Influence of the interaction zone between coating and paper on the dynamic mechanical properties of a coated paper

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Papers coated with pigments bonded by polymer latexes have been tested by dynamic mechanical analysis. Measurements in tension and in three-point bending have been performed to determine the influence of the interaction zone between the coating and the paper on the properties of the coated paper. Comparisons have also been made with results from measurements in torsion. Experimental values of Young's modulus and the peak height of tan δ were higher than values theoretically calculated from data obtained on the separate layers, the paper and the coating. This deviation is interpreted as being due to the influence of an interaction zone between the coating and the base paper. If the thickness of the interaction zone is taken into account in the theoretical model, a better correlation with the experimental values is obtained for the peak height of tan δ. Higher values of the experimental data for the shear modulus of coated paper than from a weight-average calculation of the shear modulus of the pure components were obtained. This can be explained as being due to an increased stiffness of the coated paper as a result of the interaction zone, that was not adjusted for in the model. Further evidence for the existence of the interaction zone was provided by the pigment and latex distributions in the cross-section of coated papers determined in a scanning electron microscope using energy dispersive X-ray analysis.

1 Introduction

A coated paper is a layered composite consisting of a paper sheet as a middle layer with porous clay-based polymer coatings. The coating is applied to give a smooth surface for good printability and a high surface gloss [1].

During processing and use, coated papers are exposed to different dynamic processes such as calendering and printing, which makes it important to investigate their dynamic mechanical properties. Dynamic mechanical analysis is a powerful method for the study of such properties. Measurements in different modes of deformation, e.g. in torsion, tension or bending, have different sensitivities to different parts of the specimen and thus make it possible to estimate properties of inner and outer layers of the specimen. Studies of fibre–matrix interactions in composites are an example of a widely reported application of dynamic mechanical analysis [2–4].

Because dynamic mechanical test methods are sensitive to small changes in polymer content and differences in structure, particularly in the case of materials with secondary transitions like glass transition temperatures, this technique is very useful for studying differences in properties of coated papers.

In the coated paper, an interaction zone is developed between the paper and coating. Such a fibre–matrix interaction generally decreases the mechanical damping [2], tan δ, and increases the stiffness of the material. The principal objectives of this work were to describe the influence of the interaction zone between the coating and the paper. By characterizing its effects on tan δ, in a temperature region where the latex polymer exhibits the glass transition, as well as the modulus values in different modes of deformation together with theoretical comparisons using lamination theory, it is possible to obtain a deeper understanding of how the paper and the coating cooperate in a coated paper.

2. Experimental procedure

2.1. Materials and specimen preparation

The outer layers or coatings of the paper consist of pigments bonded by polymer latexes. Two different polymer latexes were used, latex A (Acronal D810, BASF), an acrylate–styrene–butadiene copolymer with a glass transition temperature of 25° C [5] (peak maximum of E'' at 1 Hz) and latex B (DL955, DOW), a carboxylated styrene–butadiene copolymer with a glass transition temperature of 18° C [6] (DSC, 10° C min^{-1}). The content of latex, expressed as parts per hundred parts of pigment (p.p.h.) in the coating was varied between 3.5 and 80 p.p.h. The high latex contents are not realistic for practical purposes, but are of interest in this study because the broad interval studied makes it easier to explain certain phenomena.

The polymer compounds also contained a dispersing agent (Polysalz S), 0.2–0.45 vol %, and a thickener (carboxymethylcellulose, CMC, Blanose 7L1C1), 1–4 vol %. The pigment (SPS Kaolin, ECC International), is a plate-like mineral pigment with an equivalent spherical diameter between 0.2 and 3 μm. The coatings were applied from aqueous suspensions and then dried for 2–3 min at 180° C. It should be emphasized that the coatings are porous [7, 8]. A coating layer of 10 p.p.h. latex has a density of approximately 1490 $kg\,m^{-3}$ compared to a density of approximately 2250 $kg\,m^{-3}$ for the pure clay-based polymer.

The middle layer, the paper sheet, was made of a mechanical pulp. The paper had a density of 700 $kg\,m^{-3}$ compared to a density of approximately 1500 $kg\,m^{-3}$ for a homogeneous wood fibre wall material [9].

The paper is anisotropic due to the preferred orientation of the fibres in the machine direction. Specimens of both the coated and the uncoated paper were cut with the longitudinal axis in the cross direction (CD) as well as with the longitudinal axis in the machine direction (MD). For comparison, the uncoated paper was treated with water in the same manner as the paper in the coating procedure, in order to release some of the drying stresses that influence the mechanical properties of the paper [10].

