

# Creep Fatigue in Engineered Wood Fiber and Plastic Compositions

M. M. SAIN,<sup>1</sup> J. BALATINECZ,<sup>2</sup> S. LAW<sup>2</sup>

<sup>1</sup> Pulp and Paper Research Centre, University of New Brunswick, Fredericton, Canada

<sup>2</sup> Department of Forestry, University of Toronto, Toronto, Canada

Received 10 March 1999; accepted 7 September 1999

**ABSTRACT:** Creep behaviour of unmodified and functionally modified thermoplastic-wood fibre composites was studied. For PVC, PE and PP-based composites creep is strongly dependent on the amount of load, time and temperature. A small rise in the temperature above ambient temperature increased creep significantly for PVC-wood-fiber composites. Instantaneous creep resistance of woodfibre-filled PP is higher than that of PE-based composites. PP and PE-based wood composites were modified with maleic and maleimide compounds. Maleic or maleimide modification of woodfibre improved transient creep behaviour of PP-woodfibre composite but it did not show practically any effect on instantaneous creep. A mathematical model has been proposed to predict creep behaviour of PVC, PP and PE-based wood fiber composites. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 260–268, 2000

**Key words:** creep fatigue; wood fiber and plastic composites

## INTRODUCTION

With recent advancements in the science and technology of wood fiber (WF) and plastic composites and the parallel increasing industrial interest in advanced WF and plastic materials, such as in construction, building, and automotive components, the subject of viscoelasticity has recently gained strong momentum in the realm of process engineering and applications. It is often considered that the response behavior of a viscoelastic material is a fundamental property of its molecular structure. However, this is an oversimplification of the actual flow process occurring in the real, complex microstructure of a viscoelastic material system such as WF and plastic composites. It is now recognized that such materials behave in a manner that primarily depends on the mate-

rial source, microstructure, and the previous history, in addition to the current state of loading and environmental conditions such as humidity and temperature.

The behavior of WF and plastic composite materials in a monotonic state of deformation is becoming an important issue for load-bearing applications. They creep when stressed and the overall creep behavior of such a material is sensitive to the geometric and rheological details of the processing stage and to the subsequent thermal history. Because of the nature of the material and its complexity there is no general agreement, strategy, or tactic of how to experimentally measure the creep behavior of these composite materials. On the other hand, a significant understanding of the creep of inorganic filler and plastic composites was already accomplished and it can be used as a first hand guide to examine the creep behavior of WF and plastic composites. The creep of a unidirectional and randomly oriented glass fiber and plastic composite and silica-epoxy system were

---

Correspondence to: M. Sain (msain@unb.ca).

*Journal of Applied Polymer Science*, Vol. 77, 260–268 (2000)  
© 2000 John Wiley & Sons, Inc.

studied in the past.<sup>1,2</sup> In general, the creep of fibers guides the creep of a unidirectionally oriented fiber composite if the fibers are in the loading direction. On the other hand, the creep performance of short-fiber reinforced thermoplastics is greatly affected by the nature of the stress transfer. Stress transfer in a fiber-plastic composite again depends on the fiber-matrix interfacial force of interaction, as well as on the nature of the interface. Anticipating a relatively large role for the interface in performance composites, the critical factors governing the creep of WF and plastic composite materials needs to be determined. A data base on the tensile and flexural creep behaviors as a function of interfacial properties, chemical composition, stress level, time, and temperature helps to predict the short- and long-term creep behavior of such materials. Because most of the research related to WF and plastic composites in the past 15 years was directed to develop a formulation, very little was done on a practical level to develop a standard method and then generate data on the long-term performance of such products. This article takes the first step to predict the long-term viscoelastic performance of WF and plastic composites by considering the monotonic creep behavior of various samples under flexural loading conditions. The work also attempts to derive mathematical models for flexural creep behavior by computing experimental findings, which helps to predict the creep of such materials as a function of material composition, load-bearing ability, and environmental conditions.

