

DMA Analysis of PVAc Latex Reinforced with Cellulose Nanofibrils

Francisco López-Suevos, Christian Eyholzer and Nico Bordeanu
Wood Laboratory
Swiss Federal Laboratories for Materials Testing and Research
Dübendorf, Switzerland

Abstract

Suspensions of commercial refined and bleached beech wood pulp (RBP) were further processed through mechanical disintegration (MD-RBP), chemical modification (CM-RBP), or through chemical modification followed by mechanical disintegration (CM-MD-RBP). Nanocomposites were prepared by compounding a poly(vinyl acetate) (PVAc) latex adhesive with increasing contents of the untreated RBP or the processed nanofibrils, and the resulting nanocomposites were analyzed by dynamic mechanical analysis (DMA). The presence of cellulose nanofibrils had a strong influence on the viscoelastic properties of PVAc latex films. For all nanocomposites, increasing amounts of cellulose nanofibrils led to increasing reinforcing effects in the glassy, glass transition and rubbery plateau regions. At any given concentration, the CM-MD-RBP cellulose nanofibrils showed superior reinforcing potential, especially in the glass transitions of PVAc and polyvinyl alcohol (PVOH), and in the rubbery plateau. The untreated RBP fibrils that were only mechanically disintegrated showed higher reinforcement effect than those that were only chemically modified. Most interestingly, the reinforcing action of the CM-MD-RBP (at 5, 10 and 20% concentrations) in the high temperature region was superior to the sum of the separate effects of the CM-RBP and MD-RBP, indicating a synergistic effect.

Keywords: Cellulose nanofibrils, carboxymethylation, mechanical disintegration, PVAc latex, reinforcement, DMA

Introduction

Cellulose nanofibrils derived from biomass resources are renewable and biodegradable materials with a strong potential for polymer composite reinforcement (Zimmermann et al. 2004). In addition to adequate fibril/matrix chemical affinity, attainable reinforcement levels are closely related to the degree of mechanical disintegration of the fibrils. The mechanical properties of nanocomposites can be modified by properly processing and refining the cellulose nanofibrils. The evaluation of the resulting mechanical properties can be efficiently conducted by dynamic mechanical thermal analysis (DMA) as a function of time/frequency and temperature. Moreover, DMA is specially suited to identify fibril/matrix interactions or changes in the viscoelastic properties of nanocomposites in the glassy, glass transition (T_g) or rubbery plateau regions. For instance, Kvien and Oksman (2007) used DMA to show a significant difference in storage modulus in the glassy region (i.e. below the T_g) of a PVOH matrix when using cellulose nanowhiskers (CNW) oriented in parallel or transverse directions. Also, the different alignment of CNW altered the breadth of the tan delta peaks through the glass transition evidencing a CNW-PVOH interaction. Dalmas et al. (2007) showed that cellulose nanofibrils obtained from sugar beet pulp provided a large mechanical reinforcement in the rubbery plateau region (i.e. above the T_g) of an amorphous poly (styrene-co-butyl acrylate) matrix. These studies demonstrate the potential of the DMA technique to evaluate reinforcement effects in the glassy, glass transition or in the rubbery plateau regions of cellulose nanocomposites.

In the present work, suspensions of commercial refined beech pulp (RBP) were further processed through chemical modification (CM-RBP), mechanical disintegration (MD-RBP) and through chemical modification followed by mechanical disintegration (CM-MD-RBP). Nanocomposites were prepared by mixing a poly (vinyl acetate) (PVAc) latex with different concentrations of the untreated or the processed RBP. The resulting nanocomposites were analyzed by DMA to investigate the influence of the different cellulose nanofibrils on their viscoelastic properties.

Experimental

Modification of Refined Beech Wood Pulp

Suspensions of refined and bleached beech wood pulp, RBP, (Arbocel B1011, J. Rettenmaier & Söhne GmbH+CO.KG, Germany) were further processed through: 1) mechanical disintegration (MD-RBP), 2) chemical modification (CM-RBP) and 3) chemical modification followed by mechanical disintegration (CM-MD-RBP). The treatments were conducted as follows.

