Electronic Supplementary Material (ESI) for Soft Matter

Supplementary Information

Nanostructured biocomposites of high toughness – a wood cellulose nanofiber network in ductile hydroxyethylcellulose matrix

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S1. Table of parameters

Table 1: Table of parameters used in Equations 1-9

term	Refers to	Determined by
ρ_{ce}	Experimental composite density	Calculated from measurements in this work
w_a	Weight of sample in air	Measured in this work
w_{Hg}	Weight of sample in mercury	Measured in this work
ρ_{air}	Air density	Litterature value
ρ_{Hg}	Mercury density	Litterature value
V_V	Porosity (Volume fraction of voids)	Calculated from measurements (2), (4), (5)
V_f	Volume fraction of NFC	
V_m	Volume fraction of HEC	
W_f	Weight fraction of NFC	Measured in this work
ρ_f	Density of NFC fibrils	Litterature value [1]
ρ_m	Density of the HEC	Litterature value [2]
ρ_{ct}	Composite theoritical density if no voids	Calculated from above data
E_c	Experimental composite modulus	Measured in this work
E_l	Theoritical longitudinal modulus for composite of unidirectional fiber	Equation expressed in (6)
E_t	Theoritical transversal modulus of composite of unidirectional fiber	Calculated from (8) and (9)
$E_{l,NFC}$	Modulus of NFC in the longitudinal direction	Estimated from (7)
$E_{t,NFC}$	Modulus of NFC in the transversal direction	Taken as 15 GPa [3]

S2. Creep and creep recovery fitting for neat HEC film and NFC/HEC (34/51) biocomposites.

Experimental strain values for creep and creep recovery were fitted using a nonlinear viscoelastic equation (Schapery model[4]). This power law model was successfully used for several fibre composites[5-7] and is used in the present study as it represents the behavior of the present materials. The constitutive equations for strains as a function of time for the Schapery model are:

Creep: $$\varepsilon(t) = \varepsilon_0 + \varepsilon_1.(1 - \exp(-t/\tau)) + (c.t)^n \quad \text{(a)}$$

Creep recovery: $$\varepsilon_r(t) = \varepsilon'_0 - \varepsilon'_1.\left(1 - \exp\left(-\frac{t - t_r}{\tau'}\right)\right) - (c'.(t - t_r))^{n'} \quad \text{(b)}$$

The experimental data of creep and creep recovery were fitted to the two equations a and b using an algorithm for least-squares optimization of nonlinear parameters for the determination of the different parameters of the equations (ε_1, ε_1',τ, τ',c ,c',n, n'). The elastic strain ε_0 was determined experimentally as the strain immediately after applying the load. ε'_0 was taken as the strain immediately after removing the load. t_r is the starting time for the recovery test (600 min). Table 2 and Table 3 present the parameters obtained and Figure 1 show fitting results obtained using experimental data.

Table 2: Creep fitting parameters

NFC/HEC	T (°C)	ε_0 (%)	ε_1 (%)	τ (min)	c (% min^{-1})	n
0/96	28	0.486	0.035	0.33	2.3E-4	0.436
34/51	28	0.139	0.004	2.13	4.4E-7	0.313
34/51	80	0.168	0.037	57.07	5.1E-6	0.313
34/51	120	0.343	0.164	36.41	2.2E-4	0.296
34/51	200	0.984	1.228	7.99	1.5E0	0.222

Table 3: Creep recovery fitting parameters

NFC/HEC	T (°C)	ε'_0 (%)	ε'_1 (%)	τ' (min)	c' (% min^{-1})	n'
0/96	28	0.555	0.035	22.21	7.1E-6	0.237
34/51	28	0.085	0.012	15.86	5.6E-10	0.215
34/51	80	0.214	0.009	31.06	1.4E-7	0.270
34/51	120	0.773	0.037	28.15	9.1E-6	0.267
34/51	200	6.252	0.043	30.66	6.1E-4	0.357

