Dynamic Mechanical Studies of a Highly Filled Composite Structure: A Lightweight Coated Paper

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SYNOPSIS

A composite sandwich structure, consisting of a paper sheet as a middle layer and two porous coating layers of a highly filled acrylate-styrene-butadiene copolymer, has been studied by means of a dynamic mechanical test in torsion. Stiffness and mechanical damping, tan δ, were recorded over the temperature region where the latex polymer exhibits a glass transition. The mechanical damping decreases with increasing filler content in the coating. Variations in the thickness of the coating layers did not influence the mechanical damping. The glass transition temperature of the latex polymer increases with increasing volume fraction of filler at high filler contents as an effect of filler-matrix interaction. The outer layers partly penetrate into the middle layer, as indicated by thickness measurements on the coated paper. A theoretical comparison of the peak heights of the mechanical damping using lamination theory shows a discrepancy in the experimental results. If penetration of the outer layer is allowed for, i.e., if using a thicker outer layer of the composite in the calculations, a favorable correlation between the theoretical and the experimental results is obtained.

INTRODUCTION

A lightweight coated paper may be regarded as being a sandwich material composed of a paper sheet as a middle layer with porous outer layers of a highly mineral-filled latex polymer. In such a filled polymer structure, the mechanical properties are dependent on the properties of the individual components and the interfacial interaction between the components. Both matrix-paper interactions and filler-matrix and filler-filler interactions, depending on shape, size, and amount of filler,[1,2] will influence the properties of the polymer. At the filler surfaces, a boundary layer of the polymer is built up, giving these polymer chains reduced mobility.[1,3]

Studies of the mechanical behavior of clay-based coating films in the region of the latex polymer softening temperature have shown a decrease in the peak height of the mechanical loss factor, tan δ, for the filled latex with increasing filler content.[1,4] The position of the peak, often taken as a measure of the glass transition temperature T_g of the latex polymer is usually shifted to higher temperatures with increasing filler content. For an acrylate-styrene-butadiene latex, a shift of a few degrees Celsius compared with the temperature for the unfilled latex has been observed when the latex is filled with 75 vol % kaolin.[4] Some broadening of the transition also occurs due to polymer-filler interaction.[4,5]

In order to obtain a deeper understanding of how the polymer and the filler cooperate within these clay-based coatings, a wider range of filler contents than those used commercially has here been studied. Dynamic mechanical studies in torsion on a coated paper make it possible to study effects of interaction between the different components in the outer layer of the composite, as the testing method exhibits a high response to the properties of the outermost part of the specimen.[6] The use of different types of paper as a mechanical inert support have been described in the literature.[7-9] However, in these cases the polymer is impregnated into the paper.

Experimental studies in torsion of the uncoated and the polymer-coated paper have been performed

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in order to study the properties as a function of composition. To examine the polymer coating alone, polymer suspensions were impregnated on glass fiber braids used as support. The behavior of the coated layer is compared with micromechanical theories for particulate composite materials.

EXPERIMENTAL

Materials and Specimen Preparation

The outer layers or coatings were made from a highly-filled polymer latex based on an acrylate–styrene–butadiene copolymer (Acronal D810, BASF) with a glass transition temperature of 25°C (peak maximum of E'' at 1 Hz[10]). The polymer compound also contained a dispersing agent (Polysalz S), 0.2–0.45 vol %, and a thickener (CMC, Blanose 7L1C1), 1–4 vol %. The filler (SPS Kaolin, ECC International) is a platelike mineral pigment with an equivalent spherical diameter between 0.2 and 3 μm. The volume fraction of filler was varied between 30 and 90 vol %. The coatings were applied from aqueous suspensions and then dried for 2–3 min at 180°C. The average thickness of the coating layers was 4.5 μm. It should also be pointed out that such coatings are porous. A coating layer with a filler content of 77 vol % has a density of approximately 740 kg/m^3 compared to the density of approximately 2250 kg/m^3 for the unporous filled coating latex.

