MECHANICAL, DIFFUSION AND DEGRADATION PROPERTIES OF BLENDS OF CELLULOSE AND RECYCLED LOW DENSITY POLYETHYLENE

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Abstract
This paper discusses the effect of Cellulose (CEL) concentration on mechanical, diffusion and degradation properties of Recycled Low Density Polyethylene (RHDPE). Injection molded blends of RLDPE and CEL were prepared in percentage ratios of 100:0, 95:5, 90:10, 85:15 and 80:20. Dynamic mechanical analysis, creep, diffusion, thermal degradation and biodegradation measurements were carried out on the molded samples. Three relaxation processes namely; α, β_1 and β_2 were observed. The α process is assigned to large scale chain motion where as β_1 and β_2 suggest lamellae shear of two different thicknesses. The intensities of the processes decreased with increase in cellulose loading whereas the temperature shifts were not observed. Creep strain increased moderately with increasing loading intakes while recovery decreased. Deformation behavior follows WLF law suggesting that free volume plays a crucial role. Water uptake was found to increase with cellulose loading. Weight change profiles for the blends at room temperature indicated that the diffusion is Fickian. Diffusion coefficient increased with CEL intake. Thermo-gravimetric analysis (TGA) showed that the decomposition trend shifted from one stage to two stage with increasing CEL intake. The models of analysis for DMA and Creep data were VFT and WLF respectively. Thermal degradation data was analyzed using Arrhenius laws while Fick's laws were used in diffusion measurements. Energy is distributed through the three transitions on impact. Creep increases with CEL intake whereas recovery is improved. Diffusivity increases while thermal stability as well as toxic byproducts decreased with CEL intake. Degradation was enhanced with CEL intake thus the composites can be adopted by policy makers to minimize environmental pollution.

Key words: Recycled Low Density Polyethylene (RLDPE), cellulose (CEL), Thermo-gravimetric analysis (TGA), William Landel Ferry (WLF), Dynamic Mechanical Analysis (DMA)

1.0   Introduction
The world rate of production of plastics is approximately 100 million tonnes per annum (Hannequart, 2004). This will eventually be disposed and will result in a significant proportion in municipal solid waste. RLDPE in its pure form is extremely resistant to environmental degradation (Arvanitojannis, 1999). Incineration would always produce a large amount of carbon dioxide and other toxic gases which eventually contribute to global pollution.

Based on these backgrounds, there is an urgent need for the development of ''green polymeric materials'' that do not involve the use of toxic or noxious components in their manufacture and that can degrade into natural environmental products faster. The addition of biodegradable components facilitates the destruction of RLDPE materials under the influence of microorganisms and environmental actions (Huang, 1984 and Coutinho *et al.,* 2000). Cellulose is one of the strongest and stiffest fibers available and it has a high potential to act as reinforcing agent in biopolymers (Huda *et al.,* 2005 and Harikumar *et al.,* 1999). RLDPE-CEL blends therefore offer a new class of materials which can minimize pollution. Permeation of solvent through a polymeric membrane is commonly used in several industrial processes. There is need to investigate diffusivity in RLDPE-CEL blends. These results will be useful for perfecting our membrane design method (George *et al*., 1998). Thermal stability, strength, diffusivity and biodegradability are among the properties that can be improved by these blends.

Several studies on the molecular dynamics of RLDPE have been reported (Cowle*,* 1991). However, identifying the molecular origin of these secondary relaxations has proven to be a difficult task. In this respect the presence of the hydroxyl groups in CEL creates an environment which influences the relaxation processes (Peng *et al.,* 2002). DMA monitored relaxation processes, creep monitored strain at constant stress, dipping the samples in pure water revealed diffusivity while TGA and soil burial test revealed thermal degradation and biodegradability respectively.

2.0 Materials and Methods

RLDPE in chips form and gray in colour was obtained from Kenplast Plastic Company in Nairobi. Mixtures of RLDPE and powdered CEL were obtained in percentage ratios of 100:0, 95:5, 90:10, 85:15 and 80:20 (by mass) through injection molding process. The mold was then allowed to cool at room temperature for 10 minutes.

