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Thermochimica Acta 367–368 (2001) 407–414

thermochimica acta

www.elsevier.com/locate/tca

Dynamic mechanical spectroscopy of paper

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Received 5 November 1999; accepted 20 July 2000

Abstract

The viscoelastic properties of base-stock and coated papers are conveniently evaluated using DMA in a film-tension mode. Measurements of storage modulus (E') and loss modulus (E'') give good reproducibility and yield distinct patterns for paper types. Factors that mediate paper strength in the production environment can be simulated using DMA. Analysis of the individual components, base paper, latex and coated paper gives significant insights into the composite nature of paper. Measured glass transitions in papers with mixed coatings give characteristic peaks that are attributable to the pure latex T_g's. SEM photomicrographs show changes in surface morphology for coated papers and provide supportive data for DMA.

Keywords: Paper; Latex; Coating; DMA; Rheology

1. Introduction

Paper is a complex composite of cellulose, lignin, mineral fillers and organic binders. Commercial applications require high strength with surface properties that afford good printability. Polymeric latexes are typically coated onto paper to improve strength and to optimize the various printing and color-image processes.

The strength and viscoelastic properties of paper are conveniently analyzed using dynamic mechanical analyzers (DMA) in a film-tension mode. This 'direct-pull' experiment best simulates forces on sheet paper in a production environment. DMA devices provide measurements of storage modulus (E') and loss modulus (E'') with a calculation of $\tan\delta = E''/E'$ over a wide temperature range at selected frequencies and amplitudes. Tan δ is a sensitive measure of the energy-loss to energy-stored. A low $\tan\delta$ is usually indicative of a stiff but elastic material that loses little energy. In contrast, materials with higher $\tan\delta$ exhibit increasing viscous (or flow) effects and show significant energy loss. In some cases they retain the geometry of the deformed state. In the autostrain mode a DMA is 'force-tracking', and adjusts strain to maintain amplitude. This mode of operation enables one to record sample elongation or shrinkage.

2. Experimental

For this project, a TA Instruments DMA Model 2980 was employed in the film-tension mode. The instrument was programmed to measure E' and E'' over the range of -50 to 200°C at 2°C/min (20 μm amplitude, 1 Hz). Calibrations for force, mass, position and temperature were made in accordance with TA procedures. Paper samples were sampled from the center of the sheet and cut using a die and razor blade

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0040-6031/01/$ – see front matter
PII: S0040-6031(00)00666-3

(machine direction, MD). Each sample was measured for length, width and thickness before mounting.

Results are presented in units of megapascals (MPa). For the purpose of units conversion, $1\,Pa = 1\,N/m^2$ ($1\,MPa = 1\,N/mm^2$) and $101.325\,kPa = 14.7\,psi$.

3. Results and discussion

Base papers without surface coatings show four distinct regions in E' as illustrated in Fig. 1. In region 1, below $-20^{\circ}C$, a vitreous state exists in which the paper is very stiff. Applied stress at low heating rates ($2^{\circ}C$/min, 1 Hz, N_2 sweep) causes a linear decrease in E'. In region 2, devitrification occurs with a more rapid drop in E'. A broad alpha transition, spanning 50°, follows in which the lignin structures lose rigidity. In this region the loss modulus E'' exhibits one or more peak values. Region 3 is characterized by a plateau, and frequently an increase in E', which is attributed to changes in void volumes [1,2]. This region may span $50–60^{\circ}$ and is characterized by shrinkage as illustrated in Fig. 2. In region 4, E' begins a gradual decline and reflects bond disruption in the cellulose and lignin structures.

Select papers are illustrated in Fig. 3 and plotted as storage modulus (E') vs. temperature. All samples were cut in the MD. These curves, adjusted for density, depict the highest strength for papers with high hardwood-to-softwood ratio. The 100% rag content paper normally contains short fibers and no lignin.

The following series of experiments were designed to test the individual components of a composite consisting of base paper, the coating and finally the coated paper. Fig. 4 illustrates the DMA pattern for a base-stock paper cut in the MD. The data from -50 to $180^{\circ}C$ shows a major loss modulus (E'') peak at $-1.1^{\circ}C$ with a minor peak at $45^{\circ}C$. The maximum in tan δ indicates a phase lag of 1.4°.