The middle layer, the paper sheet, was made of a mechanical pulp. This paper had a density of 700 kg/m^3 compared to the density of approximately 1500 kg/m^3 for the homogeneous wood fiber wall material.[11]

The paper is anisotropic due to the preferred orientation of the fibers in the machine direction. Specimens of both the coated and the uncoated paper were cut with the longitudinal axes in the cross direction of the sheets to enhance the signal of the polymer as the stiffness of the paper is lower in the cross direction. The uncoated paper was for comparison treated with water in the same manner as the paper in the coating procedure. Specimens were 30 mm in length and 0.7 mm in width, having thicknesses of 79 and 70 μm for the coated and uncoated paper, respectively. The thicknesses were measured by means of a mechanical sensor, which gives an integrated mean value of the thickness.[12]

Specimens for determining the behavior of the polymer coating were prepared by impregnating a glass fiber braid with polymer suspensions having the same filler content as the outer layer of the coated paper. The torsional glass fiber braids consist of about 40 fibers each, having a length of 15 mm and a diameter of 7 μm. The mechanical properties of the braid itself is negligible in comparison with the coated braid and therefore suitable as support.[13]

Since paper is hygroscopic and water influences the mechanical properties of paper, all specimens were conditioned at 20°C in a dry nitrogen atmosphere for 12 h before being tested. The moisture content was below 0.5%, and no further change in mechanical properties could be detected with increased drying. Measurements were performed with a heating rate of 0.5°C/min in a temperature interval between 0 and 70°C. The natural frequency range of the oscillation with these specimens is 0.5–2 Hz.

Apparatus and Principle of Evaluation

The torsion pendulum or torsional braid used for these studies, shown schematically in Figure 1, has been described by Kolseth.[14] The specimen is clamped at its upper end, and an inertia disc is freely suspended from the lower end. The sample holder is located in a chamber for temperature and humidity control. It is possible to study four specimens simultaneously.

The angular displacement of the pendulum is monitored with a light source and a photocell placed below the inertia disc, by the change in reflected light from the inertia disc, which is half-coated with a reflecting mirror. The transducer signal is linear with angular displacement.[14] The signal from the photocell is amplified and recorded by a computer.

The loss factor, tan δ, is defined by

$$\tan \delta = G''/G' = \Delta/\pi \tag{1}$$

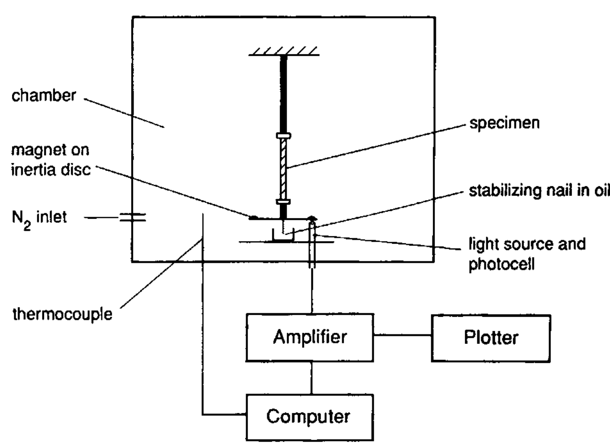


Figure 1 Schematic diagram of the torsion pendulum.

where

$$\Delta = (1/n)\ln(A_n/A_{n+1}) \quad (2)$$

G' is the storage shear modulus, G'' is the loss shear modulus, Δ is the logarithmic decrement, and A_n and A_{n+1} are the amplitudes of the nth and $(n+1)$th swings.

The torsional stiffness is directly proportional to the square of the frequency of the oscillation. The mass of the inertia disc causes an axial load on the specimen that increases the torsional stiffness,[15] which makes it difficult to measure absolute values of the shear modulus. The degree of the softening may still be compared from the relative stiffness above and below T_g as $\log(\alpha G_g/\alpha G_r)$, where α incorporates the moment of inertia and the geometry of the specimen, which is assumed not to change with temperature. The use of logarithmic values of the stiffness also means that the porosities of the paper and of the coating layer have no direct influence on the relative modulus change.