2.2. Instrumentation and test procedure

Dynamic mechanical properties were measured using a Perkin–Elmer DMA-7 with a stainless steel three-point bending measurement system as well as an extension measuring system. Specimens were cut with dimensions of 5 mm × 2 mm for the bending measurements and 12 mm × 2 mm for the tension measurements. Temperature scans were performed at a heating rate of 2° C min^{-1} between 0 and 70° C. Stress scans were performed isothermally at a force rate of 25 mN min^{-1}. The frequency of the measurement was 1 Hz. Because paper is hygroscopic and water influences the mechanical properties of paper, all specimens were conditioned at 105° C in a dry helium atmosphere for 1 h before being tested (a standard procedure for drying paper). The specimen were exposed to a dry helium atmosphere throughout the run.

The dynamic mechanical measurements in torsion were performed with a torsional pendulum described elsewhere [11, 12]. Measurements were performed at a heating rate of 0.5° C min^{-1} from 0–70° C. The natural frequency range of the oscillation with these specimens was 0.5–2 Hz. All specimens were conditioned at 20° C in a dry nitrogen atmosphere for 12 h before being tested, and were tested in this atmosphere. The moisture content was below 0.5%, as has been shown to be sufficient for measurements with this equipment, because no further change in mechanical properties could be detected with increasing drying.

The thicknesses of the specimens were measured by means of a mechanical sensor, which gives an integrated mean value of the thickness [13].

The distribution of pigment and coating polymer in the thickness direction of the paper, z-direction, was determined with a scanning electron microscope (SEM) using electron dispersive X-ray analysis (EDXA) [14, 15]. The polymer was tagged by osmium tetroxide (OsO_4) in order to make it detectable [15].

3. Results and discussion

3.1. Dynamic mechanical analysis of tan δ

In dynamic mechanical analysis, the specimen is subjected to a sinusoidal deformation and a responding dynamic stress is measured or vice versa. It is, however, necessary to observe a linear viscoelastic behaviour to obtain accurate and comparable data. For the coated paper, the glass transition of the coating polymer was studied by temperature scans observing the mechanical damping, $(\tan\delta)_{max}$, as in Fig. 1. The tan δ peak values may be calculated either from the zero level ($\tan\delta = 0$) including the damping of the paper, $(\tan\delta)^0_{max}$, or from a baseline taken as the damping level well outside the peak region to determine only the influence of the coating polymer, $(\tan\delta)^b_{max}$. In Fig 2, $(\tan\delta)_{max}$ according to the two definitions from

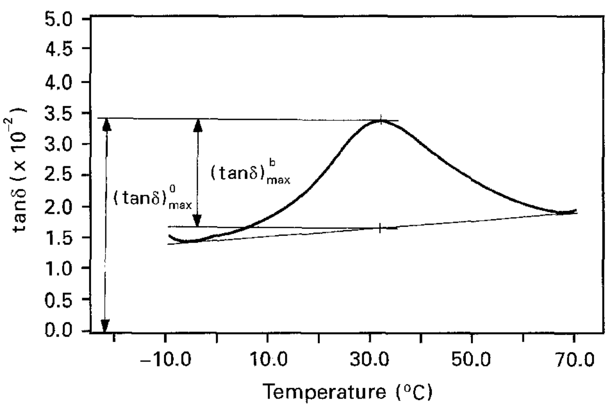

Figure 1 The mechanical damping, tan δ, in tension versus temperature for a coated paper (CD) with 10 p.p.h. latex B in the coating. The peak height at the glass transition temperature may be determined in two ways as indicated, from the zero level, $(\tan\delta)^0_{max}$, and from a baseline taken well outside the peak region, $(\tan\delta)^b_{max}$.