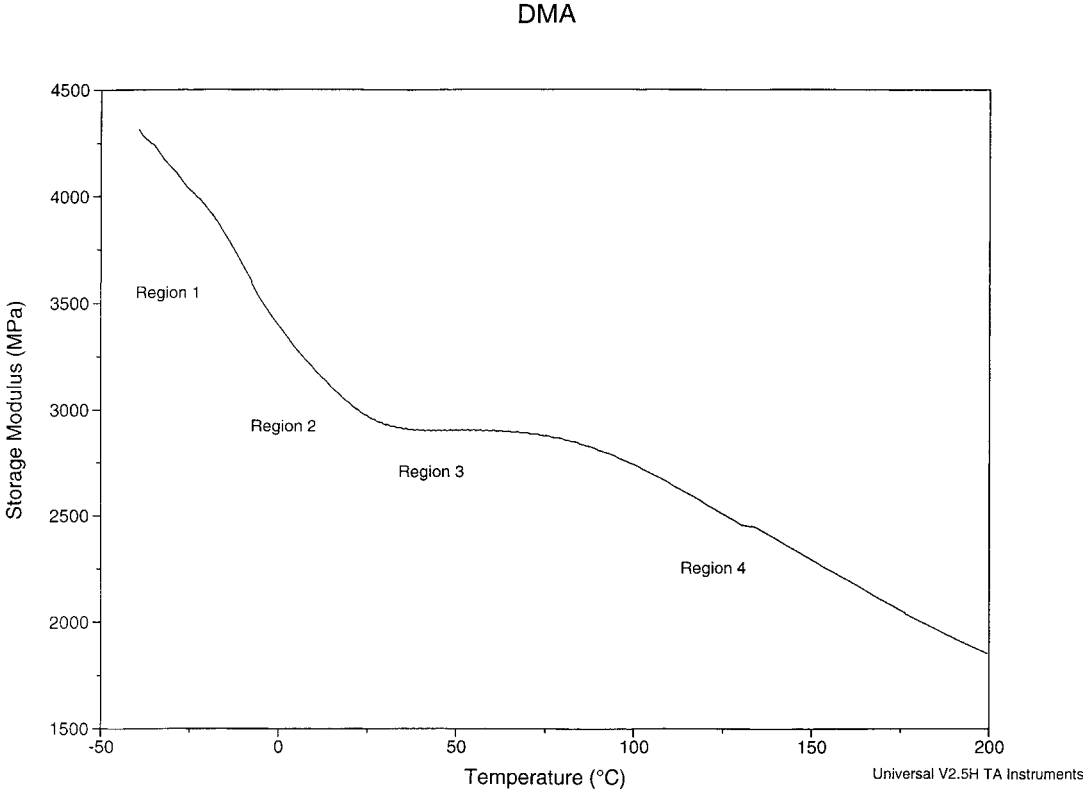

Fig. 1.

