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Mechanical and Degradation Behavior of Castor Oil Seed Shells - Recycled Low Density Polyethylene Composites

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ABSTRACT

Low density polyethylene is among the most used polymers globally due to its desirable properties. This work investigated the effect of blending recycled low density polyethylene with castor oil seed shells. The focus was on mechanical and creep behavior of RLDPE/ cellulose composites. Samples of RLDPE/ cellulose composites were prepared in the weight ratio 10:0, 9.5:0.5, 9:1, 8.5:1.5, 8:2 by injection molding process. Analysis of dynamic mechanical behavior was carried out using torsional pendulum method within temperature range of 30 °C to 100 °C. Creep strain as well as creep recovery testing were performed at 25°C, 40 °C, 50 °C and 60 °C by exerting a fixed stress for 12 minutes for each respectively. DMA data was analyzed by Fouss-Kirkwood law. Short-term creep strain and creep recovery were analyzed using Burger law and Weibull distribution function, respectively. The long-term creep was analyzed with William-Landle-Ferry law. DMA results showed that between 5-15% strong interactions between cellulose hydroxyl groups and RLDPE chains stiffens the composite which leads to increase in shear storage modulus. The results also showed that between 5-10%, there is increase in loss modulus which is attributed to viscosity increase. Creep measurement showed that for 5% cellulose intake, percentage creep strain decreases due to stiffening of the matrix. Above this, the opposite is seen. The long-term creep results indicated that the effect of cellulose on free volume in relation to temperature was lacking.

Key words: Recycled low density polyethylene; Polypropylene; Castor oil seed shell; Cellulose; Composites; Dynamic mechanical analysis

INTRODUCTION

Polymer blending has been used in material production for a long time to provide a large range of benefits that would otherwise be unattainable or prohibitively expensive. Global production of plastics is estimated to be over 368 million tonnes per year with the expectation of doubling in the next 20 years (Walker and Fequet, 2023). Eventually this will be disposed resulting to a significant proportion in environmental solid wastes. Low density polyethylene is among the commonly used polymers in the world for its attractive properties. In spite of the generally versatile qualities of low density polyethylene, a lot of research focusing on modification and regulation of its properties through blending with natural polymers; such as cellulose, starch and protein origin among others, is still being done. As a result of low densities, high stiffness, low cost, non-abrasiveness, recyclability and biodegradability among other properties, organic blends have been increasingly outshining inorganic blends. Studies have shown that incorporating these organic blends to plastics, properties like stiffness, dimension stability, hardness as well as biodegradability could be improved (Hattotuwa et al., 2002). An increase in the storage modulus (E') and a decrease in damping behavior can be observed with increasing fiber content due to reinforcement between the fibers and the matrix (Amash and Zugenmaier, 1999). According to Grozdanov 2006, rice straw is good natural fiber source that can be used in reinforcement of polypropylene. The results were impressive. When polypropylene was blended with cellulose from acacia, its dynamic mechanical, diffusion properties improved greatly (Korir P. Kiprono , 2013).

Burlein *et al.* (2014) investigated morphological as well as mechanical properties of low density polyethylene (LDPE)-poly(3-hydroxybutyrate)(PHB) blend filled with castor oil cake (CC) and the study showed that higher values of Young's modulus (E) were obtained with increase in proportion of PHB or CC added to the binary mixture. According to Nwigbo *et al.* (2013) investigation on the mechanical properties of castor seed shell-polyester matrix composites found that addition of filler content in the matrix, resulted into improved tensile strength. Use of natural fibers in blending of RLDPE has gained momentum in research due to their environmental friendliness and versatile properties; and therefore castor seed shells being an excellent natural fiber, was to improve the general properties of neat RLDPE. The objective of the study was to investigate the dynamic mechanical, creep (deformation) properties of RLDPE/cellulose composites.

