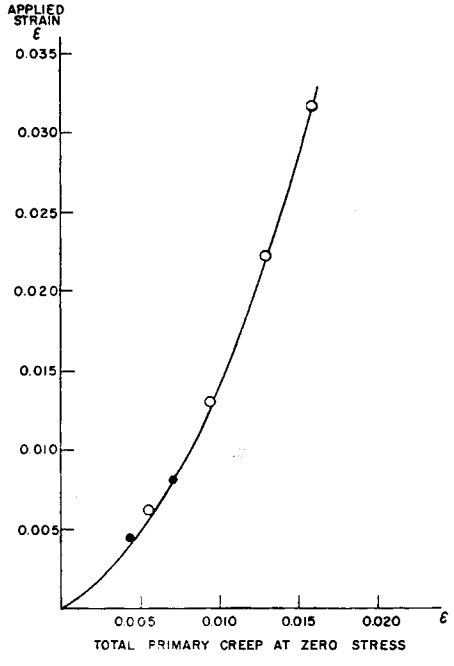

Fig. 14. Total primary creep vs. applied strain of alpha paper: (○) untreated; (●) treated with 50 parts 60:40 styrene–acrylate copolymer.

For a more fundamental rheological study of latex-treated papers genuine instantaneous strains would need to be imparted to the specimens to avoid any concurrent relaxation; similarly, the stress would need to be immediately removed to find the true elastic deformation. However, it is hoped that the type of data presented will have practical interest and stimulate further work in this field.

We would like to thank the Monsanto Chemical Company for their support of this work and also Dr. Van Royen of T.N.O. Delft (Vezel-Institut) for many helpful suggestions and criticisms.

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Synopsis

The effect of the amount and type of latex on the mechanical properties of the paper-polymer combinations is described in detail. The treatment with latex increases the wet and dry strength properties of the paper considerably, together with improving the folding and tearing resistance. If the polymer in latex is below its film-forming temperature, however, the beneficial effects of latex treatment are absent. Limitations to varying the rheological properties of plastic-paper combinations are imposed by the comparatively inextensible nature of the paper matrix. Methods of improving the extensibility of paper, including the use of synthetic fiber papers, are discussed, and the time-dependent nature of the properties are outlined.

Résumé

On décrit en détail l'influence de la quantité et du genre de latex sur les propriétés mécaniques des mélanges papier-polymère. Le traitement au latex augmente considérablement la résistance du papier à l'état humide et sec et améliore la résistance au pliage et au déchirement. Si le polymère dans le latex est au-dessous de sa température de formation de film, on perd les avantages du traitement au latex. Les changements dans les propriétés rhéologiques des combinaisons plastique-papier sont limités à cause de la nature relativement inextensible de la matrice de papier. Des méthodes pour améliorer l'extensibilité du papier comprenant l'emploi de fibres de papier synthétiques sont discutées et la dépendance des propriétés avec le temps est soulignée.

Zusammenfassung

Der Einfluss der Menge und des Typs von Latex auf die mechanischen Eigenschaften der Papier-Polymerkombination wird im einzelnen beschrieben. Die Behandlung mit Latex erhöht die Nass- und Trockenfestigkeit des Papiers beträchtlich und verbessert zugleich die Widerstandsfähigkeit gegen Falten und Reissen. Wenn jedoch das Polymere im Latex sich unterhalb seiner Filmbildungstemperatur befindet, treten die günstigen Einflüsse der Latexbehandlung nicht auf. Die Veränderungen der rheologischen Eigenschaften der Kombinationen von Papier mit einer plastischen Masse werden durch die vergleichsweise undehnbare Natur der Papiermatrix in engen Grenzen gehalten. Methoden zur Verbesserung der Dehnbarkeit von Papier, einschliesslich der Verwendung von Papier aus synthetischen Fasern, werden diskutiert und der zeitabhängige Charakter der Eigenschaften unterstrichen.

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