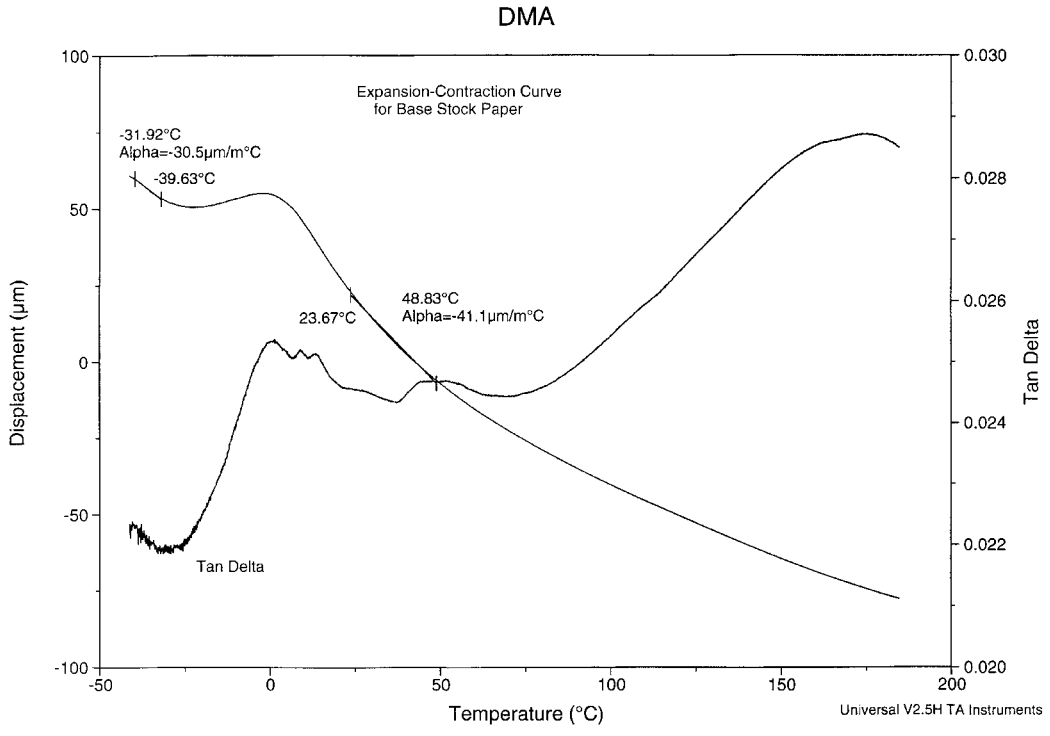
DMA
Expansion-Contraction Curve
for Base Stock Paper
-31.92°C
Alpha=-30.5µm/m°C
-39.63°C
48.83°C
Alpha=-41.1µm/m°C
23.67°C
Tan Delta
Displacement (µm)
Tan Delta
Temperature (°C)
Universal V2.5H TA Instruments

Fig. 2.

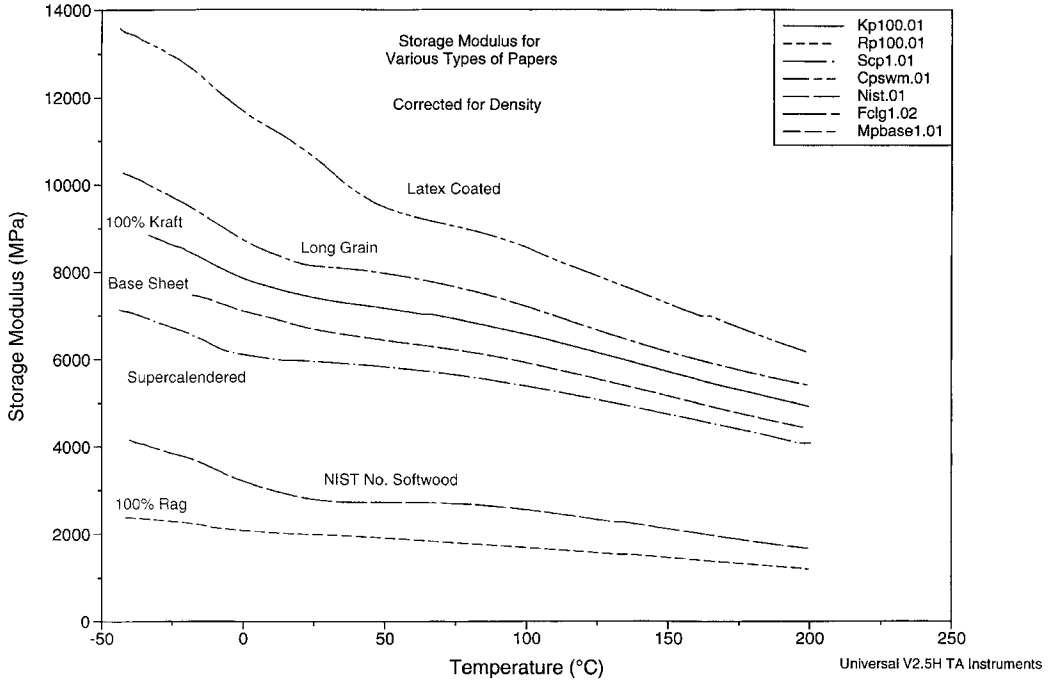
Storage Modulus for
Various Types of Papers
Corrected for Density
Kp100.01
Rp100.01
Scp1.01
Cpswm.01
Nist.01
Fclg1.02
Mpbase1.01
Latex Coated
100% Kraft
Long Grain
Base Sheet
Supercalendered
NIST No. Softwood
100% Rag
Storage Modulus (MPa)
Temperature (°C)
Universal V2.5H TA Instruments

Fig. 3.