MATERIALS AND METHODS

Recycled Low Density Polyethylene (RLDPE)

RLDPE in chips form were sourced from Kenplast plastic company in Nairobi. PE has a structure that consist of a linear repeating unit $(-CH_2-CH_2)_n$ (Cowle 1991), where n is the number of repeating units that form the polyethylene chain. Low-density polyethylene has branched chain molecules which reduce close packing and hence lowers the density

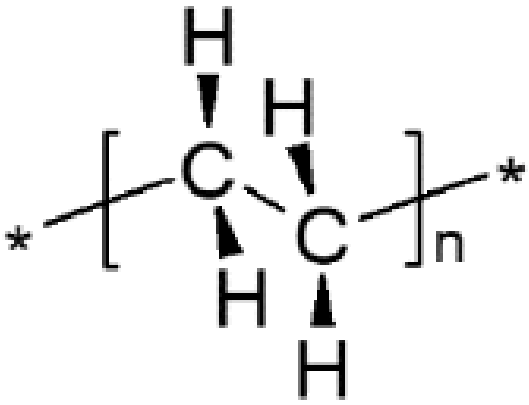

Figure1. Chemical structure of LDPE

Castor Oil Seed Shell (C)

Castor oil seed comes from castor oil plant (Ricinus communis). The castor oil seeds were sourced from farms in Mukaa sub-county in Makueni county from which the shells were obtained. Castor oil seed shell is a product with cellulose content of about 21% (Abdallah et al., 2013), which made it suitable for the study. The seeds contain cellulose whose chemical formula is $(C_6H_{10}O_5)_n$ where n is the number of repeating units. The isolated cellulose molecule is a linear condensation polymer consisting of D-anhydroglucopyranose as its basic building unit linked by β-1,4 glycosidic bonds.

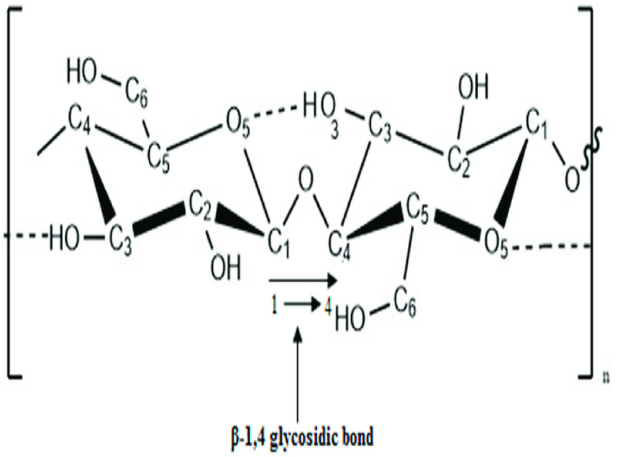

Figure 2. Chemical structure of cellulose

Composite preparation

The samples were prepared using the mold locally made at the Kenyatta University Engineering workshop. To remove excess water the seed shells were heated at 90^0 C for 8 hours after which it was ground into fine powder. The fine powder was added to the molten polyethylene in the ratio of their weight. Samples of RLDPE/Cellulose composites were prepared in the weight ratio 100:0, 95:15, 90:10, 85:15 and 80:20, respectively. The mixture was placed in a melting chamber which is cylindrical with a diameter of 18mm and a length of 168mm. the mixture was thoroughly mixed and heated to ensure homogenous blend. The composite samples were produced inform of discs and cut into slices of dimensions of 24mm×5mm×2mm.

Dynamic mechanical analysis (DMA)

In DMA, shear storage modulus (G') and shear loss modulus (G") were carried out at the range of temperatures of 30 °C to 100 °C using the torsional pendulum method. Storage modulus of a viscoelastic material is a measure of the stiffness of the material which is related to elastic energy which is stored in the material and is reversible. On the other hand, the energy which is lost as heat rom the material is referred to as loss modulus

Creep / recovery analysis

Creep measurements were carried out at 30, 40, 50 and 60 °C using beam-bending method. The time for deformation of the samples was 12 minutes and the time for recovery was as well as 12 minutes.