## EXPERIMENTAL

### Theory and Practice Issues

Various materials of the same geometry may respond differently under identical external effects. Such differences in response are often attributed to the inherent constitution of the materials. Consequently, the response behavior of a particular material, or a class of materials, is described mathematically by the so-called constitutive relations.<sup>3</sup> Thus, the creep behavior of an isotropic linear viscoelastic system can be represented by

$$\varepsilon(t) = \sigma_0 \int_0^t f(\tau) \exp(1 - t/\tau) d\tau \quad (1)$$

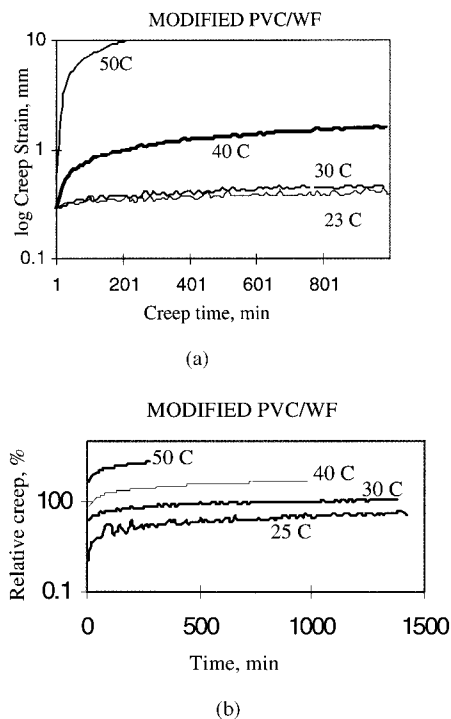
where  $\varepsilon(t)$  is the creep strain,  $t$  is time,  $\sigma_0$  is the applied stress, and  $f(\tau)$  is the distribution of the retardation times  $\tau$ .

Although it is assumed that such an expression should represent an experimental creep curve, it is actually not so because accurate information about  $f(\tau)$  is elusive. Several models were developed using the constitutive relation to explain the creep behavior of materials using a very simple elastic or viscous system and a complex combination of both.

A more commonly used model proposed by Findlay<sup>4</sup> simplifies the constitutive equation in the following simple form:

$$\varepsilon(t) = \varepsilon_0 + At^\tau \quad (2)$$

where  $\varepsilon_0$  is the initial instantaneous strain,  $A$  is the amplitude of the transient creep strain, and  $\tau$  is the time constant. The instantaneous strain, strain amplitude, and time constant are creep parameters and each can be assigned a numerical value by experimentally measuring the instantaneous and time dependent strains of a viscoelastic material and then calculating the values from eq. (2). However, values calculated from the above equation cannot be universally applied because of the oversimplification of the model, which does not take into consideration the changes in the shape of the material. The shape of a material depends on molecular mobility and is a function of the microstructure and molecular alignments during the processing of materials; and the shape from sample to sample can be influenced by other external factors such as moisture content, humidity, and temperature. Because WF and plastic composites like other viscoelastic materials are very much influenced by the factors as detailed above, the creep parameter obtainable by the creep power law model can only give an approximation of the real behavior. Figure 1 shows a typical family of creep curves plotted in the usual and convenient form of strain versus time. The shapes of the curves for different samples of a wood-plastic composite are all similar, but the magnitudes are not equal. Such a variation in magnitude is usually not explainable by a constitutive relation and it is within the constraints arising from molecular mobility. Therefore, the creep power law model that is used to predict the viscoelastic behavior of different WF and plastic composites is not a total reflection of the material property but more so for specimens taken from a



**Figure 1** Figures 1(a) and 1(b) are creep strain and relative creep of PVC-engineered woodfiber composites at three different temperatures.

particular sample of it. Keeping this limitation in mind, we model the creep behavior of WF and plastic composites by expressing the creep strain as a percent of the instantaneous strain and redefine this strain as relative strain by rearranging eq. (2):

$$\varepsilon(T)/\varepsilon_0 = 1 + (A/\varepsilon_0)t^\tau \quad (3)$$

$$\varepsilon_R = (A/\varepsilon_0)t^\tau \quad (4)$$

Therefore, by experimentally determining the strain as a function of time and then fitting it to a nonlinear expression in the form given by eq. (4), we can determine other creep parameters ( $A$  and  $\tau$ ) for a given WF and plastic composite. Such composites consist of a polymer plus a substantial volume fraction of an organic fiber phase intended to modify the mechanical behavior of the base polymer. The sample variation may reside at the level of molecular order, at a coarser macroscopic level such as the volume fraction of the extraneous component absorbed from the working environment, or at the interface between the plastic polymer and the WF phases.<sup>5</sup>

Nevertheless, for the present moment it is possibly more important to generate a data base for creep modulus values of WF and plastic composites, even without rationalizing the effects that flow geometry, thermal history, and composition have on the shape factor of  $f(\tau)$ . It is expected that WF and plastic composite manufacturers and material end users could both use this data base as a first hand tool to predict the short- and long-term deformation behaviors of such materials in a highly prospective future market targeted at various high performance applications.