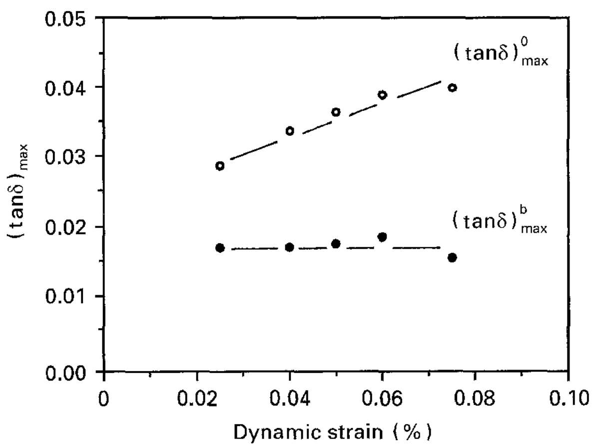

Figure 2 The peak maximum of tan δ for a coated paper (CD) with 10 p.p.h. latex in the coating layer (latex B) versus dynamic strain measured in tension. The peak values are taken both from zero level, $(\tan\delta)^0_{max}$, and from an intermediate baseline, $(\tan\delta)^b_{max}$.

tensile measurements on a coated paper of 10 p.p.h. latex B in the coating is plotted against the dynamic strain. It is here evident that $(\tan\delta)^0_{max}$ taken from the zero level is strain dependent, while $(\tan\delta)^b_{max}$ taken from the baseline is strain independent. The strain dependence appears to be associated with the paper, which has been shown to have a non-linear viscoelastic behaviour [16]. In this case, comparisons must therefore be made by extrapolating $(\tan\delta)^0_{max}$ to zero strain. For the $(\tan\delta)^b_{max}$, this is not required as the strain range studied is within the linear region of the polymer. In torsion, the dynamic amplitude is so small that the strain dependence can be neglected.

Dynamic mechanical analysis in the tension mode yields average properties over the whole cross-sectional area of the specimen, i.e. both for the paper and the coating layers, whereas measurements in the torsion mode exhibit a greater response to the properties of the outermost region of the specimen [17]. Earlier studies in torsion have shown that the latex content in the coating layer of a coated paper has a marked influence on the peak height of $\tan\delta$ [11]. A similar behaviour is here observed in the tension mode of deformation. A comparison of $(\tan\delta)^b_{max}$ for coated papers with the two different latex polymers, latex A and latex B, in Fig. 3, shows higher values for latex A than for latex B, at a given latex content. The $\tan\delta$ values are taken from an intermediate baseline, and thus depend only on the properties of the coating polymer. Although not shown, a similar behaviour is observed for measurements made on the coatings separately. A structural difference between the two polymers could explain the difference in the $\tan\delta$ peak values. It is possible that differences in adhesion properties to the pigment may also influence the peak values.

A theoretical estimate of the influence of latex content on $(\tan\delta)_{max}$ may be obtained using lamination theory, considering the coated paper as a three-ply laminate. The following expression is derived for the coated paper in tension in Appendix 1

$$\tan\delta_{tension} = \frac{\tan\delta_c}{(1 + 0.5Ak)} + \frac{\tan\delta_p}{[1 + (0.5Ak)^{-1}]} \quad (1)$$

where subscripts c and p denote coating and paper, respectively, k is the ratio of the tensile modulus for the paper to that of the coating, and A is a geometric constant.

The theoretical values of $(\tan\delta)^0_{max}$ for the coated paper (latex A) are lower than the experimental values in tension, as shown in Fig. 4. A suggested explanation for this discrepancy is that there is an interaction zone between the paper and the coating. In the coating operation, it is probable that a part of the coating has penetrated into the base paper structure giving a fibre-reinforced composite layer. A better agreement is achieved if the thickness ratio of paper and coating in the model is adjusted by 5.5 μm assuming an interaction zone with the same properties as the coating. This gives a thicker coating and a thinner base paper in the model. The adjustment by 5.5 μm should be compared with the thickness of 4.5 μm for the pure coating layer obtained by measuring the difference in thicknesses of a coated paper and an uncoated base paper.

The data from the tension experiments were also compared with similar data obtained in torsion. Values of $(\tan\delta)^0_{max}$ in torsion were obtained according to the equation [11]

$$\tan\delta_{torsion} = \frac{\tan\delta_c}{(1 + Bk)} + \frac{\tan\delta_p}{[1 + (Bk)^{-1}]} \quad (2)$$

where subscripts c and p denote coating and paper, respectively, k is the ratio of the shear modulus for the paper to that of the coating and B is a geometric constant. The theoretical values were again lower than the experimental values, as shown in Fig. 5. A better agreement with the experimental values was again obtained by introducing an interaction zone 5.5 μm thick between the coating layer and the paper in the model. In the tension mode, the adjusted theoretical values were slightly below the experimental values, and in the torsion mode the adjusted theoretical values were slightly higher than the experimental values.