RESULTS AND DISCUSSION

Storage modulus

Figure 3 below shows how shear storage modulus varied with temperature change for RLDPE/cellulose composites

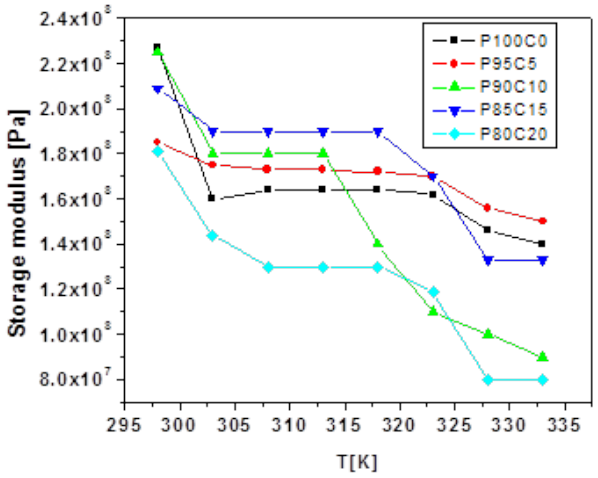

Figure 3. Storage modulus as a variant of temperature for RLDPE/cellulose composites

The shear storage modulus G'(T) of all samples decreases with increase in temperature as observed in figure3. This is attributed to softening of the composites. Between 5% to 15 % of cellulose, it is noted that, the shear storage modulus G'(T) increases. This is attributed to strong interactions between RLDPE chains and hydroxyl groups of cellulose stiffening the composite. Above 15% of cellulose, shear storage modulus G'(T) decreases as particles coalesce weakening interactions between RLDPE chains and hydroxyl groups of cellulose which leads to softening of the composite.

Loss modulus

Figure 4 below represents variation of shear loss modulus with temperature change.

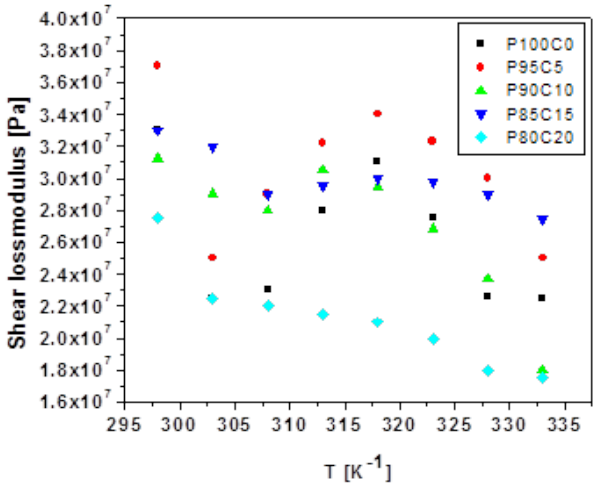

Figure 4. Shear loss modulus as a variant of temperature for RLDPE/cellulose composites

Shear loss modulus, represents non recoverable energy loss as heat or molecular rearrangements during one loading cycle or the viscous nature of polymer. From the figure 4 above, between 5% to 15% of the filler, shear loss modulus increases since the viscosity of the composites increases. This is because of limited molecular movements in the matrix. Above 15% of the filler, the loss modulus decreases due to decrease in viscosity which results from enhanced molecular movement.

The temperature dependence of shear loss modulus is given by Fouss-Kirkwood relation

$$G''(T) = \frac{G''_{max}(T)}{\cosh\left[\frac{mE_a}{R}\left(\frac{1}{T}-\frac{1}{T_m}\right)\right]} \quad (1)$$

Where m is a broadening parameter representing distribution of relaxation times, E_a is activation energy and T_m is the temperature at maximum value of loss modulus ($G"_{max}$). A plot of shear loss modulus versus inverse temperature for all samples is shown in Figure 5.The solid lines represent the Fouss-Kirkwood fits.

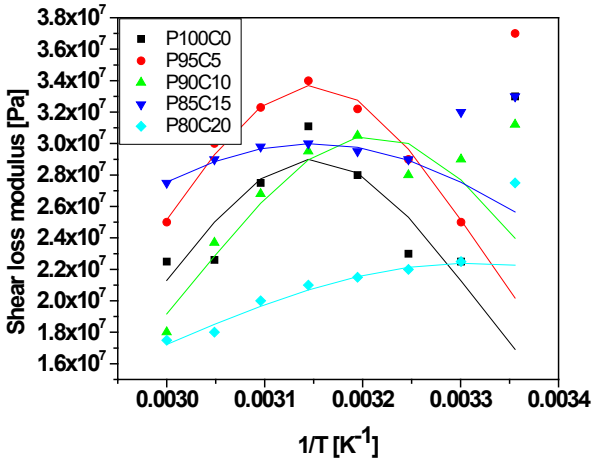

Figure 5. Variation of loss modulus with inverse temperature for RLDPE/cellulose composites.