## MATERIALS AND METHODS

### Sampling

The WFs and plastics were mixed in a K-Mixer using a high shear force at 170–200°C for 2 min. For a poly(vinyl chloride) (PVC)-WF composite first the powder form of PVC and other ingredients including stabilizer were mixed in a Gelimat and then it was mixed with unmodified WF. The WFs were modified *in situ* in the K-Mixer where a modifier was introduced along with the plastic and WFs. These modifiers were maleated polyethylene (PE) or polypropylene (PP) or a bismaleimide compound. For PVC the WF was treated with an aqueous solution containing an alkyl cyanocompound. After treatment the Wfs were dried and then mixed with PVC powdered compound in the K-Mixer.

The present work strategy took into consideration the following issues in the WF and plastic composite sampling in order to minimize the error between the experimental data and the mathematical model:

1. use test samples that approximately correspond in flow geometry to service items,
2. use samples with uniform moisture content,
3. use a modified interface between the WF and plastic in order to generate data on interfacial factors influencing creep, and
4. use an increasing temperature profile in the creep measurements to obtain more information on the distribution of retardation times  $[f(\tau)]$ .

These strategic sampling tactics were combined with a standard testing practice that considers measurement in a stable and closely con-

**Table I** Temperature Dependence of Creep Parameters for Modified PVC-Wood Fiber Composites

Temp. (°C)	Creep Strain			Relative Creep		
	Intercept	Slope	$R^2$	$A/\varepsilon_0$	$\tau$	$R^2$
23	+0.210	0.028	0.66	-24.6	8.1	0.72
30	+0.84	0.049	0.84	-29.7	18.5	0.89
40	+0.33	0.256	0.88	-168	86.5	0.88
50	-1.5	2.01	0.87	-164	339.8	0.85

trolled state to ensure that it remains essentially unchanged during the course of the investigation; the test results are then likely to be self-consistent and reproducible.

### Sample Collection

Test samples were collected from manufacturing processes, which are used industrially for preparing WF and plastic composite materials. Specimens were cut either from injection molded or extruded products. Samples were prepared for deformation by beam flexure measurement according to ASTM D 2990.

### Creep Testing

Creep tests were performed with flexural creep equipment having a span to specimen depth ratio of 16:1 according to ASTM D 2990. The creep devices consisted of five sets of linear displacement transducers and flexural test rigs. The voltages of all transducers were measured using a voltmeter. Prior to testing, all transducers were calibrated using gauge blocks and a calibration best-fit line was obtained. The slope of this line provided a conversion from the measured electrical voltage to the deflection at midspan of the test specimen. Creep strains were calculated using the following relationship:

$$\varepsilon(t) = 6D(t)d/S^2$$

where  $D$  is the deflection,  $d$  is the specimen depth, and  $S$  is the length of the span. The strain due to creep was added to the instantaneous (elastic) strain to give the total strain. The elastic strain was the strain measured 30 s after the load application.

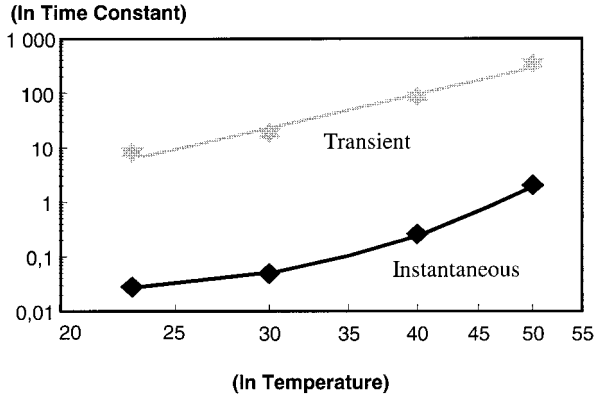
The static flexural tests were carried out to determine the ultimate flexural strength of the specimens according to ASTM D 790. The average

