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Stress-relaxation behavior of lignocellulosic high-density polyethylene composites

Babak Mirzaei[1], Mehdi Tajvidi[1], Robert H. Falk[2] and Colin Felton[3]

Abstract

In this study, stress-relaxation performance of HDPE-based injection-molded composites containing four types of natural fibers (i.e., wood flour, rice hulls, newsprint, and kenaf fiber) at 25 and 50 wt% contents, and the effect of prescribed strain levels were investigated. The results indicated that incorporating more filler causes lower relaxation values and rates, and stress retention and prescribed strain level were reversely correlated. Among the studied filler types, wood flour and kenaf fiber presented more similar behaviors, whereas newsprint resembled rice hulls performance. Strain–time superposition was applied to the experimental data. Due to complex rheological behavior of the studied composites, single horizontal shifting method, with respect to strain levels, was found to be inadequate to satisfactorily superpose data.

Keywords

stress relaxation, composites, natural fibers, high-density polyethylene, superposition

Introduction

Commonly known under the name of wood plastic composites (WPCs), natural fiber-loaded thermoplastics are a newly developed group of materials received much attention during the past decade. This is mostly owing to the advantages of natural fibers such as renewability, lower cost, biodegradability, ease of preparation, lower energy requirements for processing, wide availability, lightness, and relative non-abrasiveness to processing equipment compared to inorganic fillers.[1,2]

Generally, thermoplastic-based composites tend to deform over time, thus, developing engineered applications necessitates the study of viscoelastic behavior of these materials. Time-dependent response of a material under prescribed stress and strain is referred to as creep and stress relaxation, respectively. Knowledge of the stress-relaxation behavior of composites enables us to predict the dimensional stability of load-supporting structures and the retention of clamping force for bolts fastened to composites.[3] Furthermore, due to inherent interdependence of viscoelastic phenomena (i.e., stress relaxation and creep) their results can be exchanged by exploiting predictive models.[4]

Compared to the voluminous literature covering different aspects of WPCs, studies conducted on their viscoelastic behavior are still infrequent among which stress-relaxation behavior is even less studied. Bhattacharyya et al. reported that the presence of wood fiber as reinforcement in the thermoplastic-based composites restricts the stress relaxation, but its effectiveness decrease with the increase in atmosphere temperature.[5] Sreekala et al. investigated various aspects affecting stress relaxation of natural fibers and phenol formaldehyde composites and found the

[1]Department of Wood and Paper Science and Technology, Faculty of Natural Resources, University of Tehran, Iran.
[2]USDA Forest Products Laboratory, USA.
[3]Campbell, CA, USA.

Corresponding author:
Mehdi Tajvidi, Department of Wood and Paper Science and Technology, Faculty of Natural Resources, University of Tehran, P. O. Box 31585-4314, Karaj, Iran
Email: mtajvidi@ut.ac.ir

relaxation rate was lowered upon hybridization with glass fiber.[3] George et al. studied stress-relaxation behavior of short pineapple-reinforced polyethylene and found that the rate of relaxation decreases with fiber content and its amount decreases with strain level. They also reported that time decay of stress takes place as a result of physical (i.e., crystallization, molecular level rearrangement and orientation of fibers) and chemical (i.e., bond breakage and reorganization) processes.[6] Geethamma et al. studied the relaxation response of short-coir-fiber-reinforced natural rubber and concluded that the strain level, fiber loading, and fiber orientation influence the rate of stress relaxation in the composites.[7]

Using composites under life cycle loads is problematic, because the long-time decay of stress should be interpreted and data should be acquired along extensive periods of time which is a tedious process. Therefore, principles such as Boltzmann and time–temperature superposition are invoked to evaluate the long-term viscoelastic behavior of materials by utilizing short-term data and constructing master curves.[8] According to time–temperature superposition principle, time–strain superposition and time–stress superposition were also employed previously by Dastoorian et al.,[9] Sreekala et al.,[3] and George et al.[6]

The objective of this study is to assess flexural stress-relaxation behavior of polyethylene-based composites, consisting of different types and contents of natural fibers, at various strain levels of their ultimate strain. Additionally, by horizontal shifting method, curves at different strain levels were superposed through which a master curve was generated in order to describe the long-time decay of stress in terms of strain fractions.