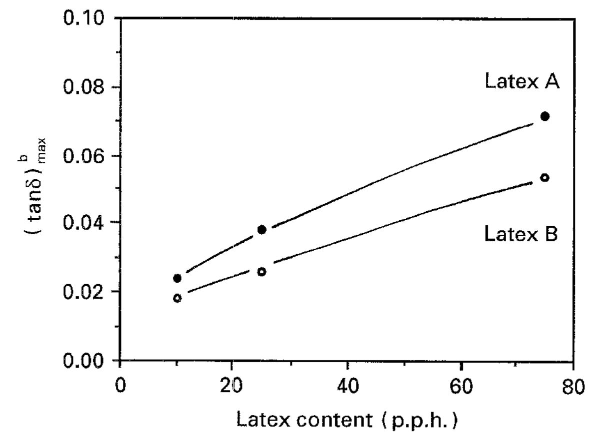

Figure 3 Experimental values of $(\tan\delta)^b_{max}$ in tension of latex A and latex B for different amounts of latex in the coating at a constant coat weight of 10 g m^{-2}.

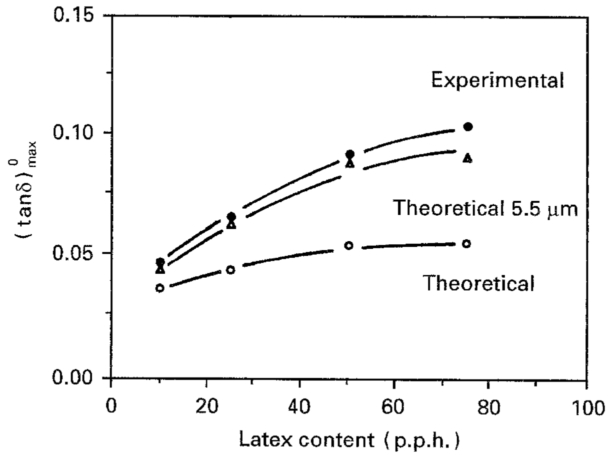

Figure 4 Experimental and theoretical values of $(\tan\delta)^0_{max}$ for coated papers (CD) in tension. Theoretical values of $(\tan\delta)^0_{max}$ assuming an interaction zone with a thickness of 5.5 μm are also shown.

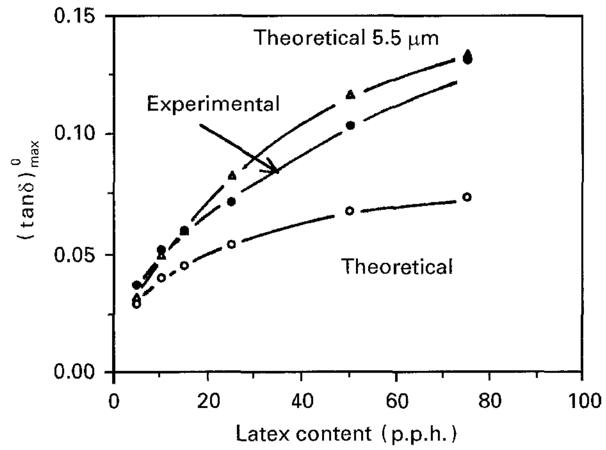

Figure 5 Experimental and theoretical values of $(\tan\delta)^0_{max}$ for coated papers (CD) in torsion. Theoretical values of $(\tan\delta)^0_{max}$ assuming an interaction zone with a thickness of 5.5 μm are also shown.

3.2. Dynamic mechanical analysis of Young's modulus in tension and bending.

Values of the tensile Young's modulus of coated papers in the MD direction with different contents of latex B in the coating are presented in Table I. Coatings with three different compositions were investigated; 10, 25 and 75 p.p.h. latex. Values are given both at − 10° C, a temperature at which the coating polymer is below its T_g, and at 70° C, a temperature above T_g for the polymer, i.e. in the rubbery region. For comparison, experimental values of the tensile Young's modulus of the water-treated base paper are given. As expected, the tensile Young's modulus increases with decreasing latex content, in other words with an increasing proportion of pigment. Because the modulus of the coating is higher than the modulus of the paper, except for blends with a very high latex content at temperatures above T_g, e.g. 75 p.p.h. at 70° C, the modulus of the corresponding coated papers are higher than the modulus of the base paper.

Theoretical calculations of the modulus of coated paper from data for the single layers, paper and coating films, considering the coated paper as a three-ply laminate, are also shown in Table I. The experimental values of the Young's modulus are higher than the theoretical values at all temperatures and latex contents. The discrepancy between the theoretical values and the experimental values may again be explained by assuming that there is an interaction zone between the coating and the paper. In the calculations, no adjustment has been made for an interaction zone with a higher modulus than the base paper, as was done in case of the theoretical calculations of $(\tan\delta)_{max}$ where the interaction zone was assumed to have properties more similar to those of the coating layer than those of the paper.