dimensions of creep samples were  $63.5 \times 12.5 \times 3.175$  mm. The applied load ranged from 10 to 50% of the ultimate flexural strength. The concentration of the wood flour in the composite was kept constant at 30 wt %. Composites with a modified interface prepared by adding coupling agents were also tested to determine the effect of the interface on creep behavior. Samples were exposed to various temperatures ranging from 22 to 60°C. Because a high temperature such as 60°C is not frequently encountered in end use applications for thermoplastic composites, most of our measurements were limited to 22 and 40°C. The creep load was applied from a few minutes to several hours, depending on the sample composition.

## RESULTS AND DISCUSSION

### PVC-WF Compositions

Within the constraints arising from the nature of  $f(\tau)$ , certain aspects of the creep behavior of plastic composites recently acquired the status of basic facts. The log of the strain usually increases with increasing time, the initial slope is very high, and then the slope possibly decreases asymptotically. In most circumstances a region of constant strain is observed, which is implicit in eq. (1). Figure 1 shows a typical family of creep curves for engineered WF and PVC (PVC-WF) composites plotted in the unusual but convenient form of log strain versus time instead of strain versus log time. We decided to use this in order to maintain clarity in data interpretation for a large variation of strain in a sample in creep. The shapes of the curves at different temperatures are all similar, but the spacing is nonlinear with respect to temperature for a given stress level of 30% of the flexural strength. Like the isochronous

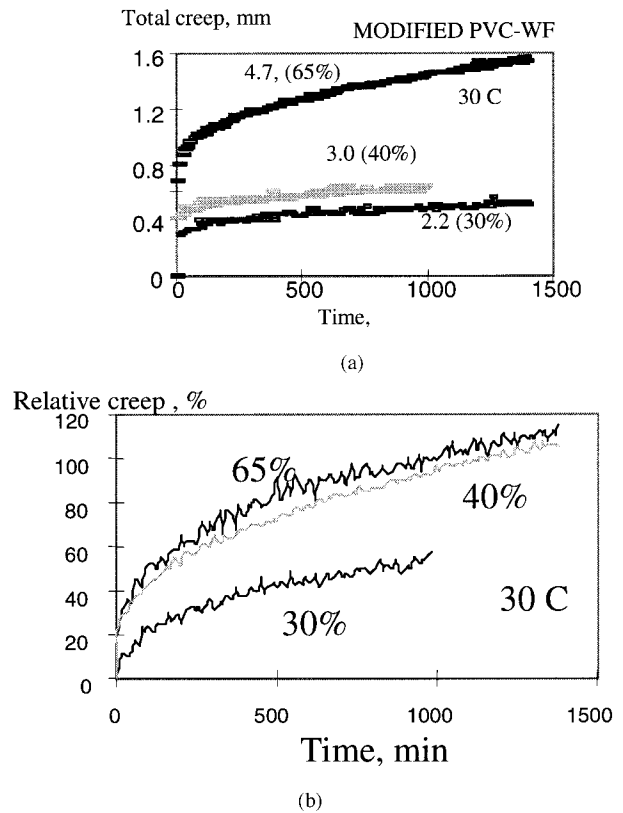


**Figure 2** Log-log plot of Time constant and temperature for PVC-woodfiber composites.

stress-strain test,<sup>6</sup> a relationship between applied temperature and flexural strain reached at some specific time can be derived from a strain-temperature curve. It is possible that a curve similar to the isochronous curve and three creep curves suffice to define creep behavior of any one sample at one stress level within the time range of the experiment.<sup>5</sup> Table I gives the slope and intercept of a logarithmic plot of the total creep (instantaneous plus transient) that could provide additional information on the total creep as a function of temperature. Like all other thermoplastic materials operating below their glass-rubber transition, the PVC-WF composite showed similar creep behavior of each component in the composite. However, such a simplistic assumption may not hold true in a real plastic-WF composition, which includes several other components such as plasticizers, compatibilizers, and stabilizers. It would be highly unrealistic that such modification processes would not have any effect on phase crystallinity and molecular rearrangement. Moreover, there is no simple route to the adjustment of data to allow for variations in interfacial interaction, moisture absorption, weathering, and so forth; the only current option in those cases is direct testing, which has always been limited in scope and popularity by the cost. Therefore, in the subsequent part of our discussion we illustrate creep behavior sample by sample without any attempt to generalize them in a single model.