Experimental

Materials

High-density polyethylene (HDPE) (HiD 9035, Chevron, The Woodlands, TX), with a melt-flow index of 40 g/10 min (190°C, 2.16 kg) and a density of 0.952 g/cm^3, was used in this study as the polymer matrix. Wood flour, kenaf fibers, newsprint, and rice hulls were used as the discontinuous phase in the composites. Wood flour was 40-mesh maple flour and was supplied by American Wood Fibers, Schofield, WI. Kenaf fibers were supplied by Kengro, Charleston, MS. They contained ~97% bast fiber. Rice hulls were 20–80 mesh ground rice hulls and were supplied by Riceland Foods, Stuttgart, AR. Newsprint fibers were obtained by grinding old newspapers in the laboratory. Maleated polyethylene (MAPE) was a Fusabond C modified polyethylene (MB-100D) and was supplied by DuPont Industrial Corp (Wilmington, DE).

Table 1. Composition of evaluated formulations (wt%)

Formulations	Fiber content	Resin content	Compatibilizer content
PE–WF-25	25	74	1
PE–WF-50	50	48	2
PE–RH-25	25	74	1
PE–RH-50	50	48	2
PE–WF-25-0	25	75	0
PE–WF-50-0	50	50	0
PE–NP-25	25	74	1
PE–NP-50	50	48	2
PE–KF-25	25	74	1
PE–KF-50	50	48	2
PE	0	100	0

PE, polyethylene; WF, wood flour; KF, kenaf fiber; RH, rice hulls; and NP, newsprint.

Sample preparation

Polymers, fibers, and the compatibilizer were initially weighed and bagged according to the various fiber contents indicated in Table 1. The composition of each formulation is also shown. The different ingredients were mixed in the proprietary mixing equipment of Teel Global Resources, Baraboo, WI. The compounded materials were then ground using a pilot scale grinder to prepare the granules. The granules were injection-molded with a 33-ton Cincinnati Milacron 32-mm reciprocating-screw injection molder (Cincinnati, OH) with a length/diameter ratio of 20:1. Before the injection, all materials were dried for at least 4 h at 105°C. Injection-molded samples were rectangular strips with dimensions of $50 \times 8 \times 2\,\mathrm{mm}^3$.

Testing

Testing was performed in an environmentally conditioned room controlled at 23°C and 50% relative humidity. All specimens were environmentally conditioned for at least 14 days prior to performing the tests. The ultimate strain values, obtained from static three-point bending tests were used as the reference strain level to determine the applied strain. The data were collected using an Instron 4486 universal testing machine. Tests were carried out on samples over a range of strains from 30% to 50% ultimate strain of each formulation. Flexural strains, at the span of 36 mm, were maintained for 240 s and the force required to maintain the prescribed strain was recorded automatically using a 10 kN Instron load cell and was then converted into stress values. For each sample, instantaneous stresses were divided by initial stress

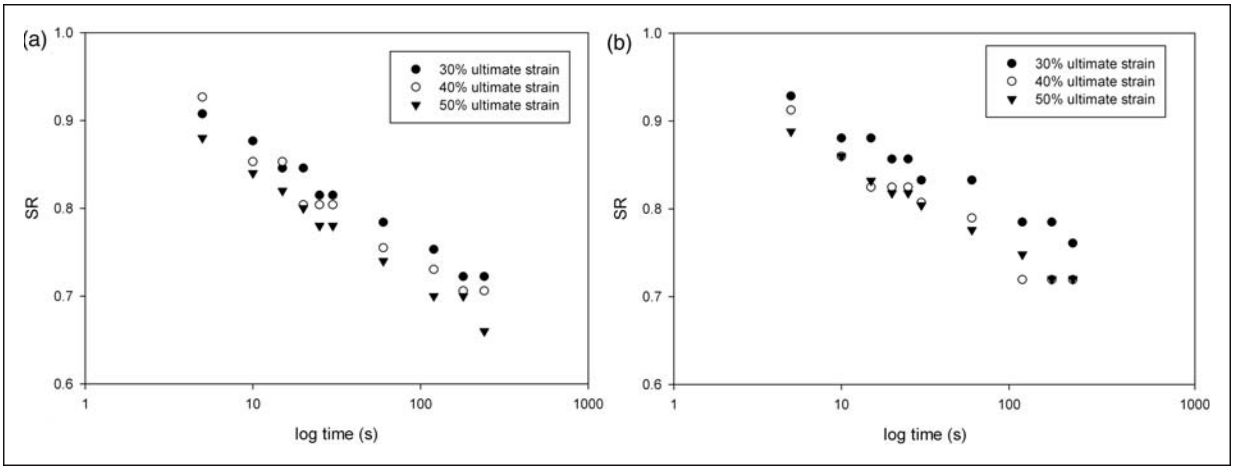

Figure 1. SR of wood flour composites at 25% (a) and 50% (b) filler contents.