RESULTS

Viscoelastic Response of the Coating Layer

The filler content in the coating layer of coated papers affects the mechanical damping over the glass transition region, as shown in Figure 2, where tan δ is given as a function of temperature. The volume fractions of filler in the coating (10 g/m^2 on each side) are 43, 60, and 77%, respectively. The height

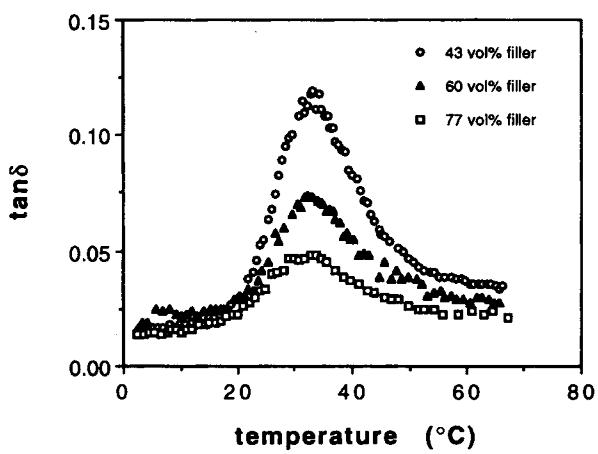


Figure 2 The mechanical damping, tan δ, versus temperature for composites with different filler contents in the outer layer. The coating weight was constant 10 g/m^2.

of the peak associated with the matrix softening decreases markedly with increasing filler content.

In order to take into account only the contribution to damping from the softening process, the peak height of tan δ is measured from a baseline taken as the damping level well outside the peak region. Figure 3 shows data of $(\tan\delta)_{max}$ versus vol % filler for coating/glass braid and coated paper specimens. The coating/glass braid specimen displays higher values of tan δ and a more pronounced increase in the mechanical damping at lower filler contents.

The influence of filler content on the glass transition temperature T_g of the polymer matrix is illustrated in Figure 4 for the coated paper. The value of T_g is taken as the position of the tan δ peak on the temperature scale. No definite trend is seen at lower filler contents. At filler contents above 70 vol %, an increase in T_g is noticed. The T_g increase is about 5°C as the filler content increases from 70 to 85 vol %. Although not shown, a similar behavior is observed for measurements made on the coating separately.

Figure 5 shows the effect of coating thickness on tan δ. The thickness of the middle layer was kept constant, 70 μm, and the filler content of the matrix was kept at 77 vol %. It is evident that the thickness of the outer layer has no major influence on the height of the tan δ peak in the range here studied. The authors have also shown that the thickness of the middle layer, the paper sheet, has a minor influence on the peak height of tan δ.[16]

The degree of softening at T_g of the polymer may also be calculated as the logarithmic difference between stiffness in the glassy region and in the rubbery region, $\log(G_g/G_r)$. G_g and G_r are taken as the intersections of two parallel lines following the stiffness curve in the glassy and that in the rubbery region, respectively, and a vertical line at T_g as indicated in Figure 6. T_g is here defined as the position of the vertical line on the temperature scale where the vertical line intersects the stiffness curve at half its height, $h/2$.

Figure 7 shows $\log(G_g/G_r)$ for both coating/glass braid specimen and coated paper specimen, for different volume fractions of filler. The influence of filler content on the logarithmic difference in stiffness is similar to that obtained for the damping height.