Table I gives the value of  $A/\epsilon_0$ , which is the ratio of the amplitude of the transient creep strain and the initial instantaneous strain, and the time constant  $\tau$ , which is derived from the logarithmic expression of the relative creep equa-

tion [(4)],  $\epsilon_r = (A/\epsilon_0)t^\tau$ , for PVC-WF composites at a given stress level of 30% of the flexural strength. The experimental data on relative creep (%) versus the creep time is illustrated in Figure 1(b). Apparently the time dependent creep function as defined by  $\epsilon_r$  is less influenced by temperature compared to the instantaneous creep. Although the shapes of the curve in both cases are the same, the spacing is more nonlinear with respect to the temperature transient creep region [Fig. 1(b)]. This is possibly more clear from the log time constant versus the log temperature plot in Figure 2. It is then possible to predict that the initial instantaneous creep mostly governs the temperature dependent creep in compatibilized PVC-WF composites. Once the equilibrium between the temperature and initial deformation is attained, the time dependent deformation behavior under the same amount of load probably leads to almost the same extent of viscous deformation; any measurable difference can possibly be accounted for by a corresponding change in molec-



**Figure 3** Figure 3(a) and 3(b) are creep strain and relative creep curves for PVC and engineered wood fiber composite at three different flexural loading conditions.

**Table II** Dependence of Creep Parameters on Load for Modified PVC-Wood Fiber Composites

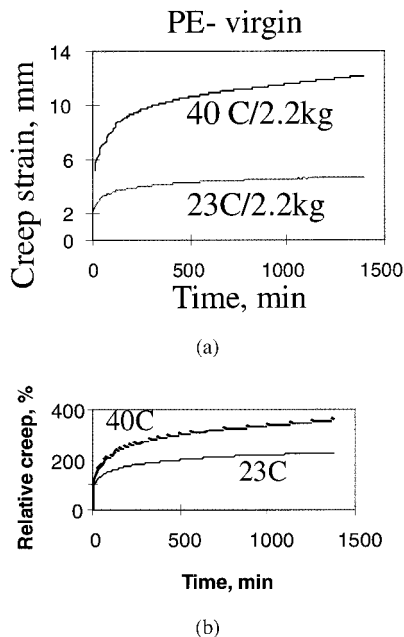
Load (% Flex. Stress)	Creep Strain			Relative Creep		
	Intercept	Slope	$R^2$	$A/\epsilon_0$	$\tau$	$R^2$
30	+0.19	0.042	0.81	—	—	—
40	+0.35	0.038	0.80	-20.3	10.1	0.87
65	+0.37	0.153	0.89	-31.1	17.6	0.86

ular chain mobility at the higher temperature. In order to quantify the temperature dependence of  $\tau$ , new exponential fit of the data in Table I for relative creep were generated having a relationship for  $\tau$  of the form  $\tau = 0.301 e^{0.147T}$ , where  $T$  is the creep exposure time.

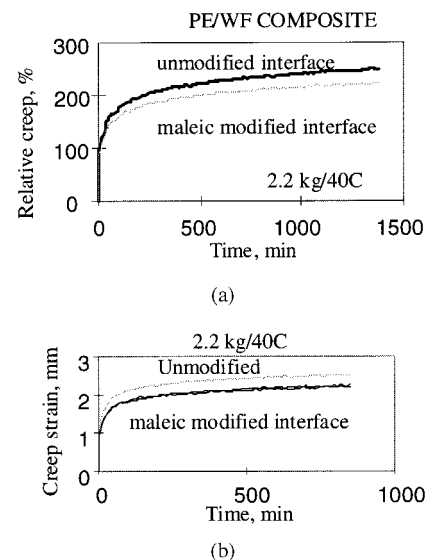
This correlation equation can be useful as a predictive tool for calculating the temperature dependence of relative creep at a given flexural load of 30% for the given PVC-WF composition. However, in practice the applied flexural load can vary over a wide range. It is then important to know the change in the creep properties of such composites under variable loading conditions.