The Fouss-Kirkwood fit parameters as given in Table 1

Table 1 Fouss-Kirwood fit parameters for RLDPE/cellulose composites

Sample	G_{max} [MPa]	m	E_a [kcal/mol]	T_m [K]
P100C0	29.0	0.62	17.8	317.4
P95C5	33.7	0.61	17.5	317.4
P90C10	30.5	0.59	16.8	311.5
P85C15	30.0	0.44	12.7	317.4
P80C20	22.4	0.41	11.9	302.1

From table 1, the decrease in E_a with cellulose intake reveals the existence of reorganization of molecular chains of the crystalline-amorphous interface having taken place which leads to low hindrance of their motion. The decrease in

m with cellulose intake indicates broadening of the loss process due to a wide distribution of relaxation times. In addition, it is evident from Fig. 5 that width of the relaxation process increases with cellulose intake.

Creep/recovery analysis

Short-term Creep analysis

The short-term creep analysis was done based on burger law;

$$\varepsilon_c(t) = \frac{\sigma_o}{E_M} + \frac{\sigma_o}{E_K}\left[1 - exp\left(-\frac{tE_k}{\eta_k}\right)\right] + \frac{\sigma_o t}{\eta_M} \qquad (2)$$

Where s_o is applied stress; E_M and h_M are modulus of Maxwell spring and viscosity of the Maxwell dashpot respectively, E_K and h_K are modulus of Kelvin spring and viscosity of Kelvin dashpot respectively. The first term in eq. 2 is the immediate elastic deformation while the second term is the delayed elastic deformation and the third term is the Newtonian flow.

Figure 6 shows the variation of % creep-recovery for all samples at 25, 40, 50 and 60 °C.

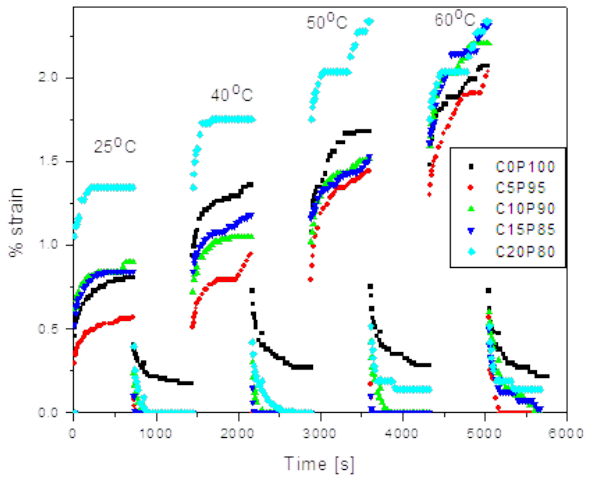

Fig. 6. Variation of % strain with time for RLDPE/cellulose composites at 25 °C, 40 °C, 50 °C and 60 °C

At 25 °C, P100C0 and P95C5 display only the immediate elastic deformation and the delayed elastic deformation. There is no evidence of the Newtonian flow or creep rupture. This due to stiffening of the matrix. For P90C10, P85C15 and P80C20 all the three deformations are evident probably due to softening of the matrix. As anticipated % creep strain increased as temperature increases in both pure RLDPE and its composites. Evidently, increasing temperature from 25 to 60 °C the peak creep strain increased by 180 %. This is because, as the temperature increases, activation barrier for bond dissociation is decreased which allows untangling of molecular chains, slipping and reorientation of chains more easily .

It can be seen that % creep strain of pure RLDPE was higher than that of P95C5 at all the temperatures showing that the performance of the material in terms of creep improved. The results further indicate the % creep strain increases with increase in cellulose, consequently reducing creep performance.

For P95C5, the attraction of microfibrils with the OH groups is maximum and thus leading to reinforcement of the structure(stiffening increases). Since cellulose resist slippage, reorientation as well as motion of polymer chains in the composite, the resistance to creep strain for cellulose composite increases (N. E. Marcovich and M. A. Villar, 2003). At higher concentrations, the % creep strain increases probably due to formation of aggregates by the filler particles. The aggregates require less energy to initiate or propagate a crack for they are regions of stress concentration and thus are potential sites for composite fractures.