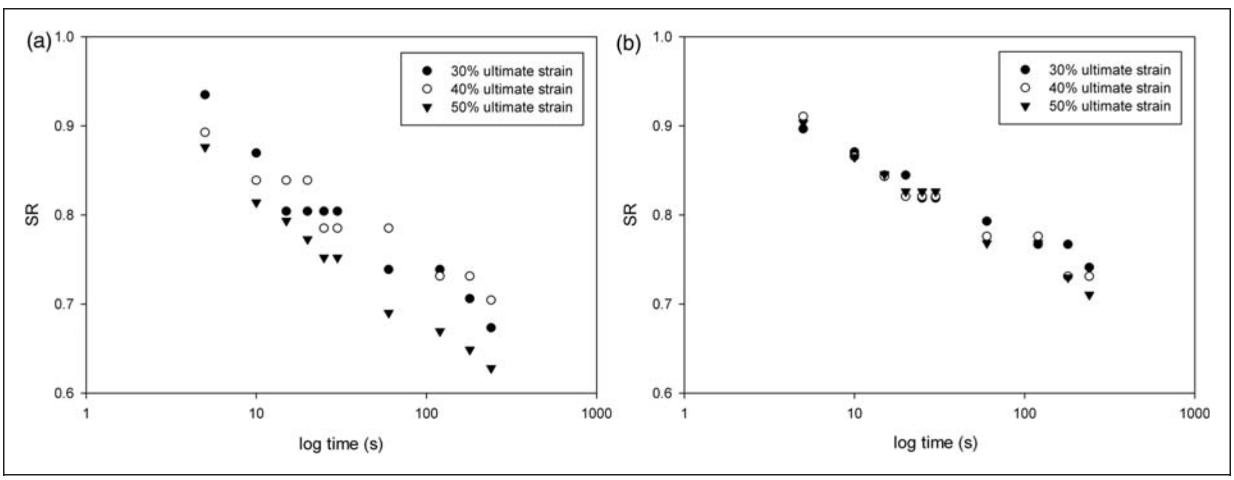

Figure 2. SR of rice hulls composites at 25% (a) and 50% (b) filler contents.

and the resulted stress ratio (SR) quantities as calculated using Equation (1) were plotted against log time axis:

$$\mathrm{SR} = \frac{\sigma_t}{\sigma_0} \tag{1}$$

where SR is the stress ratio, σ_t the stress at any given time, and σ_0 the initial stress.

Results and discussion

Values of SR at prescribed strain against log time for composites containing wood flour are shown in Figure 1. From Figure 1(a), it can be clearly seen that composites loaded by 25% filler at different strain levels have reduced SR with time, and applying higher strain levels results in decreased stress retention. Figure 1(b) shows a similar trend for 50% loaded polyethylene. This corroborates previous studies on stress relaxation and also creep behavior of materials that applied strain level and the amount of relaxation are directly correlated;[9,10] however, in the case of using low strain levels in tensile tests (i.e., under 10% of ultimate strain) the pattern has been reported to be in an opposite order.[6] By comparing part (a) and (b) of Figure 1, it can be observed that the incorporation of more wood flour generally leads to less relaxation, and this is also in agreement with creep data for WPCs.[8,10] This is mainly because wood flour obstructs reorientation and mobility of polyethylene chains, and delays relaxation process, therefore, the more filler incorporated the less relaxation observed. Bhattacharyya et al. found the same effect for introducing wood fiber to polypropylene, but the trend became reverse through increasing fiber content.[5]

The stress decay over time at different strain levels for composites containing rice hulls is presented