Figure 3 shows the creep strain and relative creep curves for PVC and the engineered WF composite at three different flexural loading conditions.

It is evident that instantaneous creep strain is more dominant than transient creep strain if the applied load is about 30% of the flexural breaking load. The transient creep becomes more significant under the application of a load of 65% of the breaking load as shown by the relative creep curve in Figure 3(b). This observation also confirms that PVC-WF composites are not suitable for use under unusually high load fatigue conditions. However, they can bear a moderate load of about 30% of the flexural failure load without a large deformation for a significantly long duration. Table II gives the values of  $A/\epsilon_0$  and the time constant for the studied compositions at a given temperature of 23°C. The ratio of the amplitude of the transient creep strain and the initial instantaneous strain is somewhat higher at higher load conditions. From Figure 3(b) it is also evident that the difference in the magnitude of the relative strain becomes more pronounced as the time of



**Figure 4** Figures 4(a) and 4(b) are creep strain and relative creep of virgin PE at two different temperatures.



**Figure 5** Figures 5(a) and 5(b) are creep strain and relative creep of unmodified and maleic modified PE-wood fibre interface.

**Table III** Effect of Maleic Modification of PE-WF Composites

Nature of Interface	Creep Strain			Relative Creep		
	Intercept	Slope	$R^2$	$A/\epsilon_0$	$\tau$	$R^2$
Unmodified	+0.99	0.25	0.99	+59.5	28.2	0.99
Maleic modified	+0.91	0.19	0.99	+58.7	22.6	0.99

retention is increased. Therefore, similar to the temperature effect, the flexural load also shows a detrimental effect on relative creep at an extended applied load time. Moreover, the effect is more significant on transient creep than instantaneous creep. This means molecular slippage is the dominant mechanism under high loading conditions. This effect is exactly the reverse if the applied load is less than 30%. In practice, these results can be used as a predictive tool where load-bearing application of PVC-WF composites is important.

#### PE-WF Composites

These composites are now used in decking, fencing, plastic lumber, and furniture applications. Because of the nature of their end use, creep in one of the important properties to consider for designing such materials. The results in Figures 4 and 5 and Table III compare the creep properties of virgin PE with PE-WF composites. Virgin PE is very sensitive to creep failure. Under a given load, instantaneous creep is more sensitive than transient creep at low operating temperatures; the transient creep strain becomes more pronounced as the operating temperature is increased. This is demonstrated in Figure 4(a,b). Figure 4(b) shows that relative creep increased by about 200% at 40°C over the corresponding creep deformation at 23°C during a time period of 20 h. Hence, virgin PE is not suitable for load-bearing applications. On the other hand, the creep properties of WF-filled PE are significantly improved, even at a higher application temperature. It is

evident from Figure 5(a,b) that the instantaneous creep strain of WF-filled PE is about one-sixth of the virgin PE. Also, the secondary creep zone is much less pronounced for filled PE. This phenomenon can be correlated to the strengthening and weakening processes under load. In the transient part of the creep, which is also the primary creep zone, the strengthening process mostly occurs. Hence, WF-based PE composites do not undergo transient strength weakening processes, which are otherwise very much evident from the rising nature of the relative creep curve for virgin PE. It is important to note that fiber modification by the maleation process does not have a sizeable effect on creep properties in general and instantaneous creep in particular. A little improvement in the primary and secondary creep of modified composites can be attributed to less viscous molecular slippage due to increased interfacial interaction between the modified fiber and PE. There is about 20–50% less secondary creep for composites prepared with modified fiber. However, it is obvious that creep properties are mostly influenced by the creep of PE wherein WFs act as discrete particles of high creep resistance embedded in the plastic matrix that partly retards both the elastic and viscous flow of polymeric chains under stress. Table III gives the regression equation of the total creep strain and relative creep for two different composite interfaces. As discussed before, these equations are useful in calculating the creep properties of modified and unmodified WF-based composites under a given load and at a given temperature. A small decrease in the  $A/\epsilon_0$  value of the