A plot of variation % creep strain with time at 60 °C is shown in Fig. 7. It is noted that 5 % cellulose intake percentage creep strain decreases which is attributed to stiffening of matrix, above which the opposite is seen.

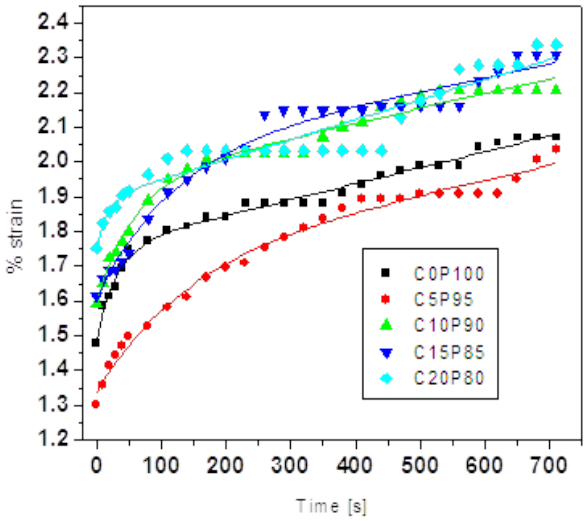

Figure 7. Variation of % creep strain with time for RLDPE/cellulose composites at 60 °C. The solid lines represent the Burger law fits

The Burger law fit parameters as given in table 2

Table 2 The Burger fit parameters for RLDPE/cellulose composites.

Sample	E_M (MPa) ±0.05	E_K (MPa) ±0.5	η_K ($\times 10^9$ s) ±0.05	η_M ($\times 10^9$ s) ±0.05
P100C0	2.08	11.4	0.349	6.67
P95C05	2.30	8.21	1.110	7.67
P90C10	1.94	8.88	0.506	7.14
P85C15	1.92	7.36	0.830	8.14
P80C20	1.76	22.3	2.50	5.33

The decrease in E_M with C intake shows less improvement in elasticity of matrix. The decrease in E_K with C shows decrease in stiffness of matrix. The increase in h_M with C shows increased flow of matrix. The increase in h_K with C shows increased viscosity of matrix.

Short-term recovery analysis

The recovery of the system after the removal of stress is different from creep, namely, instantaneous due to Maxwell element, exponential due to Kelvin-Voigt element and finally Newtonian flow.

At 25 °C, P100C0 display instantaneous and exponential recovery. P95C5, P90C10 and P85C15 display instantaneous and flow recovery; and P80C20 display instantaneous, exponential and flow recovery. At 60 °C, P100C0, P90C10, P85C15 and P80C20 display instantaneous and exponential recovery, but P95C5 display instantaneous, exponential and flow recovery probably due to stiffening of matrix. As anticipated % recovery strain increases proportionally with temperature rise in both pure RLDPE and its composites. P100C0 increased from 75 to 90 %, however, composites remained approximately 100 %. This is because, temperature increases activation barrier for bond association hence preventing chains of molecules to entangle, slip or reorient more easily.

The recovery analysis was done based on the Weibull distribution function given by equation 3

$$\varepsilon_r(t) = \varepsilon_r \left[\exp\left(-\left(\frac{t}{\eta_r}\right)^{\beta_r}\right)\right] + \varepsilon_f \qquad (3)$$

Where e_r is the recovery strain, b_r is the characteristic life parameter, h_r is shape parameter, e_f is the permanent strain depended on effects of viscous flow.

A plot of variation of % recovery strain with time at 60 °C is shown in Fig. 8. It is noted that at 5 % C intake % recovery strain increases which is attributed to stiffening of matrix, above which the opposite is seen.