Equations for Filled Composites

The modulus of a filled polymer may be predicted by a variety of models that may provide a better

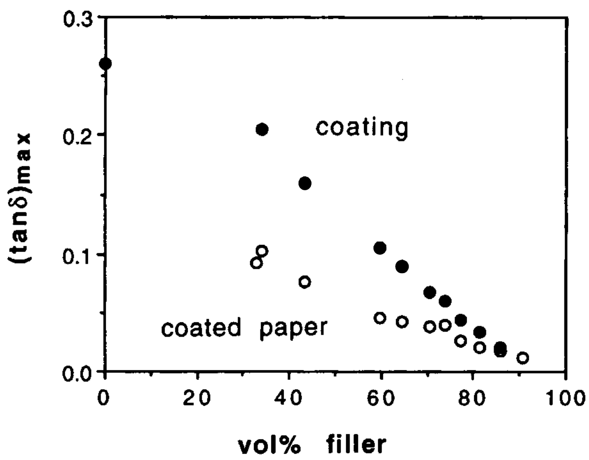


Figure 3 Peak height of the mechanical damping, tan δ, vs. volume fraction of filler for coating/glass braid and coated paper specimens.

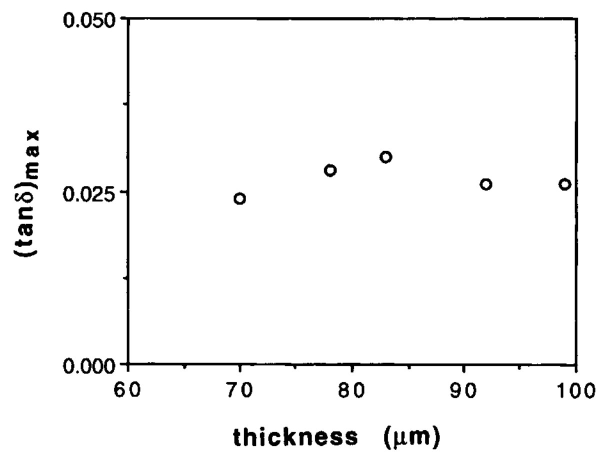


Figure 5 Peak height of the mechanical damping, tan δ, vs. thickness of the coating layer of the coated paper. The filler content in the coating was 77 vol %.

insight into the structural arrangement of the components within the composite.

Using equations such as those given in Appendix A, it is possible to estimate the degree of softening through the logarithmic difference in modulus, $\log(G_g/G_r)$, at T_g. In Figure 8, $\log(G_g/G_r)$ is plotted versus filler content for the different models and the experimental values for the coating/glass braid specimen. For the Halpin–Tsai equation, a geometric A-value of [17] 54 [$\log A = \sqrt{3}\log(\text{aspect ratio})$, where the aspect ratio of the filler platelets is assumed to be 10] and a modulus for the clay of 70 GPa were used.[18] The modulus of the acrylate-styrene–butadiene copolymer was estimated to be 2 GPa in the glassy region and 0.2 GPa in the rubbery region.[19]

As seen in Figure 8, none of the models are capable of describing the experimental results over the entire range of filler contents. The shape of the experimental curve may indicate a reorganization of the particles as the filler content increases. The most dramatic reorganization could be when the latex matrix changes from being continuous to become discontinuous in nature, merely anchoring the filler particles to each other. These two configurations of the latex can be depicted in the way presented in

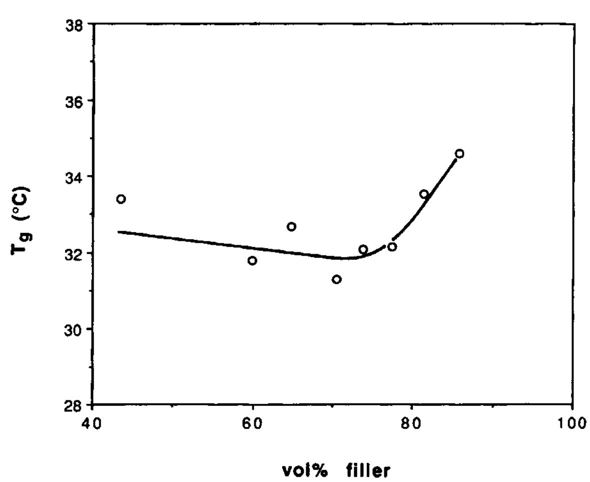


Figure 4 Softening temperature T_g vs. vol % filler in the coating layer of the coated paper. The values of T_g are estimated from the position of the tan δ peaks on the temperature scale.