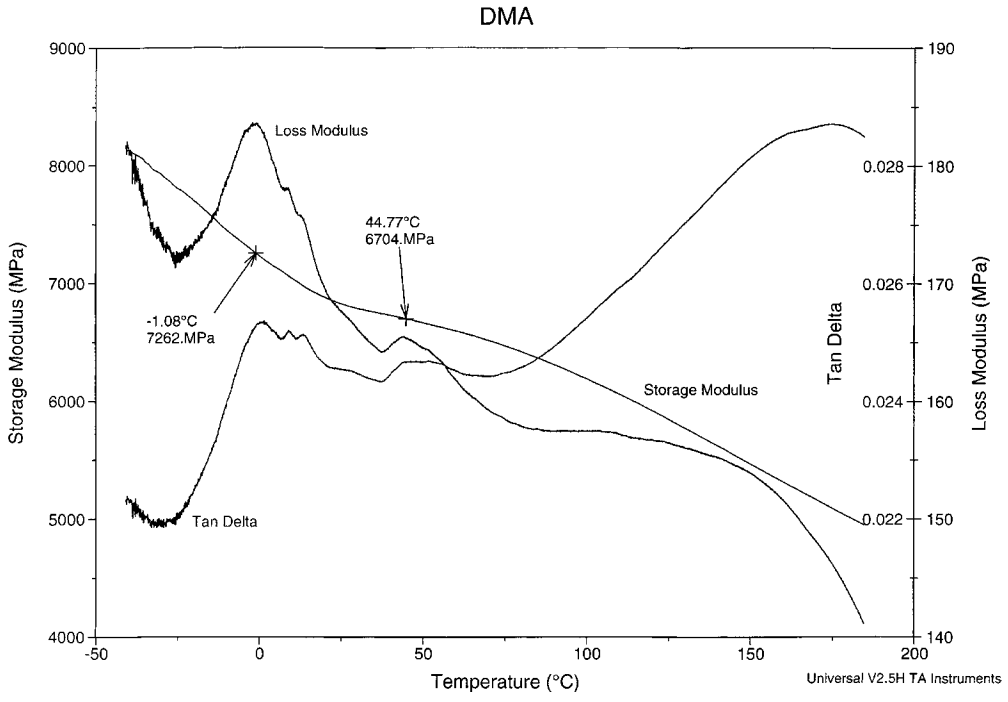
DMA
Loss Modulus
44.77°C
6704.MPa
-1.08°C
7262.MPa
Storage Modulus
Tan Delta
Storage Modulus (MPa)
Loss Modulus (MPa)
Tan Delta
Temperature (°C)
Universal V2.5H TA Instruments

Fig. 4.