**Table IV** Temperature Dependence of Creep for Virgin PP

Temp. (°C)	Creep Strain			Relative Creep		
	Intercept	Slope	$R^2$	$A/\epsilon_0$	$\tau$	$R^2$
23	+1.57	0.43	1.0	+45.3	25.0	0.99
40	+2.1	1.37	0.99	+20.9	45.5	0.95

**Table V** Effect of Interface Modification of PP-WF Composites

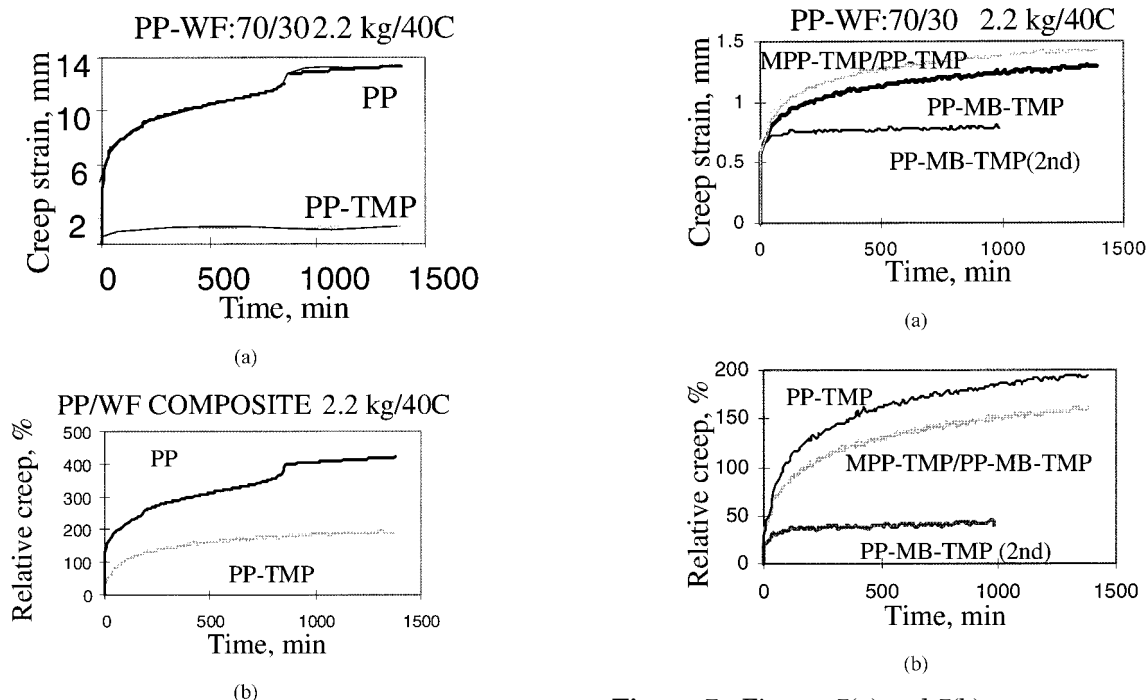
Nature of Interface	Creep Strain			Relative Creep		
	Intercept	Slope	$R^2$	$A/\varepsilon_0$	$\tau$	$R^2$
No interface (virgin PP)	+0.37	1.73	0.91	-42.5	60.9	0.85
Unmodified	+0.43	0.15	0.97	-25.1	30.1	0.96
Maleic modified	+0.32	0.15	0.97	-20.2	24.5	0.95
1st cycle MB modified	+0.34	0.13	0.97	-20.2	24.5	0.95
2nd cycle MB modified	+0.61	0.03	0.91	+17.64	3.58	0.88

modified composite over unmodified ones is the result of a small decrease in the transient creep as seen in Figure 5. As Lafeber<sup>7</sup> indicated, the mechanical behavior of any material made up of different phases is generally not given by the sum of the behavior of the different components; instead it depends on their mutual interaction and interference. The interaction is affected by the nature of the interface, as well as by the spatial arrangement of the component phases. Although the creep for solid wood is negligibly small under the given condition, the results obtained from the PE-WF compositions are not an additive function of the composition. In PE-WF composites the interface played an important role in determining

the final creep value of these composites. This result is partly evident from the change in the creep values with the change in the nature of interface from a hydrophilic one to more hydrophobic ones, which is due to the addition of maleated wax modified WF.