As in the torsion mode, dynamic mechanical analysis in the bending mode is particularly sensitive to the properties of the outermost part of the specimen, i.e. to the coating layers for coated papers. Results for coating films, uncoated paper and coated papers of various latex contents (latex B), are presented in Fig. 6.

TABLE I Tensile modulus for coated paper in machine direction, MD

Amount of latex (p.p.h.)	$E_{-10°C}$(GPa)		$E_{70°C}$(GPa)	
	Exp.	Theor.	Exp.	Theor.
10	6.5	5.4	5.1	4.3
25	6.1	5.3	4.5	4.0
75	5.5	4.4	3.4	3.2
Uncoated paper[a]	3.7		3.4	

[a]Water-treated.

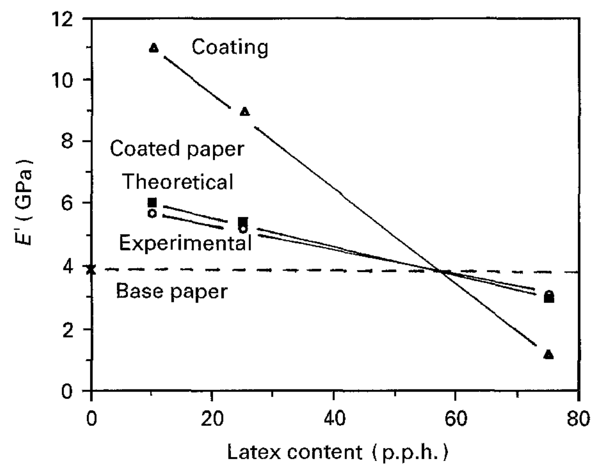

Figure 6 The Young's modulus in three-point bending for latex films, uncoated paper (MD) and coated paper (MD) as a function of latex content at 70°C. Theoretical data for coated paper based on a simple laminate approach are incorporated. (---) Modulus of the uncoated paper.

Both the coated and the uncoated paper were measured in the MD direction at a temperature of 70° C, i.e. in the rubbery region of the coating polymer. The modulus of the uncoated paper is indicated with a dotted line. At latex contents less than approximately 55 p.p.h., the Young's modulus in bending for the coating is higher than that of the paper, giving a modulus of the corresponding coated paper intermediate between these values. At latex contents above 55 p.p.h., the modulus of the coating is lower than that of the paper and the modulus of the corresponding coated paper is then lower than that of the uncoated paper.

A theoretical estimate of the Young's modulus in bending is also included in Fig. 6. The coated paper is considered as a three-ply laminate without taking into consideration the influence of any interaction zone, see Appendix 2. There is a good agreement between the theoretical and the experimental values. The discrepancy is less than that observed in the tension mode for the same materials at the same temperature. This can be explained as being due to the higher sensitivity to the coating in bending. In tension, the properties of the interaction zone have a greater influence on the behaviour of the coated paper, as the response is equally distributed over the whole cross-section of the specimen. It is noticeable that the curves for the coated paper, for the coating film and for the uncoated paper all intersect in the same point, indicating the accuracy of the experimental measurements.

3.3. Analysis of the interaction zone between coating and paper

It is obvious that the properties of a base paper with a low grammage porous structure, consisting of only a couple of fibres in the thickness direction, will change when it is coated with a clay-based polymer. The thickness of the coating layer is not, however, constant, but changes with the substrate unevenness [8], as illustrated by the scanning electron micrograph of a cross-section of a coated paper in Fig. 7.

In Fig. 8 it is evident that the thickness of a coated paper increases linearly with increasing coat weight above a value of 5 $g\,m^{-2}$ at a constant latex content of 10 p.p.h. At lower coat weights, however, the thickness is unaffected by the coat weight. At this low coat weight, the coating partially penetrates the paper structure creating a reinforced interaction zone in the structure, without leading to any increase in the total thickness.