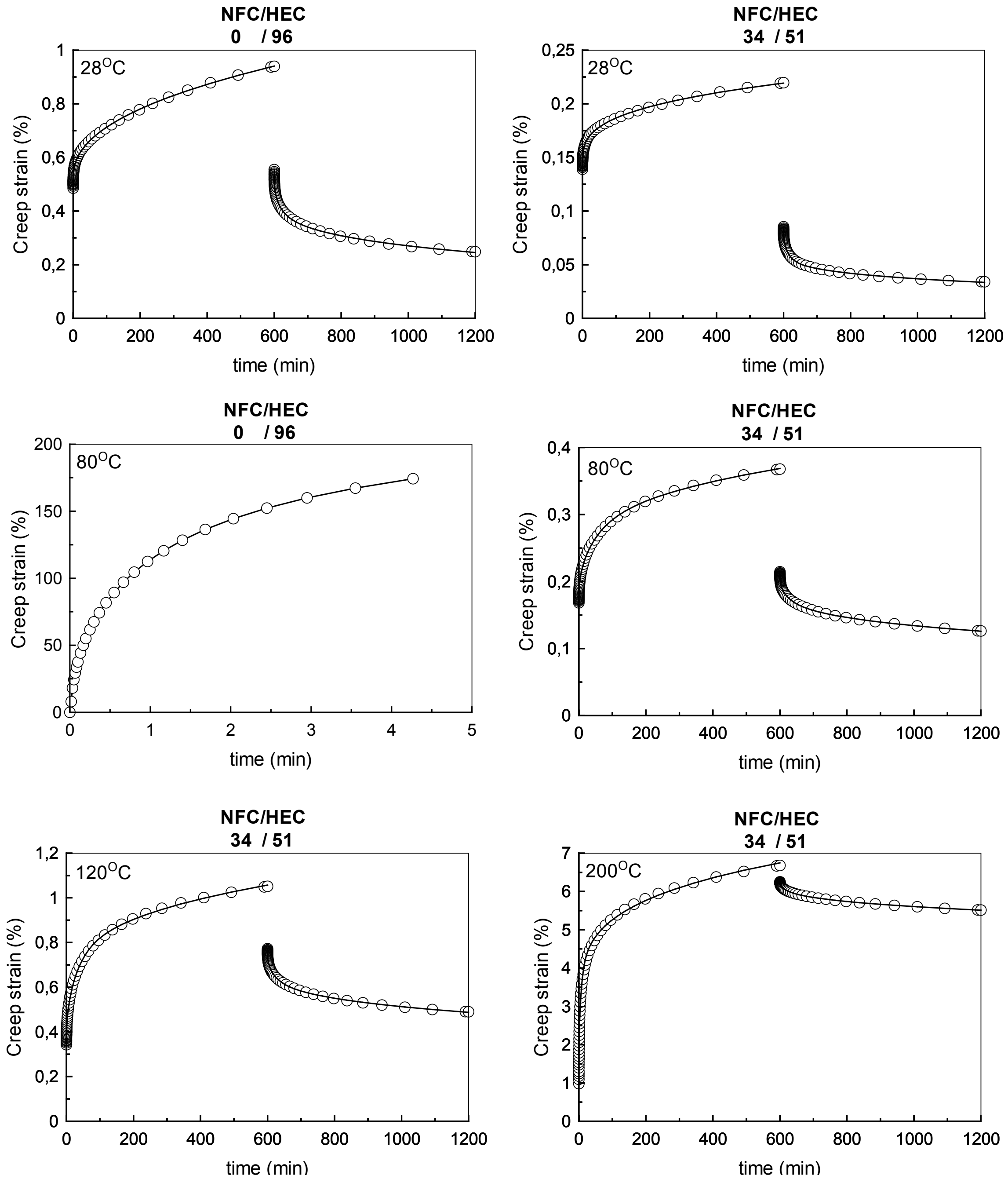

Figure 1: Creep properties at 10MPa load of neat HEC film (0/96) and 34/51 HEC/NFC biocomposite. Open circles are experimental values, solid line correspond to fitted data according to equation 1 for creep and equation 2 for creep recovery. Test temperatures are represented in the top left corner of each curve.

Figure 1 shows that equations 1 and 2 represent the experimental data well. It is generally seen that ε_0, ε'_0, ε_1, c and c' increased as the test temperature was increased, while the other parameters did not show a clear trend. The primary and secondary creep strains increase significantly by increased test temperature.