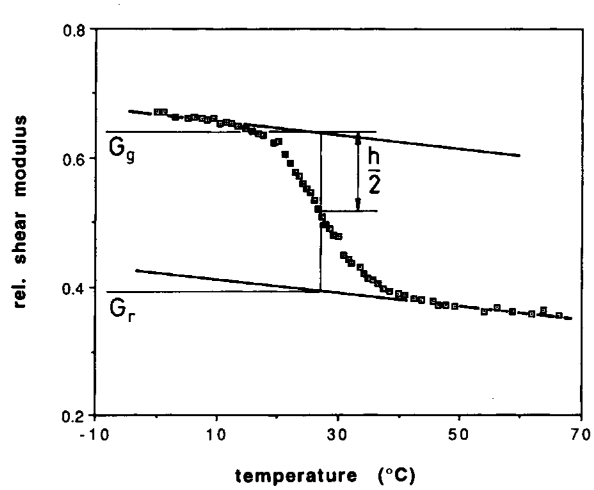


Figure 6 Relative shear modulus versus temperature for a dried polymer with 60 vol % filler/glass braid specimen. The degree of softening is calculated as indicated in the figure.

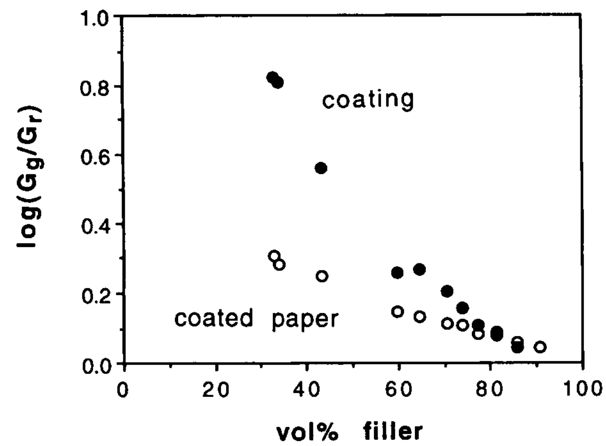


Figure 7 Effect of filler content on the logarithmic difference in stiffness for both coating/glass braid specimen and coated paper specimen.

Figure 9. This change in configuration may also be associated with the effects seen on the T_g. At high filler contents the T_g is affected by the polymer boundary layer, whereas at low filler contents it reflects the bulk matrix properties.

Paper/Coating Interactions

The interaction between paper and coating may be viewed by examining the effects of the thickness of the composite structure. Figure 10 shows that the thickness of the coated paper is unaffected by the coat weight below about 5 g/m^2, but that, at coat weights above 5 g/m^2, the thickness increases linearly with the grammage of the coating layer. Similar results have been noticed by others.[20] It seems probable that the coating layer partly penetrates the paper structure and fill voids and irregularities of the surface before contributing to the total thickness. Although not shown, it was found that the thickness of the laminate was not affected by the volume fraction of filler in the coating in the range of 34–90% here studied.

A simple analysis of the coated paper treated as a three-ply laminate is presented in Appendix B. The following expression for the mechanical damping, tan δ, is obtained:

$$\tan \delta_c = \tan \delta_o[1 + (b/a)(G'_{12})_m/(G'_{12})_o]^{-1} + \tan \delta_m[1 + (a/b)(G'_{12})_o/(G'_{12})_m]^{-1} \quad (3)$$

where subscripts c, o, and m denote coated paper, outer layer, and middle layer, respectively, a and b are geometric constants given in Appendix B, and G'_{12} is the storage shear modulus.