Mechanical Disintegration

Pretreatment: 1.40 kg of the RBP aqueous suspension (ca. 10% by weight) were initially mixed with 8 L of water and stirred with a stainless steel agitator for 30 minutes at 20°C in a 10 L reactor. The diluted RBP suspension (ca. 1.5% by weight) was then processed with an inline disperser (Megatron MT 3000, Kinematica AG, Switzerland) at 20000 rpm for 60 minutes. This pretreatment facilitated the breaking down of the RBP fibrous material into smaller parts (cellulose fibril bundles) providing a more homogeneous suspension.

High-Shear Mechanical Disintegration: 6 L of the pretreated RBP suspension were subjected to high-shear disintegration in a Microfluidizer type M-110Y (Microfluidics Corporation, USA). A stable cellulose nanofibril suspension (MD-RBP) was obtained after 6 passes through the Y and Z-shaped interaction chambers (process pressure: 1500 bar) of the Microfluidizer.

Chemical Modification

2.54 kg of the RBP aqueous suspension were mixed with 7.46 kg of a 5:3 (v/v) isopropanol:ethanol mixture in a 10 L reactor using a stainless steel agitator. The resulting mixture was then processed with the inline disperser at 15000 rpm for 30 min at 20°C. 115.02 g of chloroacetic acid (sodium salt) were added to the mixture followed by slow addition of 189.50 g of a 21% (by weight) sodium hydroxide aqueous solution under continuous stirring. After raising the temperature to 60°C, the reaction mixture was again processed with the inline disperser at 20000 rpm for 2 hours before cooling down to 20°C. The resulting suspension was neutralized with acetic acid and centrifuged at 15000 rpm for 90 min. The supernatant was discarded and the precipitate containing the carboxymethylated cellulose fibrils was washed first with distilled water several times to remove any water-soluble by-product and second with a 5:3 (v/v) isopropanol:ethanol mixture prior to drying overnight in the oven at 65°C. The resulting powdered CM-RBP fibrils are easily re-dispersible in water forming a stable gel. The degree of substitution (DS) of the CM-RBP was evaluated by conductometric titration according to a modified method from Eyster et al. (1947). A DS of 0.156 ± 0.028 was obtained from three independent evaluations, which amounts to 5.2% of the hydroxyl groups present in the cellulose fibrils being replaced by carboxyl groups.

Finally, the CM-MD-RBP fibrils were prepared by initially re-dispersing 69.2 g of the dry CM-RBP in 2.69 kg of water (ca. 2.5% by weight) with a high-shear blender (Ultra-Turrax, IKA, Germany). The resulting suspension was then transferred to the 10 L reactor and the mechanical disintegration treatment was conducted as described previously.

Adhesive

The PVAc latex used was VN 1693 (Collano AG, Switzerland). This system is an aqueous suspension of PVAc particles stabilized by PVOH and it does not contain cross-linking agents.

Preparation of the PVAc latex-cellulose fibrils nanocomposites

Composites were prepared by mixing the PVAc latex with the RBP, MD-RBP, CM-RBP or CM-MD-RBP fibrils at different concentrations, i.e. 5, 10, 20 and 30% (g of dry fibrils in 100 g of total dry material). The PVAc-fibrils mixtures were blended with the Ultra-Turrax and degassed under vacuum before casting the films onto silicon molds. The films were dried under ambient conditions for 2 days and then cut with a twin-bladed cutter to obtain 45 (length) x 10 (width) x 0.6-0.7 (thickness) mm samples. Prior to DMA analysis, all samples were dried by storage over silica gel under vacuum for at least 3 days.

DMA experiments

A GABO-Eplexor DMA 800 (GABO qualimeter Testanlagen GmbH, Germany) in tension mode was used to study the viscoelastic properties of the resulting dried films. All samples were initially conditioned at 0°C for 5 min in the DMA, and then dynamic heating scans were performed from 0 to 150°C at 2°C/min and 10Hz. The contact force, the static load strain and the dynamic load strain used in these experiments were 0.1N, 0.3% and 0.03%, respectively. Three analyses were obtained for each sample.