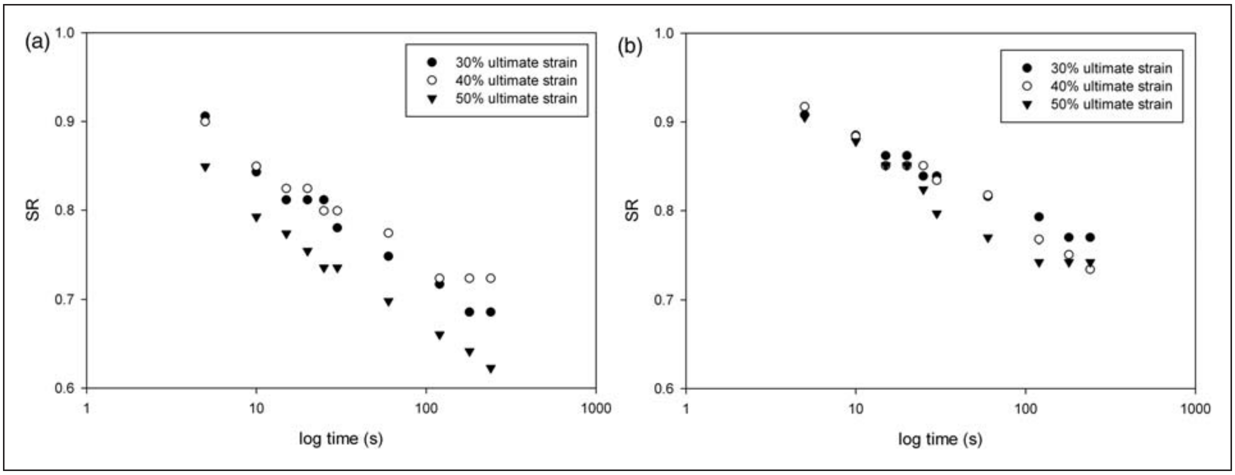

Figure 3. SR of newsprint composites at 25% (a) and 50% (b) filler contents.

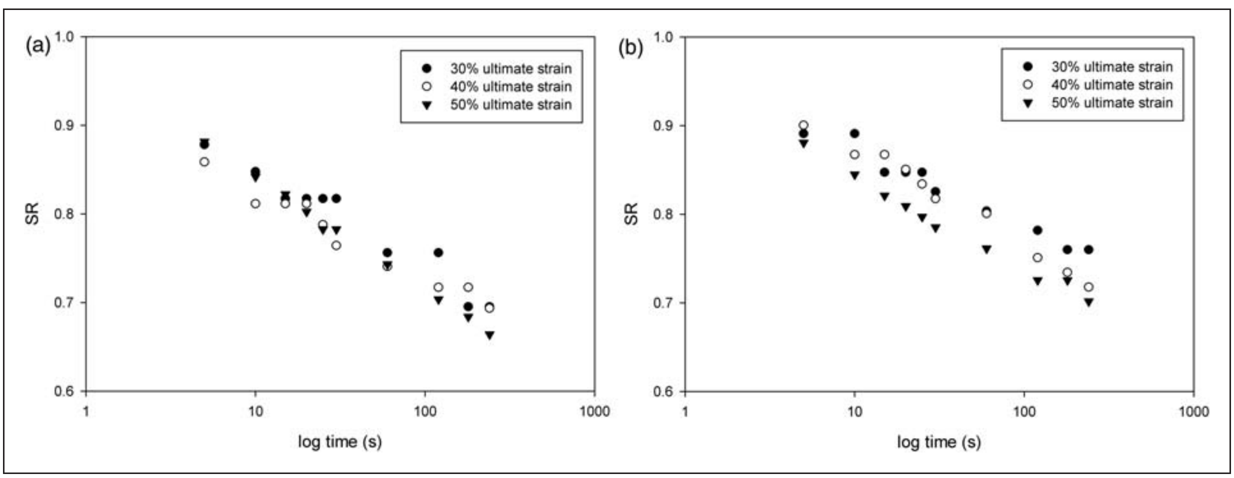

Figure 4. SR of kenaf fiber composites at 25% (a) and 50% (b) filler contents.

in Figure 2. Figure 2(a) shows the relaxation performance of 25% loaded composites as a function of time. It is evident that increasing strain level brings about more stress relaxation, and it is especially obvious at 50% ultimate strain. As exhibited in Figure 2(b), the effect of strain level on SR is less pronounced in 50% filled composites. This indicates that rice hulls decrease the dependence of SR on strain level at high concentration. As expected, adding more rice hulls resulted in general increased stress retention.

SR of newsprint-loaded composites recorded as a function of time for 25% and 50% filler contents at different strain levels is illustrated in Figure 3(a) and (b), respectively. Again at higher strain levels, higher stress relaxation is observed, and increased stress retention is characterized as a consequence of incorporating filler to the higher extent. In the stress-relaxation patterns, newsprint-loaded composites present similarities, to some degree, to their counterparts containing rice hulls, of which one can clearly detect less-pronounced strain dependence of relaxation of composites at higher filler content. It implies the same behavior of newsprint and rice hulls as filler in this regard. However, this strain dependency develops with time, and is low in early stages.