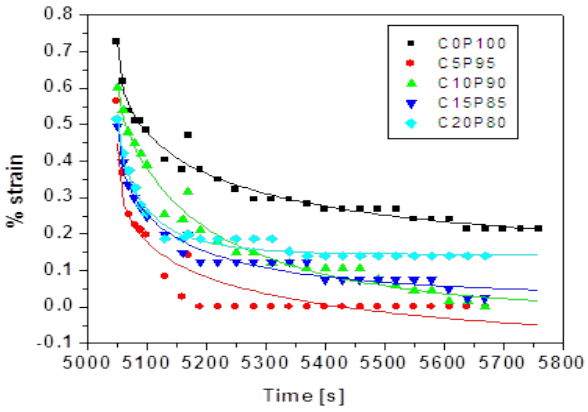

Figure 8. Variation of % recovery strain with time for RLDPE/cellulose composites at 60 °C. The solid lines represent the Weibull distribution function fits

The Weibull distribution function fit parameters as presented in table 3.

Table 3. Weibull distribution function fit parameters for RLDPE/cellulose composites

Sample	ε_r	η_r	β_r	ε_r
P100C0	0.58	160.9	0.50	0.14
P95C5	0.58	160.9	0.42	0.08
P90C10	0.63	152.7	0.69	0.02
P85C15	0.48	87.8	0.54	0.03
P80C20	0.38	43.8	0.72	0.08

From the table, there is decrease in e_r and e_f with cellulose loading. This signifies enhanced recovery performance. As it is noted that, there is decrease of h_r with cellulose intake, this implies decrease in viscosity in the composites. Increase of b_r with cellulose loading, shows change of creep rate of the composites. Generally adding cellulose to the matrix leads to decrease in viscosity of the composites

Long-term creep analysis

Figure 9 gives the master curves for long term creep analysis as described by William-Landel-Ferry in equation 4

$$\log(a_T) = \frac{-C_1(T-T_0)}{C_2+(T-T_0)} \qquad (4)$$

where C_1 and C_2 are fit parameters which vary depending on specific morphology or structure of a given material.

Eq. 4 was chosen since measurements were done over the RLDPE glass transition temperature.

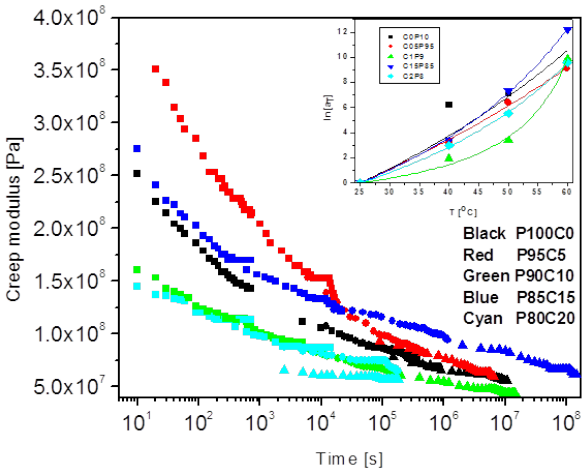

Fig. 9. Master curves presenting creep modulus as a variant of time for RLDPE/cellulose composites. Inset shows logarithm of shift factor varying with temperature. The solid lines represent WLF fits.

Table 4. WLF fit parameters for RLDPE/cellulose composites

Sample	C_1 (± 0.5)	C_1 (± 0.5)	T_o (°C) (± 0.1)
P100C0	30.4	-135.6	25.2
P95C5	38.3	-180.8	24.8
P90C10	3.0	-45.7	24.9
P85C15	15.8	-80.0	25.3
P80C20	12.8	-82.0	25.4

From the master curves, prediction of the long term properties extends up to more than 1.4×10^{8} s in time scale. At 10 and 20% of cellulose creep modulus is lower than that of pure RLDPE. This indicates reinforcement of effectiveness of the filler. From Table 4, the values of C_1 and C_2 presents some trends that lack consistence with cellulose intake showing that cellulose has no effect on free volume in relation to temperature.

CONCLUSIONS

Dynamic mechanical investigations showed that between 5 to 15% of the cellulose, strong interactions between cellulose hydroxyl groups and RLDPE chains, stiffens the composite thus leading to increase in shear storage modulus. The investigations also revealed that between 5 to 15% of the filler, the shear loss modulus increases due to increase in viscosity resulting from limited molecular movement.

The creep measurements showed that, for 5% cellulose intake, percentage creep strain decreases due to stiffening of the matrix above which the opposite is seen. It was also revealed that, at 25 °C % recovery strain of all composites is improved which worsen with increase in temperature.

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