Results and Discussion

Figure 1 shows the viscoelastic response (storage modulus and $\tan \delta$) for all PVAc nanocomposites prepared in this work. First of all, the reproducibility of the response was very good, as demonstrated by the nearly perfect overlap of three repeat curves for each sample type. Spanning from low to high temperatures, three different regions could be identified: the glassy state, the glass transition, and the rubbery plateau. The neat films (open star symbols) exhibited two major transitions above the glassy temperature region: one near 45°C ($\tan \delta$ peak) that corresponds to the PVAc glass transition, and another near 80°C ($\tan \delta$ peak) associated to the PVOH glass transition (Brandrup and Immergut 1989, López-Suevos and Frazier 2006). Through these two glass transitions the neat films dramatically softened as showed by the almost four decade reduction in storage modulus. Above the glass transition the material became rubbery; although a clear distinction of the rubbery plateau that followed the PVAc softening was not possible since this region overlapped with the subsequent PVOH glass transition.

As it can be seen from Figure 1 the presence of the cellulose nanofibrils, regardless of the treatment or concentration, had a significant effect on the viscoelastic properties of the resulting nanocomposites. For all the different nanofibrils, in the glassy region (see inset graphs), the storage modulus moderately increased with increasing contents of cellulose nanofibrils. This effect was more pronounced for the treated ones, i.e. the CM-RBP, MD-RBP and CM-MD-RBP. It is thought that these treatments break down the RBP fibrous material into smaller parts which increases stiffness of nanocomposites in the glassy region.

In the PVAc glass transition we saw an increase in storage modulus up to nearly two decades and a decrease in the damping intensity ($\tan \delta$ peak) from 0.85 to 0.2-0.3, depending on the fibril type and concentration. This suggested that the presence of cellulose fibrils reduced the flexibility of the PVAc chains leading to the increase in storage modulus. On the other hand, the presence of cellulose fibrils did not significantly alter the PVAc glass transition temperature ($\pm 2^\circ\text{C}$ from $\tan \delta$ peak) suggesting, according to similar studies (Backman and Lindberg 2004), a weak interaction between the bulk PVAc and the fibrils. Most interesting is that the PVOH softening was gradually erased as the fibril concentration in the nanocomposites increased. This was associated with the segmental motions of the PVOH chains being increasingly restricted by the presence of the nanofibrils. Since the PVOH is the interfacial dispersing agent used to prepare the vinyl acetate emulsion polymerization, this finding suggests that the fibrils primarily act at the particle boundaries where PVOH is believed to be located.