Table I shows for comparison the estimated values of the mechanical damping for the laminated structure, tan δ_c, based on eq. (3), and the experimental results. Here, the absolute values of the tan δ peak for both coating and coated paper are taken as the measured values from zero level of the abscissa, as given in eq. (3). The theoretical values are slightly lower than the experimental data but the dependence on filler content seems to be consistent with the measured values. However, a better

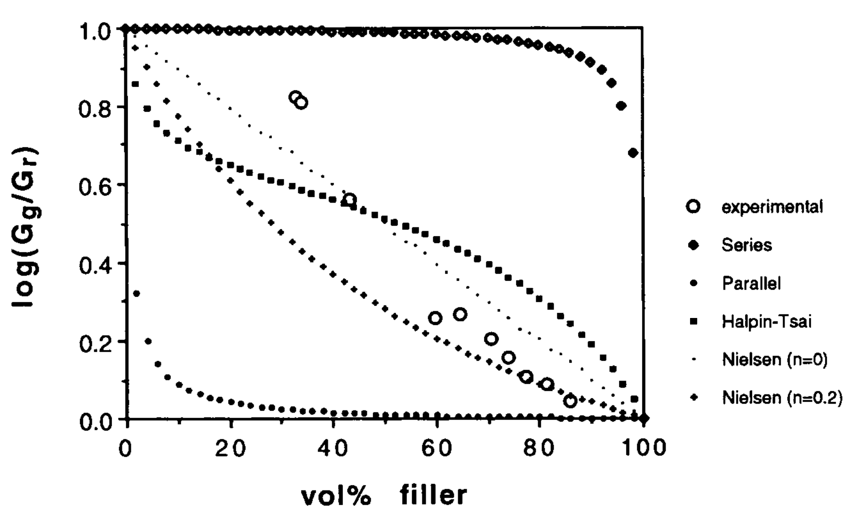


Figure 8 The experimental data are for the coating/glass fiber braid specimen and for calculated values from different models.

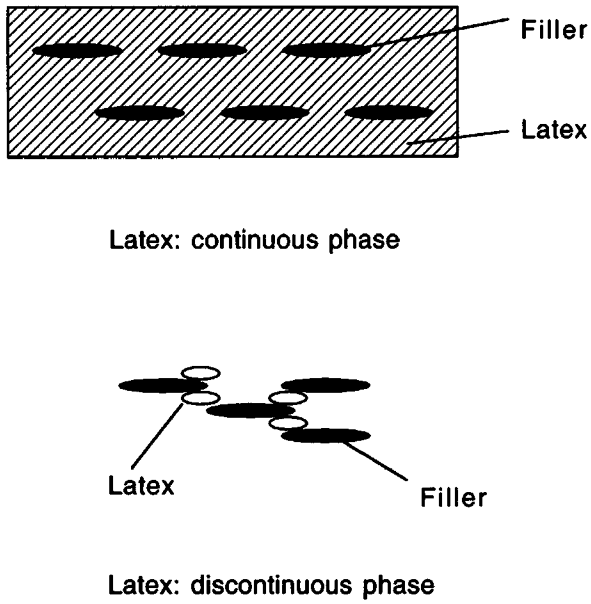


Figure 9 Schematic models of the continuous phase and the discontinuous phase of a filler/latex system.

correlation is obtained if a thicker outer layer and a corresponding reduction in the thickness of the base paper are assumed. Thickness measurements indicate that the amount of penetrated coating material corresponds to a thickness of about 6 μm, i.e., 3 μm on each side (see Fig. 10). If it is assumed that this interpenetrating layer has properties corresponding to those of the outer layer, it would be appropriate to estimate tan δ with a higher value for the outer layer. Calculations of tan δ based on this increased thickness of the outer layer and a corresponding decrease in thickness of the base paper are also shown in Table I. The total thickness of the composite is kept constant at 79 μm.