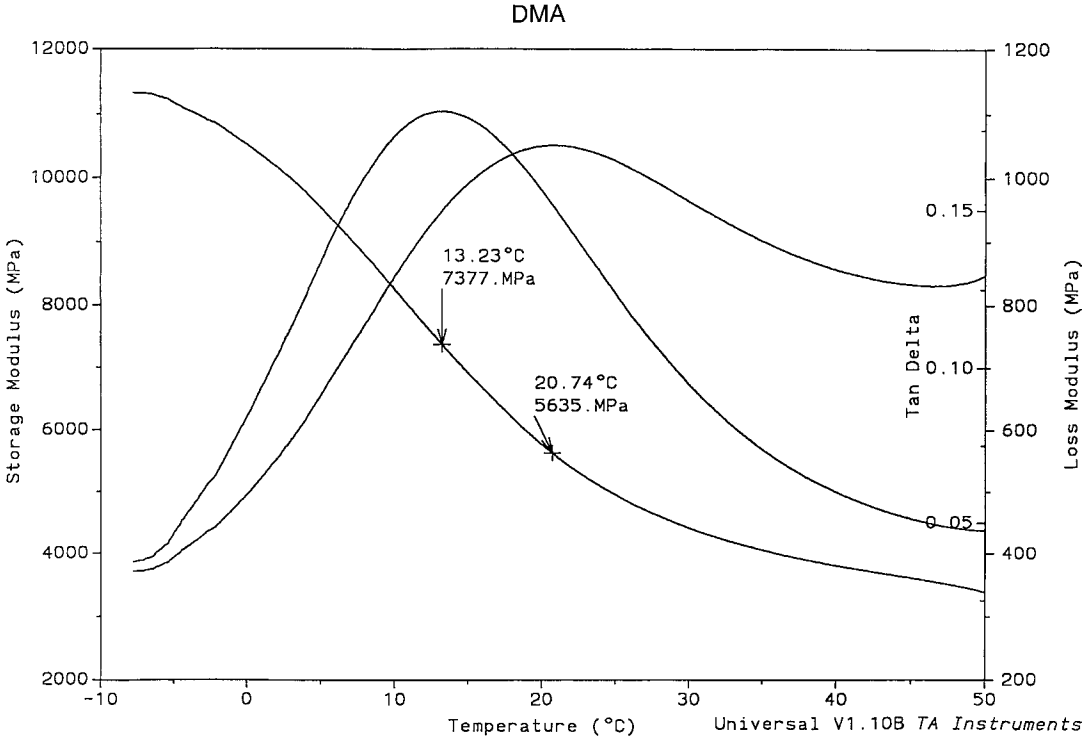
DMA
13.23°C
7377.MPa
20.74°C
5635.MPa
Storage Modulus (MPa)
Loss Modulus (MPa)
Tan Delta
Temperature (°C)
Universal V1.10B TA Instruments

Fig. 5.

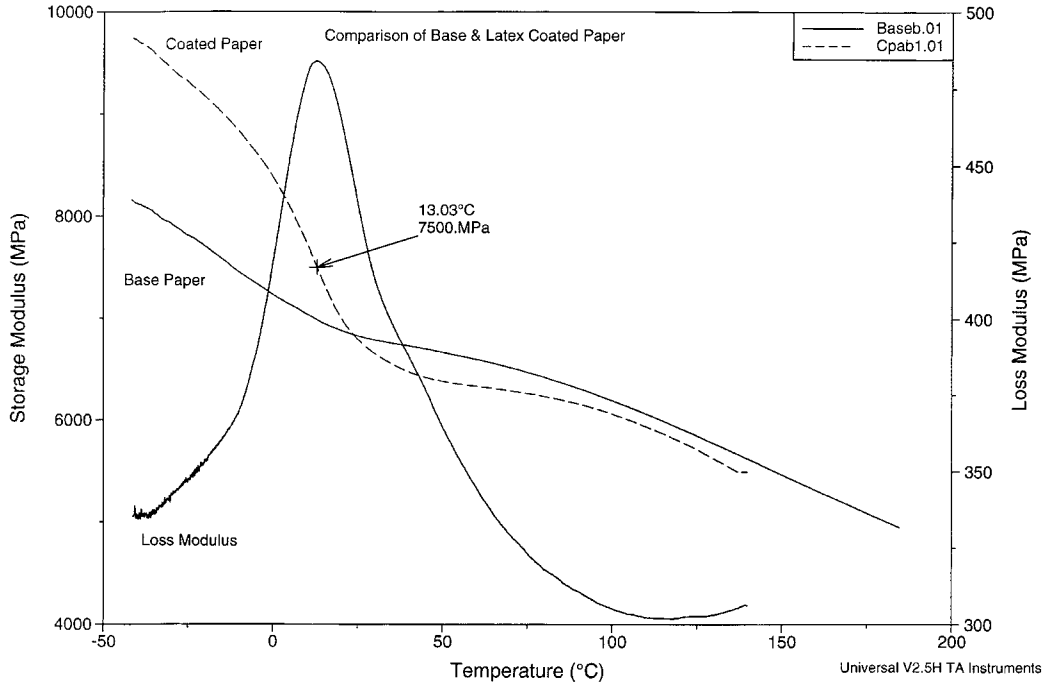
Comparison of Base & Latex Coated Paper
Baseb.01
Cpab1.01
Coated Paper
13.03°C
7500.MPa
Base Paper
Loss Modulus
Storage Modulus (MPa)
Loss Modulus (MPa)
Temperature (°C)
Universal V2.5H TA Instruments

Fig. 6.