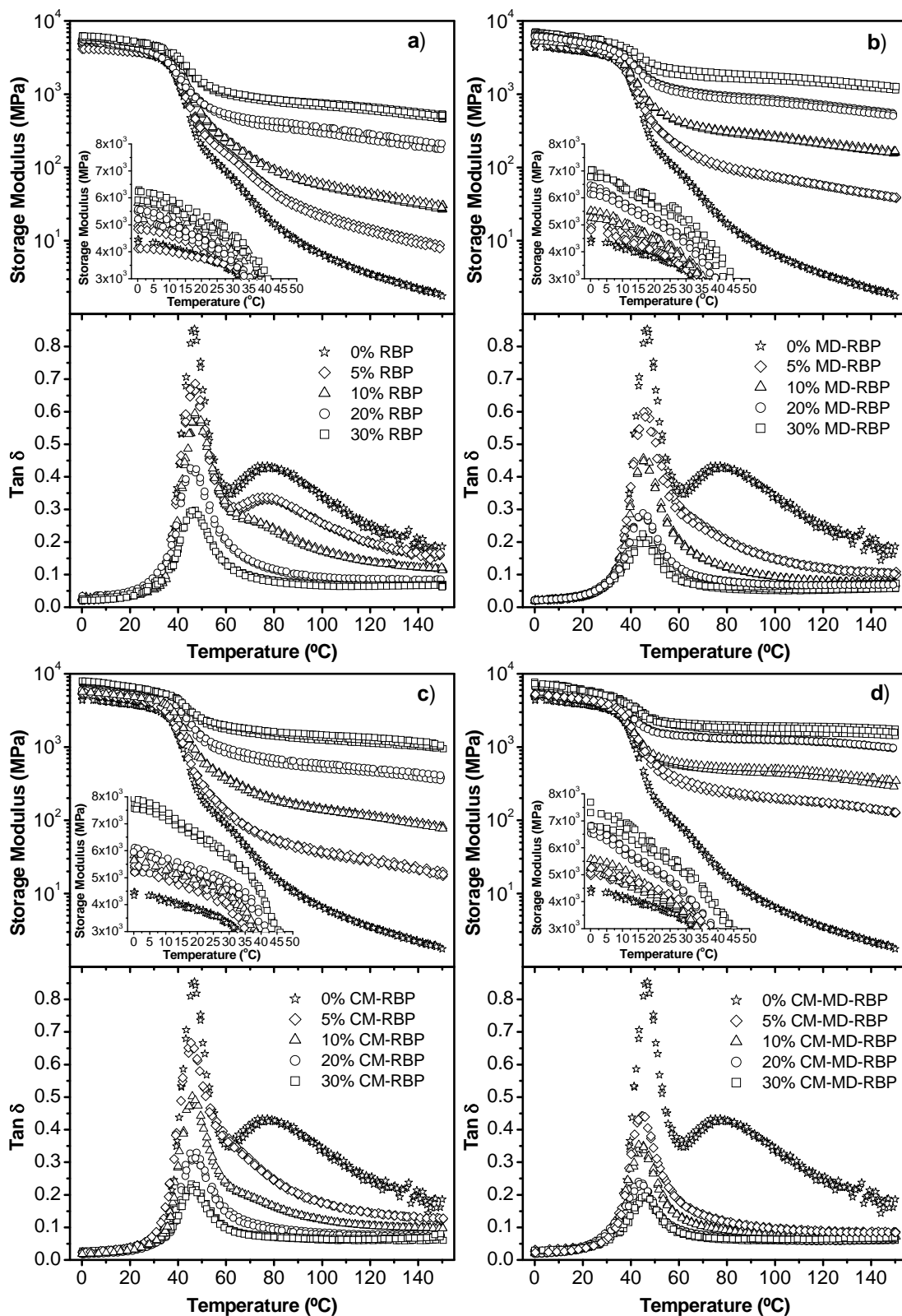


Figure 1 Dynamic heating scans showing the storage modulus and $\tan \delta$ for PVAc composites prepared with different concentrations of the RBP (a), MD-RBP (b), CM-RBP (c) and CM-RBP-MD (d) cellulose nanofibrils. Three repetitions at each concentration are shown.

Finally, we observed an outstanding reinforcing effect in the high temperature region (rubbery plateau) due to the presence of the different nanofibrils. For example, the storage modulus of the neat film at 150°C was 1.75 MPa, and this value was increased to 130, 345, 975 and 1590 MPa when adding 5, 10, 20 and 30% of CM-MD-RBP, respectively, which amounts to increases up to nearly 3 orders of magnitude. Although similar trends were found for all the different fibrils used, the differences among the treated ones were also very marked when compared at the same concentration as shown in Figure 2.