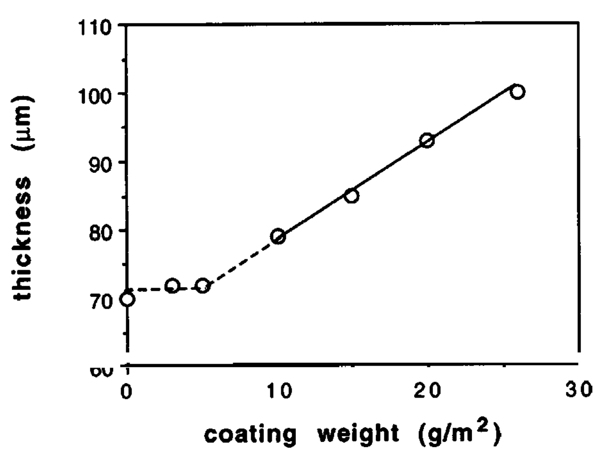


Figure 10 Thickness of the coated paper with different amounts of coating in the outer layer. The filler content was 77%.

Table I Experimental and Theoretical Values of tan δ for the Composite

Vol % Filler	$\tan\delta_{exp}$	$\tan\delta_{theor}$[a]	$\tan\delta_{theor2}$[a,b]
34	0.132	0.074	0.107
43	0.104	0.068	0.096
60	0.072	0.054	0.071
70	0.060	0.045	0.054
77	0.052	0.040	0.047
86	0.037	0.029	0.031

[a] Calculated from eq. (3).
[b] Corrected thicknesses of the different plies.

The improved agreement between the theoretical and the experimental data indicate that the interpenetrating zone has properties more resembling those of the coating layer than those of the paper.

CONCLUSIONS

This study of dynamic-mechanical properties in torsion of a polymer-coated paper shows that the thickness of the coating only marginally influences the peak value of tan δ at the softening temperature of the polymer latex. The filler content in the coating, however, has a marked influence on the peak height on tan δ. With increasing filler content, there is a nonlinear decrease in tan δ, the form of which is dependent on the kind of interaction occurring in the composite system. The linear decrease in tan δ with increasing filler content reported for such systems[21] may thus be only an approximation of the general behavior.

The increase in softening temperature with increasing volume fraction of filler at high filler contents is probably an effect of filler–polymer interaction. In the interfacial region of the filled polymers, chains are immobilized by interaction with filler surfaces, leading to an increase in T_g.

The shapes of the experimental curves of the logarithmic difference in stiffness, $\log(G_g/G_r)$, a measure of the degree of softening at T_g, as a function of filler fraction are similar to those of the curves for the tan δ peak heights. From the comparison with the theoretical calculations in Figure 8, it is seen that the composite behaves more as a series or a lower bound model at low filler contents, whereas in the highly filled region the behavior is closer to that described by a parallel model.

In a coated paper, an interphase is formed between the middle and outer layer, as is evident from the thickness measurements on the composites with different amounts of coating. Penetration of coating components into the paper form an interaction zone with mechanical properties different from those of the other layers. The discrepancy between the experimental and the theoretical values of tan δ is indeed smaller if the thicknesses of the outer layer and of the middle layer are compensated for by considering a penetration of the coating layer into the paper substrate.

APPENDIX A: EQUATIONS FOR FILLED COMPOSITES

Limiting values for the mean properties in a filled composite may be given by the parallel model,

$$G = (1 - v_f)G_m + v_f G_f \quad (A.1)$$

or by the series model,

$$G = [(1 - v_f)/G_m + v_f/G_f]^{-1} \quad (A.2)$$

where G_m and G_f are the shear moduli of matrix and filler, respectively, and v_f is the volume fraction of the filler.