Stress-relaxation behavior of kenaf fiber-reinforced composites subjected to different strain levels is shown in Figure 4. As expected, higher stress relaxation corresponds to higher prescribed strain level. Figure 4(a) and (b) give the relaxation process for 25% and 50% reinforced composites, respectively. It can be detected that the composite reinforced by 50% kenaf fiber exhibited higher stress retention than that of its 25% counterpart. The efficiency of kenaf fiber in terms of composite relaxation behavior resembles the one of wood flour.

It is worth mentioning that incorporation of more filler also led to general decreased relaxation rate of composites. By a comparison between part (a) and (b) of Figures 1–4, it can be observed that the slopes of

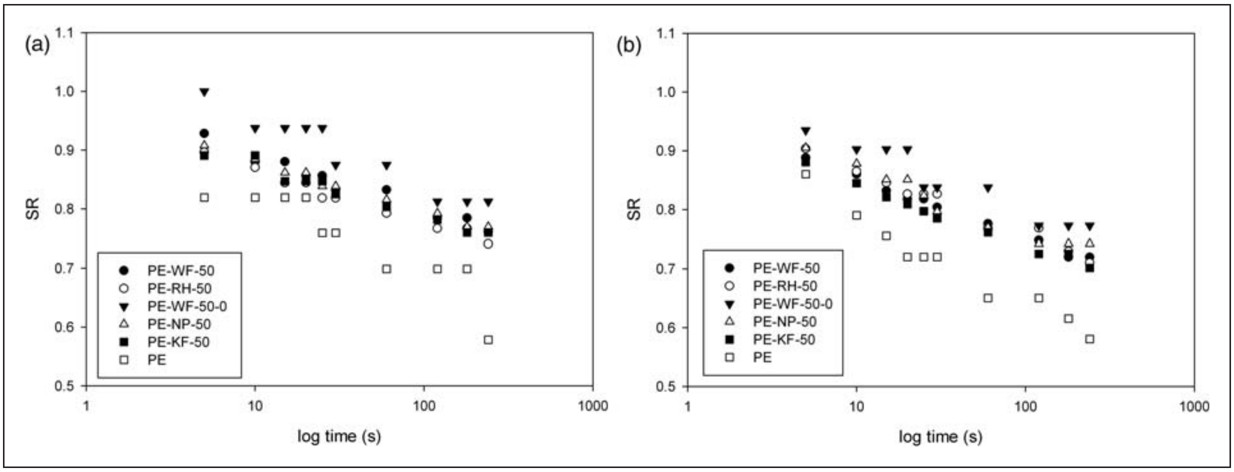

Figure 5. SR of 50% filled composites at 30% (a) and 50% (b) ultimate strains.

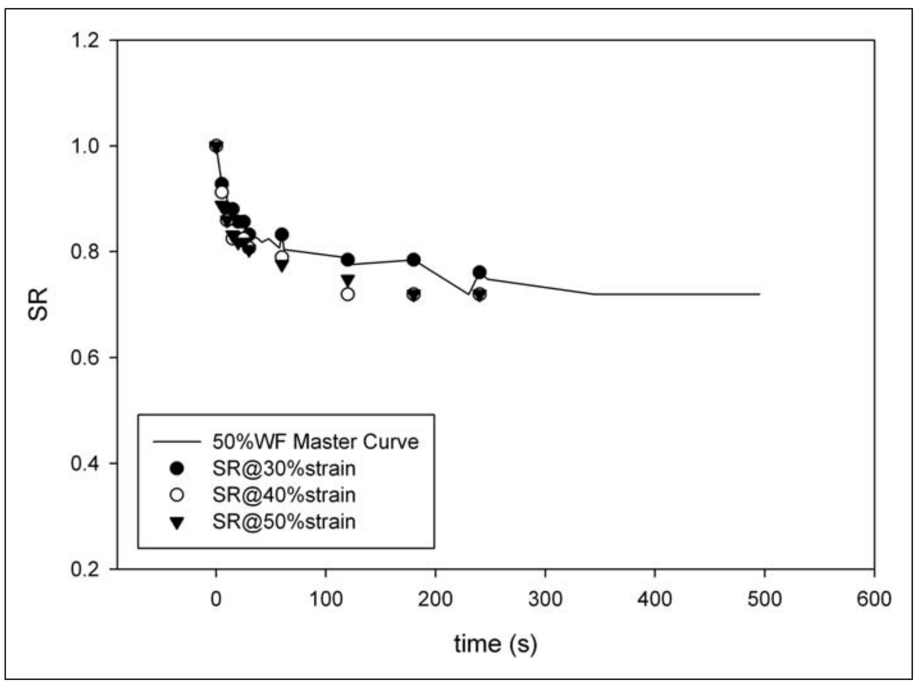

Figure 6. The master curve for 50% wood flour composite at 30% ultimate strain.

