EFFECT OF MOLAR RATIO AND FILLERS ON CREEP BEHAVIOR OF PHENOL-FORMALDEHYDE AND MELAMINE-UREA-FORMALDEHYDE THERMOSETTING ADHESIVES

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This paper investigates the effect of molar ratio and three kinds of fillers (poplar wood flour, wheat flour and glass particles) on the creep behavior of two thermosetting adhesives used for wood-based panels – phenol-formaldehyde (PF) and melamine-urea-formaldehyde (MUF) – by dynamic mechanical analysis (DMA). The results obtained indicate that the ability of high molar ratio PF or MUF adhesives to resist deformation is largely superior to that of low molar ratio adhesives. In high molar ratio PF and MUF adhesives (P/F=1:2.20 and (M+U)/F=1:2.26), all fillers had a negative effect on the creep behavior. However, the fillers could markedly improve the creep behavior of PF and MUF adhesives with low molar ratio (P/F=1:1.98 and (M+U)/F=1:1.50). Moreover, glass particles and poplar wood flour proved to have a stronger effect, compared to wheat flour. The results obtained provide insights into easy ways to improve the creep behavior of wood adhesives for structural purposes.

Keywords: creep behavior, phenol-formaldehyde, melamine-urea-formaldehyde, molar ratio, filler

INTRODUCTION

Adhesive bonding technology has played an important role in the development of wood-based panels and therefore it has been the subject of numerous studies. In load-bearing timber structures, adhesives must be both capable of withstanding a continuous load with minimal creep or deformation, similar to solid wood, and durable to ensure a long life span of the structure.[1,2] As a result, creep resistance or the ability of an adhesive to resist deformation under load under service conditions is one of the key considerations in the building codes around the world.

Alternative adhesives, such as isocyanate-based polyurethanes,[3] aqueous polymeric emulsions[4] and epoxy[5,6] etc, have been improved and, in some cases, they may provide a viable option for structural timber members. The lack of long-term performance, especially regarding the creep values, has led to restrictions in some cases. Formaldehyde-containing resins, which are synthetic resins derived from a condensation reaction involving formaldehyde, have been used for over 70 years for structural timber, as its performance has set a very high performance benchmark that the ultimate consumer can have confidence in. Also, the cost and production efficiencies and low health and environmental impacts of formaldehyde-based adhesives have been largely discussed in recent years.

The formaldehyde-based adhesive family includes two groups: phenolics and amino plastics.[7] Phenolic resins are formed *via* an irreversible crosslinking reaction. They have a rate of expansion and contraction similar to solid wood, which makes them an excellent adhesive for structural applications. Amino plastic resins are generally made by a reversible crosslinking reaction, which can sometimes be followed by hydrolysis in the presence of moisture or an acid, and therefore may be succeptible to bond failures over time. Melamine formaldehyde resins, however, have good resistance to hydrolysis, as well as a rate of expansion and contraction similar to solid wood. Thus, melamine hybrid based adhesives have been developed for glulam.[8] Phenolic resins, as well as some melamine and its hybrid adhesives, were used under exterior or harsh climatic conditions, while urea-formaldehyde – for structural purposes.

Normally, related to manufacturing and bonding, it is known that the composition, structure, network and fillers have a remarkable influence on the performance of the resin. However, there no available data on the influence of molar ratio and of common fillers on the creep of PF and MUF, which could help eliminate or at least minimize the deformation during the life of products.

In this paper, the effect of molar ratio and three kinds of fillers (poplar wood flour, wheat flour and glass particles) on the creep behavior of two thermosetting adhesives, PF and MUF, used for structure wood-based panels were investigated by DMA. It was shown that PF and MUF adhesives with different molar ratio and filler exhibited different creep under the temperature conditions tested.