#### PP-WF Composite

The creep properties of WF-PP composites were compared with virgin PP. The results are given in Tables IV and V and Figures 6 and 7. Figure 6 compares the creep strain of virgin PP with the PP-WF composite above ambient temperature. It is evident from Figure 6 and Table IV that the



**Figure 6** Figures 6(a) and 6(b) are creep strain and relative creep of PP and PP-TMP compositions.

**Figure 7** Figures 7(a) and 7(b) are creep strain and relative creep unmodified and, maleic (MPP) and maleimide modified PP-TMP interfaces.



creep of PP is sensitive to the effect of temperature. A more interesting observation was the relative change of the transient creep with respect to instantaneous creep. As the testing temperature was increased from 23 to 40°C, the time constant increased from 25 to 45.5. Therefore, virgin PP is practically unusable for load-bearing applications and it is more so above ambient temperature. Unlike virgin PP, the addition of 30% by weight of thermomechanical pulp reduced creep strain significantly, even under elevated temperature conditions. Yet the measured creep strain was still much higher than solid wood; solid wood showed less than 1% creep under similar experimental conditions. A comparison of the creep strain value and percentage relative creep in Figure 6(a,b) suggests that WF addition helps to significantly reduce the instantaneous creep of virgin PP. Time dependent transient creep of PP is less influenced by the presence of WF. This observation on the variable effect of WF on instantaneous and transient creep prompted us to study the effect of the nature of the WF-PP interface on creep deformation. It is evident that the effect of the chemical nature of the interface on creep properties is not strong. Although maleimide modified WF is apparently more resistant to creep, maleic modified WF showed marginally superior relative creep to unmodified fiber. Moreover, this difference in creep resistance was only evident in the transient creep region. In other words, the nature of the interface has hardly any effect on instantaneous creep. It is further noted that the cyclical loading for the short or long term mostly affects instantaneous creep as is evident from Figure 7(a,b). When the maleimide modified composition was subjected to repeated loading cycles under flexural bending conditions, the instantaneous creep almost remained constant but the transient creep strain decreased significantly during the second load application. This was also evident from a significant change in the  $A/\epsilon_0$  value after repeated loading as demonstrated in Table V.

Thus, a comparison of the creep behavior of various thermoplastic and WF composites re-

vealed that PVC-WF composites are the most resistant to creep fatigue and PE-WF composites are the least resistant to creep. The creep resistance of PP-WF composites can only be marginally improved by improving the interfacial interaction between the fiber and plastic.

## CONCLUSION

Creep behavior of plastic composites is a strong function of the loading condition and temperature. High load and elevated temperature both have a detrimental effect on creep behavior of thermoplastic and WF composites. An increase in the flexural load from 40 to 65% of the failure load almost doubled the time constant of PVC-WF composites. A similar rise in the temperature from 30 to 40°C increased the time constant by more than 5 times, and the creep of filled PVC at 40°C was almost equal to the creep of unfilled PVC at 30°C. The creep resistance of WF-filled PE was very low for unmodified and modified compositions. Unlike PE, WF-filled PP was reasonably resistant to instantaneous creep. On the other hand, the time dependent and transient creep behavior of PP-WF composites were only marginally superior to virgin PP. Maleic or maleimide modification of WF resulted in a marginal improvement of the transient creep behavior of PP-WF composites, but such modifications had a negligible effect on instantaneous creep.

## REFERENCES

1. Mallick, P. K. *Composites* 1988, 19, 283.
2. Rey, S. F. (to Exxon). U.S. Pat. 4,548,961, 1985.
3. Hunter, S. C. *Mechanics of Continuous Media*; Ellis Horwood: Chichester, U.K., 1976.
4. (a) Findlay, W. N. *SPE J* 1960, 16, 57; (b) Findlay, W. N. *SPE J* 1960, 16, 192, 198.
5. Moore, D. R.; Turner, S. *Plast Rubber Compos Process Applic* 1994, 21, 33.
6. Turner, S. *Trans Plast Inst* 1963, 31(93), 60.
7. Lefeber, D. *Geology* 1966, 1, 261.