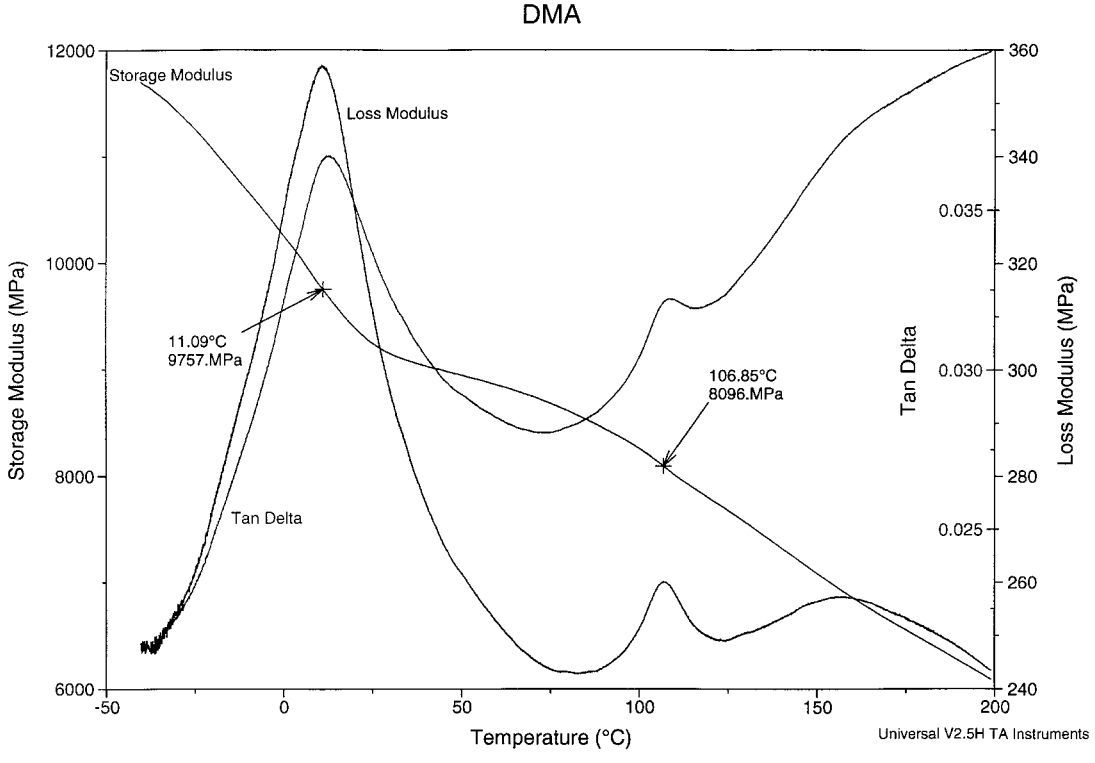
DMA
Storage Modulus
Loss Modulus
11.09°C
9757.MPa
106.85°C
8096.MPa
Tan Delta
Storage Modulus (MPa)
Tan Delta
Loss Modulus (MPa)
Temperature (°C)
Universal V2.5H TA Instruments

Fig. 7.

A polymeric latex coating, cast as a film, was analyzed using the same procedure with results shown in Fig. 5. The strength of the latex is somewhat higher at the low temperature end, but falls off more rapidly with increasing temperature. A T_g of 13.2°C is indicated via E'' and the $\tan\delta$ $T_g = 20.7$°C indicating a phase lag of 9.9° (more viscous).

When the coating is applied to the surface of the base paper at the 2% level, with calendering, the paper becomes a composite and now shows increased strength at the low end and a T_g of 13°C (Fig. 6). The peak in $\tan\delta$ (phase lag = 3.7°) indicates an increase in viscous effect and produces a more flexible paper than the base sheet.