S3. FE-SEM micrographs of the surfaces of NFC nanopaper and NFC/HEC biocomposite samples.

Surface micrographs of the NFC/HEC biocomposites and nanopaper sample are shown in Figure 2. The percolated network formed by the fibrils can be seen in all images (even at 8% volume fraction of NFC) and relates to the high aspect ratio of the nanofibers. These surface images also show that the pores become less apparent when going from the pure nanopaper sample (Figure 2.a) to the 8/64 NFC/HEC biocomposite (Figure 2.d). This is due to the HEC matrix filling the pores.

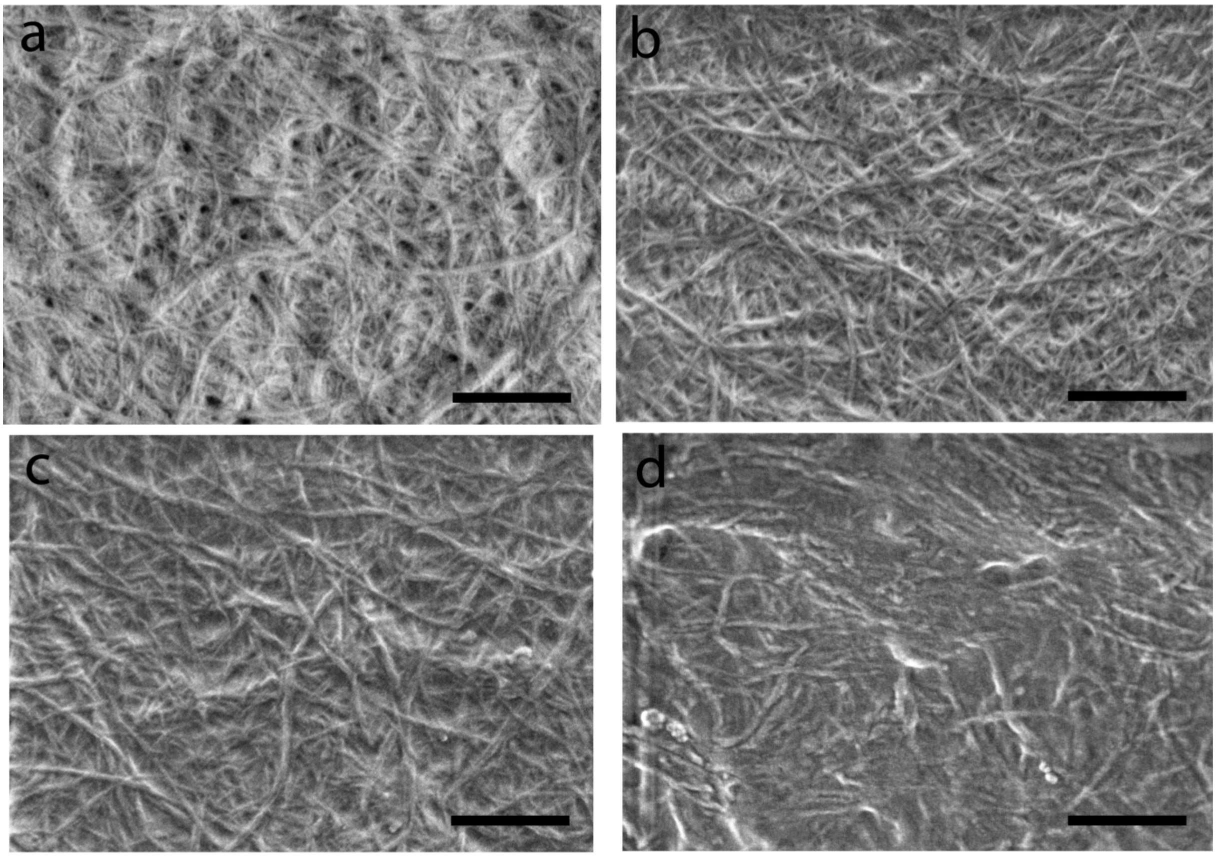

Figure 2: FE-SEM micrographs of the surfaces of NFC nanopaper (a), and NFC/HEC biocomposite samples of NFC/HEC volume fraction ratio of 54/28 (b), 31/56 (c) and 8/64 (d). Scale bar is 500 nm.

References

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