2.1 Dynamic Mechanical Analysis Measurement Procedure

Dynamic mechanical testing was done using DMA 2980 TA instrument in the DMA Multi-Frequency - Single Cantilever mode on film samples of about 25 mm x 4 mm x 2 mm that were cut from the blend samples of RLDPE-CEL. The storage and loss moduli were recorded in a DMA multi-frequency single cantilever mode system in the frequency range of 1 to 30 Hz, in the temperature range -30 to 90 ^{o}C and with a heating rate of 5 ^{o}C/ min.

2.2 Creep Measurement

The creep and recovery behavior of the polymer blends of dimensions 25 mm x 4 mm x 2 mm were evaluated using DMA 2980 in a multi-frequency single cantilever mode at a constant span of 12 minutes. The oven was set to a desired temperature and the sample was allowed to equilibrate for 12 minutes. The creep measurements were initiated by setting the machine to displace at 1 MPa and equilibrate for 20 minutes at 30 °C, 40 ^{o}C, 50 °C and 60 °C.

2.3 Diffusion

The molded specimens (10 mm $\times$ 5 mm $\times$ 2 mm) of each composition were dried in an oven for 6 hours at a temperature of 50 $\pm$ 3 °C, cooled in a desiccators and immediately weighed until the consecutive weights were equal. The samples were placed in distilled water at room temperature (25 $\pm$ 2 °C) for 77 days. The weighing was repeated at the end of every week and the average of three values was recorded. The difference between the saturated weight and the dried weight was calculated as the water absorption.

2.4 Thermal Degradation

The TGA measurements were carried out on 0.0105 g of the samples by monitoring the mass loss after every 5 ^{o}C at a heating rate of 5 ^{o}C/ min within a temperature range of 25 ^{o}C - 550 ^{o}C using a thermogravimetric analyzer (Model Lindberg / Blue tube furnace) in oxygen atmosphere and the kinetic parameters were obtained.

2.5 Biodegradation

The RLDPE-CEL samples in percentage ratios of 100:0, 95:5, 90:10, 85:15 and 80:20 weighing 0.15 g each were dried in an oven for 6 hours at a temperature of 50 $\pm$ 1 °C until a constant mass was obtained and then buried 20 cm beneath the ground. A control box that contained only samples and no soil was also maintained for comparative studies. The moisture content was at 20-50 % and the soil pH was measured as 6.4. The samples were removed from the soil every 7 days. After removal, samples were washed in distilled water and dried at 50 $\pm$ 3 °C until a constant mass was obtained.

3.0 Results and Discussions
3.1 Dynamic Mechanical Analysis

Storage modulus, *E*' determines the ability of the material to absorb or store energy; high storage modulus indicates more rigid material while loss modulus, *E*" determines the ability of a material to dissipate energy (McCrum *et al.,* 2003). The DMA results were obtained in terms of storage modulus, *E*' and loss modulus, *E*'' from -30 ^{o}C to 90 ^{o}C and presented in Figure 1 and Figure 2.

3.2 Storage Modulus and Loss Modulus

Figure 1 shows the variation of storage modulus and loss modulus with temperature for pure RLDPE at different frequencies. The loss factor spectra *E*" was quantitatively described by a superposition of model function and given in equation 1 (Vauderschueren *et al.*, 1979).

$$E^{"}(T) = \sum_{i=1}^{2} A_i \exp\left\{-\frac{E_i}{kT} - \frac{T^2}{T_{m_i}^2} \exp\left[\frac{E_i}{k}\left(\frac{1}{T_{m_i}} - \frac{1}{T}\right)\right]\right\} \dots\dots\dots\dots\dots \text{(1)}$$