Papers designed for specific end-use applications will contain a variety of additives including, clay, opacifiers, organic pigments and latexes. Acrylic and styrene–butadiene latexes are commonly selected for flexibility and strength at the lower temperatures and polystyrene latex for good surface strength and printability at the higher temperatures. As a result, the rheology of the composite becomes more complex which increases the probability of interactions between phases [1].

A DMA plot for a finished commercial paper containing a mixture of latexes is illustrated in Fig. 7. The paper has high strength up to 100°C and shows well-resolved T_g's at 11°C, typical for S/B latex of specific composition, and at 107°C, which is attributed to the presence of polystyrene latex and polymeric pigment. SEM photomicrographs, (courtesy of Mr. Kevin Battjes, MMI) Figs. 8–10, show differences

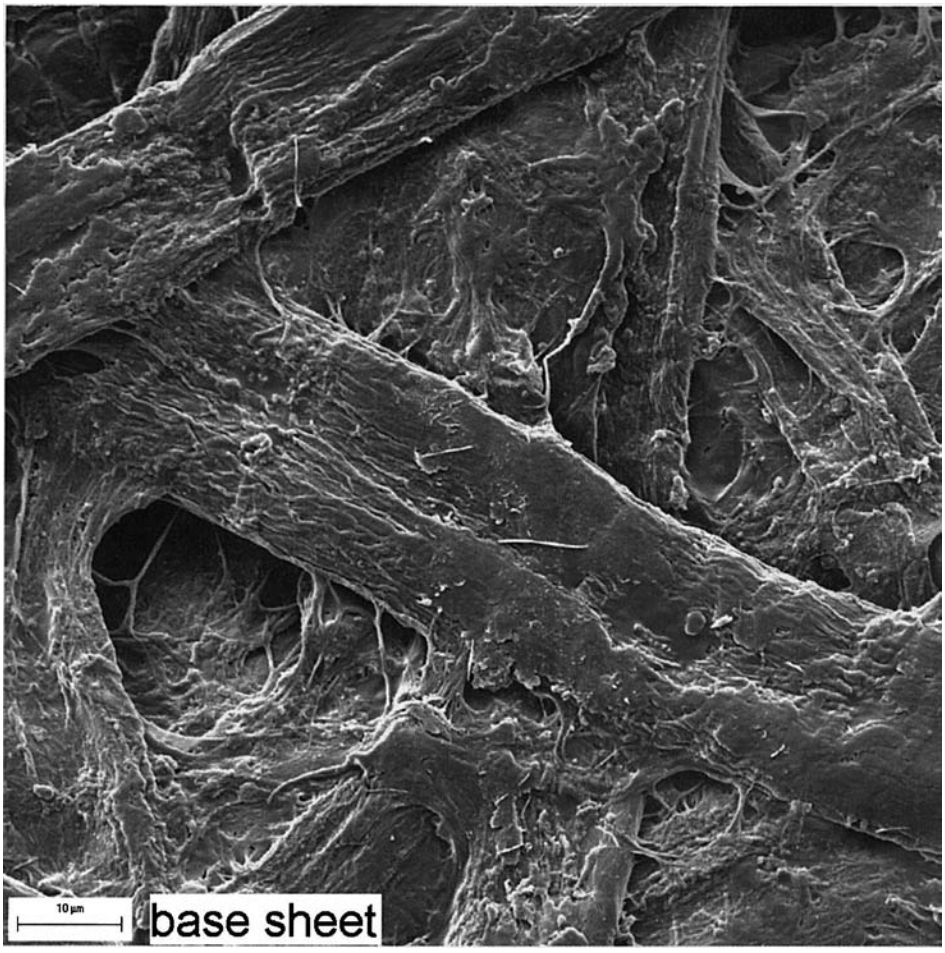

Fig. 8.