Another general mixing equation for composites has been proposed by Nielsen[22]:

$$G^n = v_f G_f^n - (1 - v_f)G_m^n, \quad \text{where } -1 \le n \le 1 \quad (A.3)$$

The constant n is related to the morphology of the system, and it has been shown that, for the shear modulus of semicrystalline polymers, $n = 0.2$.[22]

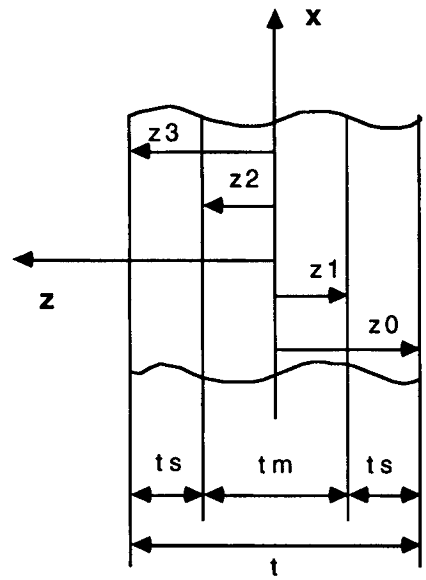
The Halpin–Tsai[17] equation is an empirical expression containing a geometric reinforcement factor A:

$$G_c/G_m = (1 + ABv_f)/(1 - Bv_f) \quad (A.4)$$

where

$$B = (G_f/G_m - 1)/(G_f/G_m + A)$$

APPENDIX B: EQUATIONS FOR TORSIONAL MODULI OF THREE-PLY LAMINATES



The torsional stiffness per unit width, D_{66}, of a layered composite is given by

$$D_{66} = (1/3) \sum (Q_{ij})_k (z_k^3 - z_{k-1}^3) \quad (B.1)$$

where $(Q_{ij})k$ is the stiffness element for the kth ply. After insertion of layer coordinates and using the relation $Q_{66} = G_{12}$, where G_{12} is the shear modulus, D_{66} may be written as

$$D_{66} = (2/3)(G_{12})_o[t_o^3 + (3/2)t_o^2 t_m + (3/4)t_o t_m^2] + (G_{12})_m t_m^3/12 \quad (B.2)$$

where subscripts o and m denote outer layer and middle layer, respectively. The torsional stiffness T can be expressed as

$$T = 2D_{66}/L \quad (B.3)$$

giving

$$T = a(G_{12})_o + b(G_{12})_m \quad (B.4)$$

where

$$a = 4/(3L)[t_o^3 + (3/2)t_o^2 t_m + (3/4)t_o t_m^2] \quad (B.5)$$

and

$$b = 2t_m^3/(12L) \quad (B.6)$$

The viscoelastic correspondence principle[23] gives

$$T' = a(G'_{12})_o + b(G'_{12})_m \quad (B.7)$$

$$T'' = a(G''_{12})_o + b(G''_{12})_m \quad (B.8)$$

also

$$\tan \delta_T = T''/T' = \tan \delta_o[1 + (b/a)(G'_{12})_m/(G'_{12})_o]^{-1} + \tan \delta_m[1 + (a/b)(G'_{12})_o/(G'_{12})_m]^{-1} \quad (B.9)$$

where

$$a/b = 8(t_o^3 + (3/2)t_o^2 t_m + (3/4)t_o t_m^2)/t_m^3 \quad (B.10)$$

The ratio $(G'_{12})_o/(G'_{12})_m$ is estimated by the corresponding ratio $(E'_{12})_o/(E'_{12})_m$, where $(E'_{12})_o$ and $(E'_{12})_m$ are the Young's moduli of the outer layer and the middle layer, respectively.[19] This assumption is valid if the difference in Poisson ratio between the paper and the matrix is small. If the Poisson ratios are assumed to be 0.15 for the paper sheet[24] and 0.3 for the matrix,[25] it follows that $(G'_{12})_o/(G'_{12})_m = 1.15\ E_o/1.3\ E_m \approx (E'_{12})_o/(E'_{12})_m$.

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