EXPERIMENTAL

PF adhesive with molar ratios of P/F=1:2.20 and 1:1.98, and MUF adhesive with molar ratios of (M+U)/F=1:2.25 and 1:1.50 were synthesized in our lab. DMA was carried out on a DMA242C Dynamic Mechanical Analyzer (NETZSCH, Germany). Poplar veneers of dimensions 60×5×0.5 mm were covered with a quantity of 200 g/m^2 of the PF or MUF adhesives with 1 wt% NH_4Cl as hardener, in the absence and presence of filler with particle size above 100 mesh (10 wt% of poplar wood flour or 10 wt% of wheat flour or 1 wt% glass particles, respectively), and then bonded under pressure and temperature. Triplicate samples were also tested in the isothermal mode at 60 °C in three-point bending, exerting a static force of 1.0 N on the specimens at a frequency of 5 Hz.

RESULTS AND DISCUSSION

Effect of molar ratio on PF and MUF adhesives

Figure 1 shows the effect of molar ratio of PF and MUF adhesives on creep behavior at 60 °C. It is obvious that the deformations of PF and MUF of different molar ratios show similar curves, indicating that both strains increase in time and stabilize after 20 min. The ability of PF or MUF adhesives with high molar ratio (P/F=1:2.20 and (M+U)/F=1:2.26) to resist deformation was superior to that of the low molar ratio adhesives (P/F=1:1.98 and (M+U)/F=1:1.50). It is easy to understand that high molar ratio PF and MUF adhesives would create more crosslinking sites than the low molar ratio ones in the crosslinking network, which would be the main reason for the resistance against deformation exhibited by the high molar ratio adhesives – this is also a popular explanation for the behavior of other thermosetting adhesives. Also, the creep resistance of PF indicated a lower strain than that of the MUF adhesive, at all molar ratios and under the same conditions. The existence of some segments of UF in the main chain of MUF was accounted for by the larger deformation, compared to that of PF, which is also consistent with the results of our previous study.[9]

Effect of fillers on PF and MUF adhesives

PF and MUF adhesives with high molar ratio

Figure 2a shows the effect of fillers, such as poplar wood flour, wheat flour and glass particles, on the deflection of the PF adhesive with high molar ratio (P/F=1:2.20), which indicates that all the fillers could increase the strain or creep under the same conditions. Moreover, the influence of glass particles is more remarkable than that of poplar wood flour and wheat flour, which possibly results from the weak adhesion between glass particles and the PF matrix, which hinders the crosslinking between the PF chains. Thus, glass particles present a larger creep, compared to poplar wood and wheat flour. Wheat flour is characterized by flexible chains which is different from the phenol ring in the PF matrix. It also has a notable influence on the creep. However, the poplar flour, which combined the rigidity of glass particles and the hydroxyl groups of wheat flour, showed a minimal effect on the creep. Therefore, poplar flour added into the PF adhesive with high molar ratio is a suitable filler for cost saving. The same behavior was observed for the MUF adhesive with high molar ratio

((M+U)/F=1:2.26), as shown in Figure 2b.