Further indications of an interaction zone between the coating and the paper are provided by a determination of the pigment and latex distributions in cross-sections of coated papers using the SEM–EDXA technique. Fig. 9 shows distribution curves for a coated paper with a latex content of 10 p.p.h. and a coat weight of 10 $g\,m^{-2}$. The intensities have been normalized by dividing the values by the total integrated area below the respective curve. The vertical dotted lines in the figure indicate a theoretical value of the thickness of the coatings on each side of the paper, calculated from the difference in thickness of the coated and uncoated papers. As seen in the figure, both pigment and polymer are present at a distance

Figure 7 Scanning electron micrograph of a cross-section of a coated paper. Coating data: 10 p.p.h. of latex A and 10 $g\,m^{-2}$.

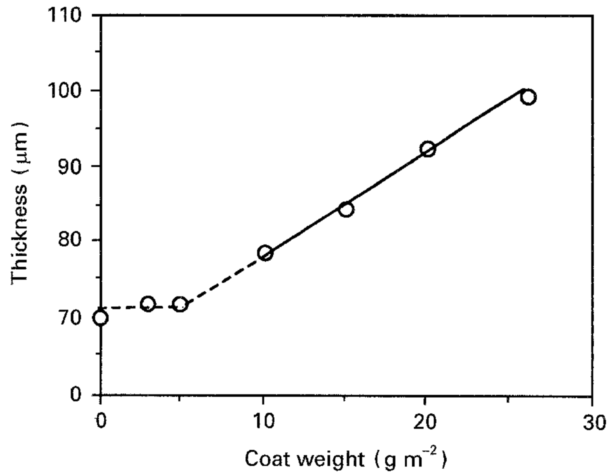

Figure 8 The thickness of a coated paper as a function of the coat weight at a constant amount of latex polymer A, 10 p.p.h.

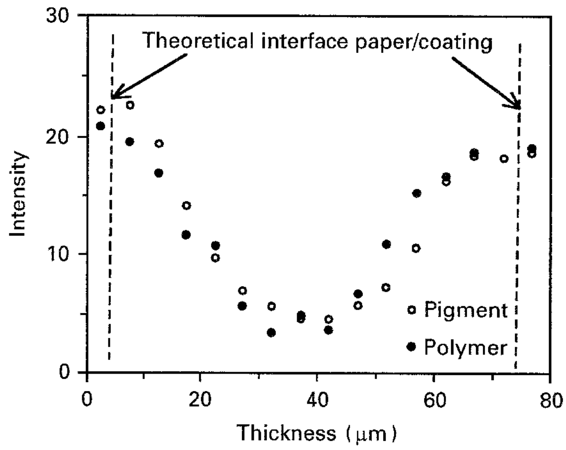

Figure 9 Latex and pigment distributions in the cross-section of a coated paper (10 p.p.h. latex B, 10 $g\,m^{-2}$).

further into the paper than the distance given by the calculated thickness of the coating layers, indicating that the coating has penetrated into the paper structure. For this latex system, it was also found that pigment and polymer have almost the same distribution in the cross-section of the coated paper. Similar behaviour was observed for coating systems with higher latex contents.

A comparison of the latex and pigment distributions in coated papers with those of coating systems based on latex A and latex B, shows that the coating system with latex A has more pigment and polymer in the surface of the sheet than systems based on latex B, where a larger amount of the coating has penetrated into the paper structure. Pigment distributions of the two coating systems are shown in Fig. 10. Because the coating procedure was performed in two steps, the intensities are different on the two sides of the paper. The side coated first has the greatest penetration and this reduces the penetration from the other side.

The effect of the penetration of the coating into the paper is further manifested in changes in elastic properties. Because the mass of the inertia disc of the torsional pendulum causes an axial load on the specimen that increases the torsional stiffness, it is difficult to measure absolute values of the shear modulus. Here

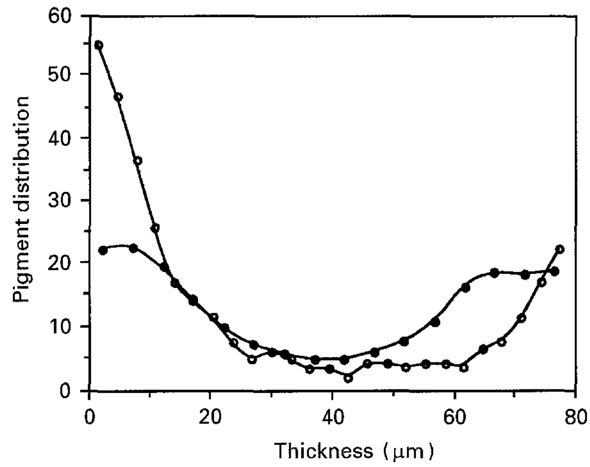

Figure 10 The distribution of pigment in the cross-section of coated papers. A comparison of two coating systems, (○) latex A and (●) latex B (10 p.p.h. 10 g m^{-2}).