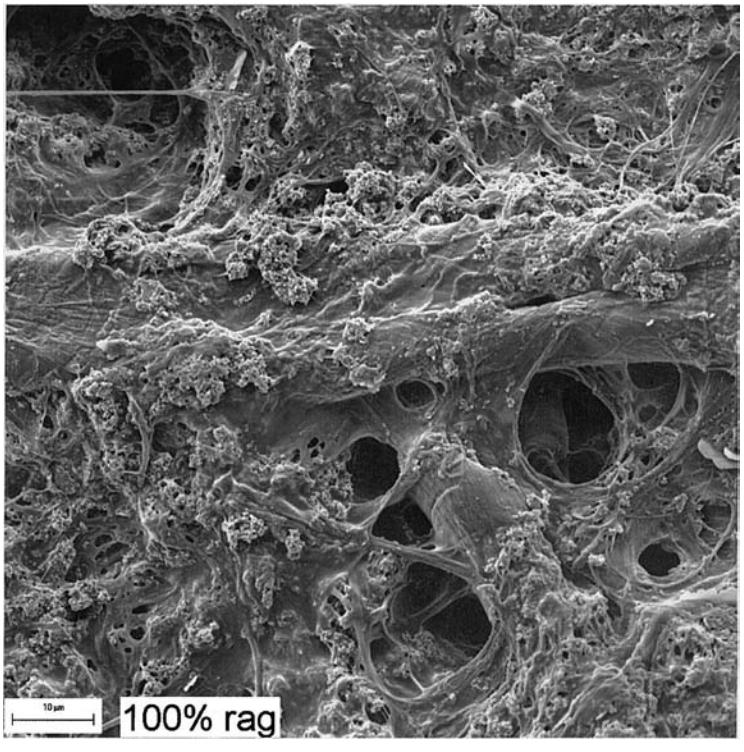

Fig. 9.

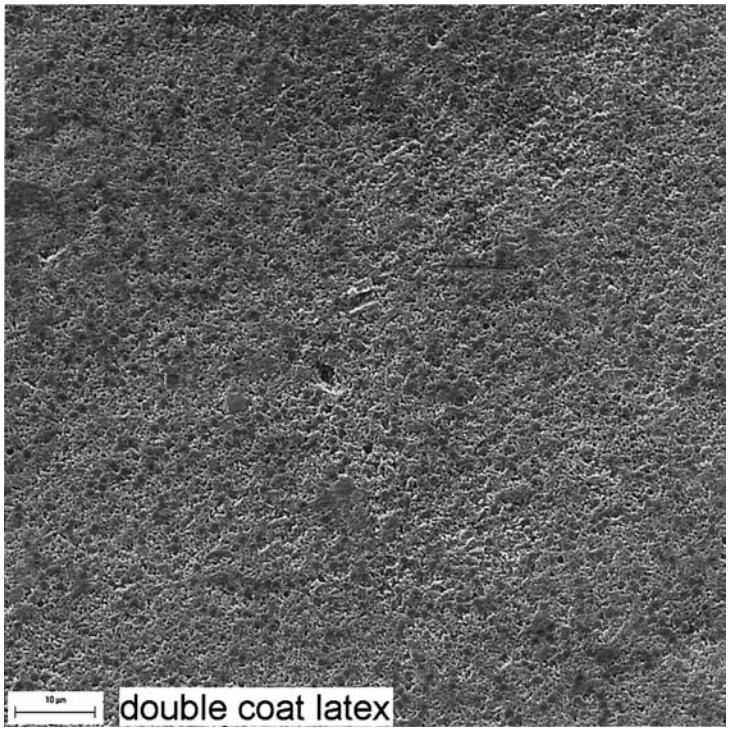

Fig. 10.

in structure between base sheet and 100% rag paper. When the base paper is coated with latex, and calendered, the surface appears largely filled in and provides a new rheological continuum.

4. Conclusions

The viscoelastic properties of paper over a wide range of conditions are conveniently evaluated using DMA. Measurements of storage modulus (E') and loss modulus (E'') give good reproducibility and produce a 'rheological fingerprint' for commercial papers. Factors that mediate paper strength in the production environment can be simulated using DMA. Analysis of the individual components in coated papers gives significant insights into the composite nature of paper. Glass transitions in papers with mixed coatings give characteristic peaks that are attributable to the pure latex T_g's.

References

[1] C.S. Kan, L.H. Kim, D.I. Lee, R.L. van Gilder, TAPPI J. 80 (1997) (5).
[2] Y. Yamaguchi, et al., TAPPI Notes: Advanced Coating Fundamentals, 1993