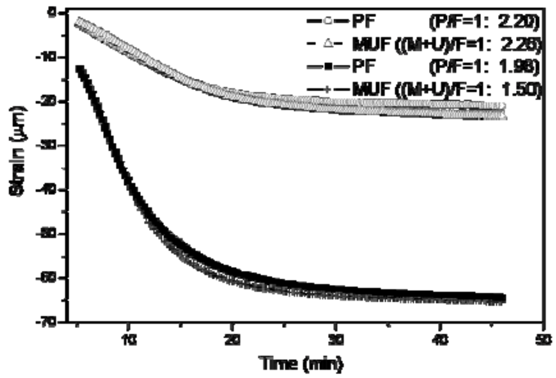

Figure 1: Deflection of PF and MUF resins with different molar ratios

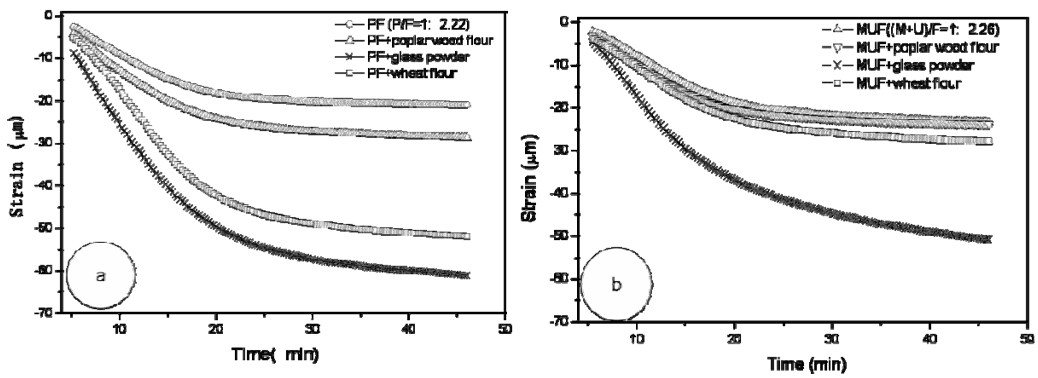

Figure 2: Effect of filler on deflection of PF and MUF adhesives with higher molar ratio (10 wt% poplar wood flour, 10 wt% wheat flour and 1 wt% glass particles, respectively)

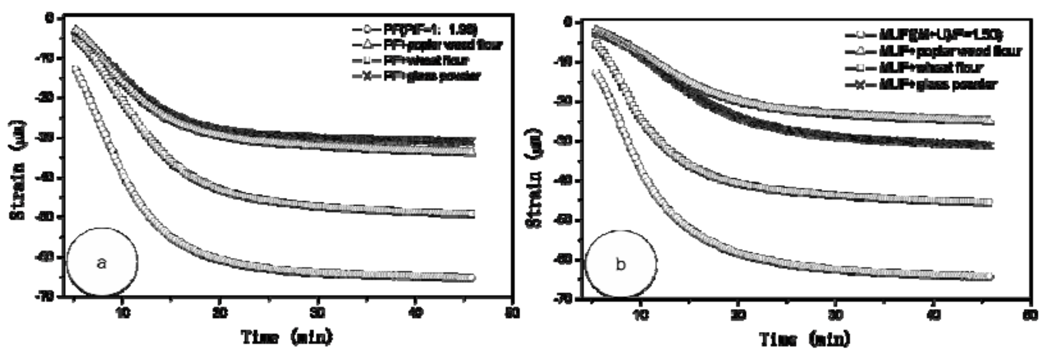

Figure 3: Effect of filler on deflection of PF and MUF adhesives with low molar ratio (10 wt% poplar wood flour, 10 wt% wheat flour and 1 wt% glass particles, respectively)

PF and MUF adhesives with low molar ratio

Figures 3 shows the effect of fillers, such as poplar wood flour, wheat flour and glass particles, on the deflection of the PF adhesive with low molar ratio (P/F=1:1.98 and (M+U)/F=1:1.50). It may be noted that the effect of fillers on the creep of the PF and MUF adhesives with low molar ratio is evidently unlike that on the PF and MUF adhesives with high molar ratio. In the case of low molar ratio, all the fillers could strengthen the PF matrix, which could be explained by building physical crosslinking sites with all fillers.

As shown in Figure 3a and b, there is a small difference between glass particles and poplar wood flour added to PF and MUF with low molar ratio, which may result from the rigidity of filler. The effect of wheat flour may be explained by the reaction of the hydroxyl groups from its molecule with the PF or MUF network.

CONCLUSION

The effect of molar ratio and three kinds of fillers (poplar wood flour, wheat flour and glass particles) on the creep behavior of two thermosetting adhesives, PF and MUF, used for structure wood-based panels, has been investigated by DMA. The results indicate that the ability of PF or MUF adhesives with high molar ratio to resist deformation is superior to that of PF or MUF with low molar ratio. In the case of PF and MUF adhesives with high molar ratio, all fillers had a negative effect on the creep behavior. However, they could markedly improve the creep behavior of PF or MUF with low molar ratio. Moreover, glass particles and poplar wood flour showed a better effect, compared to wheat flour. It should be pointed out that the effect of fillers on the creep of PF and MUF adhesives may be also due to other factors. Further studies are necessary to investigate the interaction between fillers and the PF or MUF matrix.

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