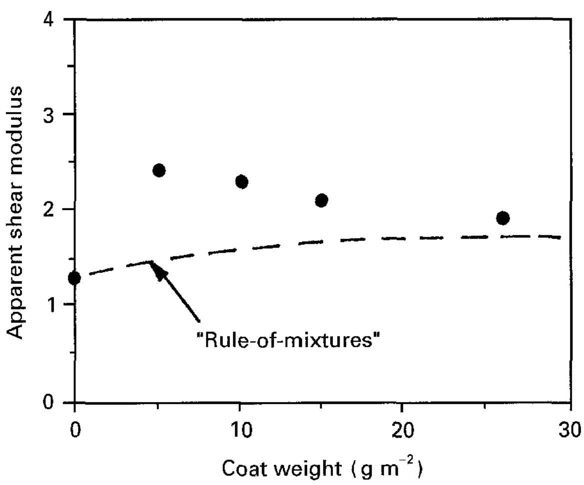

Figure 11 Apparent shear modulus of coated papers (CD) as a function of coat weight. The latex content was 10 p.p.h. (latex A).

an apparent shear modulus of coated paper is calculated by normalizing the shear stiffness to the same thickness of the coated papers. Fig. 11 shows the dependency of the apparent shear modulus in torsion on the coat weight at constant latex content, 10 p.p.h. A positive deviation from a simple weighted average (i.e. a rule of mixture) of the shear modulus of the pure components, paper and coating, is obtained. The highest experimental value is obtained at a coat weight of 5 g m^{-2}, which is in accordance with the value observed for the penetration of the coating into the paper in Fig. 8. A decrease in the shear modulus is observed as the thickness of the coating layer increases above that level. The difference between the experimental and theoretical values of the shear modulus indicates that the interaction zone has a higher shear modulus than that of the paper and the coating.

4. Conclusion

Dynamic mechanical analysis has been shown to be a useful technique for studying the properties and structure of a coated paper and its separate layers, base paper and coating layers. Using this technique, it has also been possible to demonstrate the influence of an interaction zone between the paper and the coating.

The existence of an interaction zone is revealed by the discrepancies between experimental and theoretical values of the tensile Young's modulus and the peak height of tan δ for the coated paper. By adjusting for an interphase of this type in theoretical models of tan δ, better agreement was obtained. The same adjusted thickness of the layers was used in both tension and torsion modes.

The torsional stiffness of the interaction zone is higher than that of the pure components, paper and coating. A weight average calculation of the shear modulus of the pure components without adjustment for an interaction zone, yielded values lower than the experimental values for the apparent shear modulus of the coated paper.

Thickness measurements on coated papers with increasing coat weight showed that the coating contributes to the thickness of the coated paper only above a coat weight of approximately 5 g m^{-2}. At low coat weight, the coating partially penetrates into the paper structure and fills voids and irregularities in the paper surface. The distribution of the coating components, latex polymer and pigment, was similar throughout the cross-section which implies that the coating composition was uniform throughout the paper.

Different factors may influence the penetration and the adhesion between the coating and the paper. The polymer structure and the magnitude of the attractive forces between the polymer and the fibre [14] are examples of factors that could explain the differences obtained in peak height of tan δ and the polymer and pigment distributions for the two different latex polymer systems used. The type of pigment and the gel content of the polymer latex may have an influence. The gel content can be considered to be a measure of cross-linking; higher values indicate more cross-linking [8]. Rheological differences of the coating mixes might also affect the penetration of the latexes into the paper structure. To increase the understanding of the interaction zone between the paper and the coating, the structure of the paper, e.g. its porosity and density, and possible pretreatments, e.g. calendering, are other factors that must be considered.

Acknowledgements

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Appendix 1. Equations for Young's modulus and tan δ in tension mode

The tensile stiffness of a layered composite is given by [18]

$$A_{ij} = \sum (Q_{ij})_k (z_k - z_{k-1}) \qquad \text{(A1)}$$

where $(Q_{ij})_k$ is the stiffness element for the kth ply and z_k is the distance from the mid-plane to the lower surface of the ply k. For each ply the following expressions are valid

$$Q_{11} = \frac{E_1}{1 - \nu_{12}\nu_{21}} \quad \text{(A2)}$$

$$Q_{12} = \frac{\nu_{12}E_2}{1 - \nu_{12}\nu_{21}} \quad \text{(A3)}$$

$$Q_{22} = \frac{E_2}{1 - \nu_{12}\nu_{21}} \quad \text{(A4)}$$

where ν is the Poisson's ratio and E is the Young's modulus. The tensile Young's modulus of a three-ply laminate in the machine direction (MD) is given by

$$E_x = \frac{1}{t}\left(A_{11} - \frac{A_{12}^2}{A_{22}}\right) \quad \text{(A5)}$$

where t is the thickness.