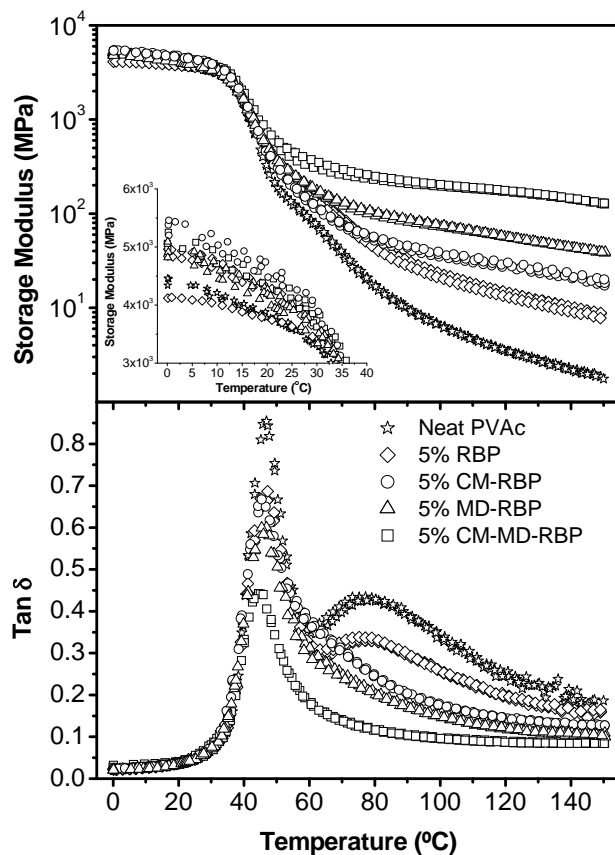


Figure 2 Dynamic heating scans showing the storage modulus and $\tan \delta$ for PVAc composites prepared with 5% concentration of the RBP (a), CM-RBP (b), MD-RBP (c) and CM-MD-RBP (d) cellulose nanofibrils. Three repetitions per sample are shown.

For instance, when comparing the storage modulus and $\tan \delta$ of PVAc nanocomposites prepared with 5% of the different types of cellulose fibrils, as it can be seen in the inset graph, the differences in storage modulus were not significantly different in the glassy region; perhaps the neat PVAc showed slightly lower storage modulus but it was marginal. However, the PVAc and PVOH glass transitions (see $\tan \delta$) were clearly altered with only 5% of the CM-MD-RBP fibrils as the PVAc damping intensity was reduced from 0.85 (neat film) to 0.45 and the PVOH transition completely disappeared. On the other side, the untreated RBP fibrils provided moderate decreases in the PVAc and PVOH damping intensities (0.70 and 0.34, respectively). Also, the remarkably different reinforcing effect observed in the storage modulus at high temperature should be highlighted. As expected, the least refined RBP fibrils provided the smallest increase in storage modulus at 150°C (8.5 MPa), followed by the CM-RBP (18.3 MPa),

MD-RBP (39.2 MPa) and CM-MD-RBP (129.5 MPa). Moreover, this order was maintained at any given concentration. Most interesting is that these results imply a synergistic effect between the treatments since the reinforcing effect of fibrils that were first chemically modified and subsequently mechanically disintegrated, i.e. the CM-MD-RBP, was greater (ca. 3 times at 5% of fibril concentration, 1.8 times at 10%, 1.6 times at 20%) than that obtained from the sum of the effects provided by each treatment (chemical or mechanical, i.e. the CM-RBP + MD-RBP) independently. However, no synergistic effect was observed at 30% of fibril concentration. The mechanism by which the synergistic effect diminished as the concentration of the nanofibrils increased needs to be further investigated.

Conclusions

The untreated and processed RBP cellulose nanofibrils used in this work showed a remarkable influence on the viscoelastic properties of PVAc latex films as demonstrated by significant changes in the storage modulus and $\tan \delta$ responses in the glassy, glass transition and rubbery plateau regions. The nanofibrils effectively reinforced the PVAc nanocomposites in all the studied temperature range, although this effect was more pronounced in the glass transition and rubbery regions. In particular, the presence of these nanofibrils dramatically reduced the PVAc glass transition and in some cases completely eliminated the PVOH glass transition. Although no significant changes in the glass transition temperatures for these two polymers were observed. Among the different cellulose nanofibrils at any given concentration in the rubbery plateau, the CM-MD-RBP provided the largest reinforcing effect followed by the MD-RBP, CM-RBP and the RBP. Moreover, the reinforcing effect of the CM-MD-RBP was as much as three times larger than the sum of the separate actions of the CM-RBP and MD-RBP, indicating a synergistic effect. This positive effect justifies the higher technical and energetic operating expenses necessary to produce the CM-MD-RBP fibrils.

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