successive points become lower as the filler content is raised, and this is especially true for newsprint composites. This result corroborates previous studies.[6]

The effect of filler type on the stress-relaxation performance of samples is presented in Figure 5. Figure 5(a) and (b) show this effect at 30% and 50% of ultimate strain, respectively. The general trends are the same for both; however, maintaining higher strain level brings about higher relaxation. It is clearly visible from the figure that the most pronounced effect corresponds to neat polyethylene, and all filled systems demonstrate considerable improvements in stress retention. In spite of its low relaxation modulus (not shown), the formulation without compatibilizer gives the highest SR values. Strain ratios used in this study were selected based on ultimate failure strains determined in the three-point bending test. As un-compatibilized formulations failed at much lower strains, the absolute strain values applied to them in stress-relaxation test was smaller as compared with those for compatibilized ones. Therefore, the higher SRs observed for these formulations can be attributed to lower strains applied. There is no distinct difference among scattered points corresponding to the other compositions. Moreover, the contrast among samples becomes more and more with time and this is particularly correct at the higher

Table 2. Details of time–strain superposition procedure applied to composite formulations

Formulations	E_a (kJ/Mol)	R^2	Ultimate strain (%)	a_ε
PE–WF-25	2463.9	0.98	40	0.735
			50	0.453
PE–WF-50	2253.4	0.66	40	0.522
			50	0.485
PE–RH-25	–	–	40	1.585
			50	1.213
PE–RH-50	–	–	40	1.214
			50	1.297
PE–WF-25-0	674.98	0.47	40	1.294
			50	0.805
PE–WF-50-0	1880.5	0.01	40	0.351
			50	0.546
PE–NP-25	4033.5	0.76	40	1.129
			50	0.273
PE–NP-50	–	–	40	1.114
			50	1.118
PE–KF-25	1675.1	0.62	40	0.609
			50	0.584
PE–KF-50	2152.5	0.89	40	0.889
			50	0.501
PE	344.63	0.01	40	0.821
			50	0.895

filler content; at the final measured time, the newsprint containing sample shows a slight advantage.

Figure 6 shows a typical master curve obtained for the composite containing 50% wood flour with compatibilizer at 30% ultimate strain. To explain the long-term relaxation pattern of composites, a master curve is constructed by considering 30% ultimate strain as the reference, and horizontally shifting curves at the other strain levels along the logarithmic time axis until they superpose. In the case of compatibilized 50% wood flour composition, the derived master curve covered approximately twice the length of the original test time. In this case, it seems that this method has limited capability to extend the time period and generate a smooth curve. This is possibly because HDPE exhibits complex rheological behavior, and incorporating natural fibers increases this complexity.[11] An Arrhenius equation was also employed to correlate the shift factor values and strain levels. Achieved activation energies for viscous flow (excluding negative ones), shift factors and R^2 values for all evaluated formulations are presented in Table 2. The highest R^2 value corresponds to the composite containing 25% wood flour with compatibilizer (0.98), and the lowest ones correspond to neat polyethylene and composite containing 50% wood flour without compatibilizer (0.01).

Conclusion

In this study, the effect of natural fiber type and content on the stress relaxation of HDPE-based composites was investigated. The results revealed that there is a reverse correlation between prescribed strain level and stress retention, and incorporating more filler results in less relaxation and also decreases relaxation rate. Among used filler types, wood flour and kenaf fiber presented more similar behaviors and newsprint performance resembled that of rice hulls. The difference between relaxation responses among different composites develop over time, especially at the high filler content. Based on the findings of this study, the composite containing 50% wood flour without compatibilizer exhibited the best stress-relaxation performance. Furthermore, a master curve was constructed with respect to strain levels by horizontal shifting method and employing Arrhenius equation. The results indicated low efficiency in the application of time–strain superposition to these composite materials.

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