By using A_{11}, A_{12} and A_{22} given by Equation A1 in Equation A5, with the stiffness elements given by Equations A2, A3 and A4 and the approximation $[1 - (\nu_{12})_p(\nu_{21})_p] \sim 1$ and $(\nu_{12})_c \sim (\nu_{21})_c$, the tensile Young's modulus can be expressed as

$$E_x = \frac{1}{t_{cp}}\left\{\frac{2(E_1)_c t_c}{1 - (\nu_{12})_c^2} + (E_1)_p t_p - \left[\frac{2(\nu_{12})_c t_c (E_2)_c}{1 - (\nu_{12})_c^2} + (\nu_{12})_p t_p (E_2)_p\right]^2 \Bigg/ \left[\frac{2t_c(E_2)_c}{1 - (\nu_{12})_c^2} + t_p(E_2)_p\right]\right\} \quad \text{(A6)}$$

where subscripts cp, c and p denote coated paper, coating and paper, respectively.

A simplification of the expression for the tensile Young's modulus of a three-ply laminate may be obtained by using only the thickness values and the modulus values of the plies, respectively, in Equation A6, and assuming minimal contribution of the Poisson's ratios in the model, giving

$$E_{cp} = \frac{1}{t_{cp}}(2E_c t_c + E_p t_p) \quad \text{(A7)}$$

The viscoelastic correspondence principle [19] gives

$$E' + iE'' = \frac{1}{t_{cp}}[2(E_c' + iE_c'')t_c + (E_p' + iE_p'')t_p] \quad \text{(A8)}$$

The real and imaginary parts of Equation A8 are written as

$$E_{cp}' = \frac{1}{t_{cp}}[2E_c' t_c + E_p' t_p] \quad \text{(A9)}$$

$$E_{cp}'' = \frac{1}{t_{cp}}[2E_c'' t_c + E_p'' t_p] \quad \text{(A10)}$$

and

$$\tan\delta_{tension} = \frac{2E_c'' t_c + E_p'' t_p}{2E_c' t_c + E_p' t_p} = \frac{2\tan\delta_c E_c' t_c + \tan\delta_p E_p' t_p}{2E_c' t_c + E_p' t_p}$$

$$= \left(\tan\delta_c + \frac{\tan\delta_p E_p' t_p}{2E_c' t_c}\right) \Bigg/ \left(1 + \frac{E_p' t_p}{2E_c' t_c}\right) \quad \text{(A11)}$$

If the ratio (E_p'/E_c') is set to be equal to k and the ratio (t_p/t_c) is set to be A, the equation may be expressed as

$$\tan\delta_{tension} = \frac{\tan\delta_c}{(1 + 0.5Ak)} + \frac{\tan\delta_p}{[1 + (0.5Ak)^{-1}]} \quad \text{(A12)}$$

Appendix 2. Equations for Young's modulus in bending for three-ply laminates

The bending stiffness of a layered composite is given by [18]

$$D_{ij} = \tfrac{1}{3}\sum (Q_{ij})_k (z_k^3 - z_{k-1}^3) \quad \text{(B1)}$$

The Young's modulus in bending in the machine direction (MD) may be expressed as

$$E_x = \frac{12}{t_{cp}^3}\left(D_{11} - \frac{D_{12}^2}{D_{22}}\right) \quad \text{(B2)}$$

After insertion of layer coordinates and stiffness elements as in tension, E_x may be written as

$$E_x = \frac{12}{t_{cp}^3}\left\{(E_1)_c A + (E_1)_p B - \frac{[(\nu_{12})_c(E_2)_c A + (\nu_{12})_p(E_2)_p B]^2}{(E_2)_c A + (E_2)_p B}\right\} \quad \text{(B3)}$$

where

$$A = \frac{2}{3}\left(t_c^3 + \frac{3}{2}t_c^2 t_p + \frac{3}{4}t_c t_p^2\right) \quad \text{(B4)}$$

and

$$B = \frac{t_p^3}{12} \quad \text{(B5)}$$

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