where A is a constant, k Boltzmann constant, T absolute temperature, T_m temperature representing maximum loss modulus, E_i is the activation energy and i refers to different processes which contribute to the mechanical response.
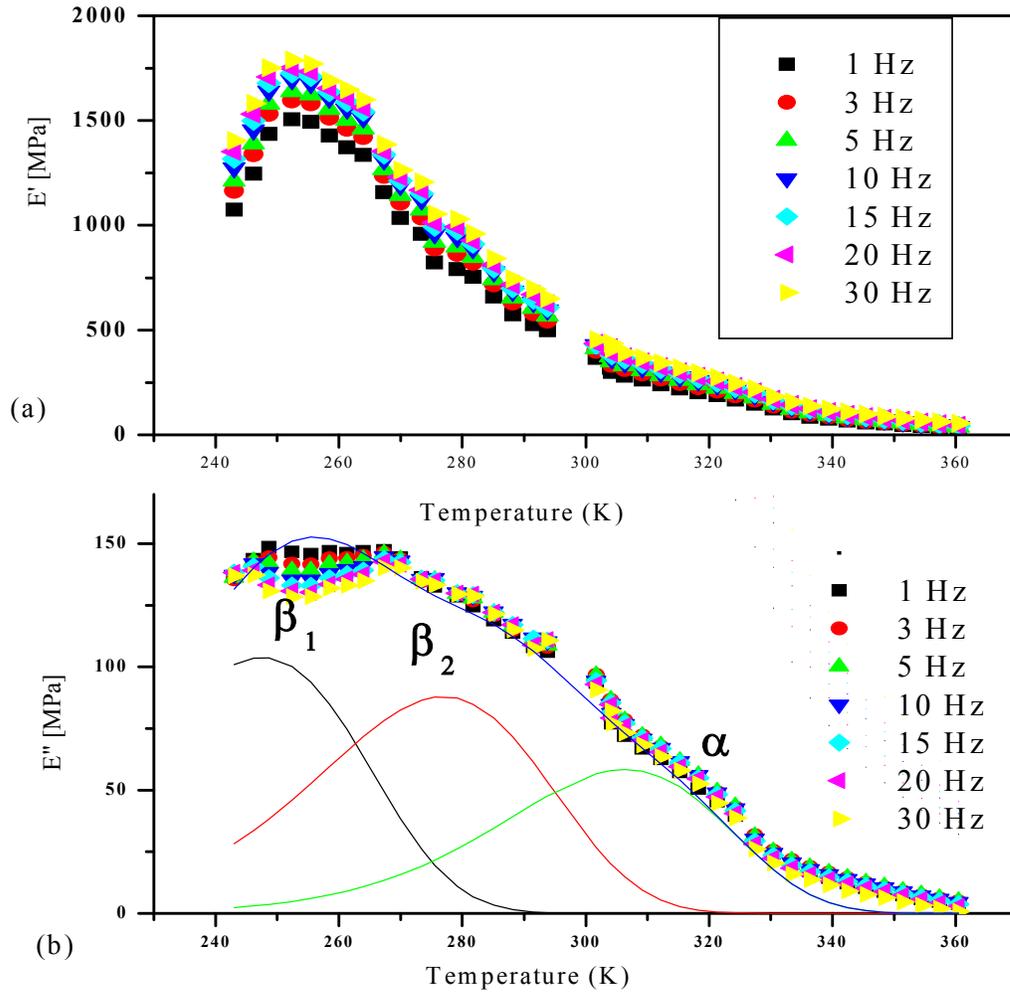
Figure 1 (a): Temperature dependence of the storage modulus of pure RLDPE (b) Temperature dependence of the loss modulus of pure RLDPE at the seven different frequencies studied

At high frequency (shorter period) the sample behave like elastic solid while at low frequency (longer period) it's rubbery. As the temperature is increased the polymer softens and large segmental motions in the amorphous regions become possible. The storage modulus decreases by increasing the temperature and increases with increasing the frequency.

Figure 1 (b) shows plots of loss modulus E'' against temperature for a pure sample at different frequencies. In the loss moduli obtained by DMA, the peaks corresponding to the β_1, β_2 and α transitions are clearly seen. The α-process is associated with large scale chain motion where as β_1 and β_2 suggest lamellae of two different thicknesses i.e β_1 and β_2 transitions are associated with branching relaxation or interlamellar shearing (Munaro and Leni,

2008). Figure 2 shows the temperature dependence of storage modulus *E'* and loss modulus *E''* for blends of different compositions at a frequency of 1 Hz.
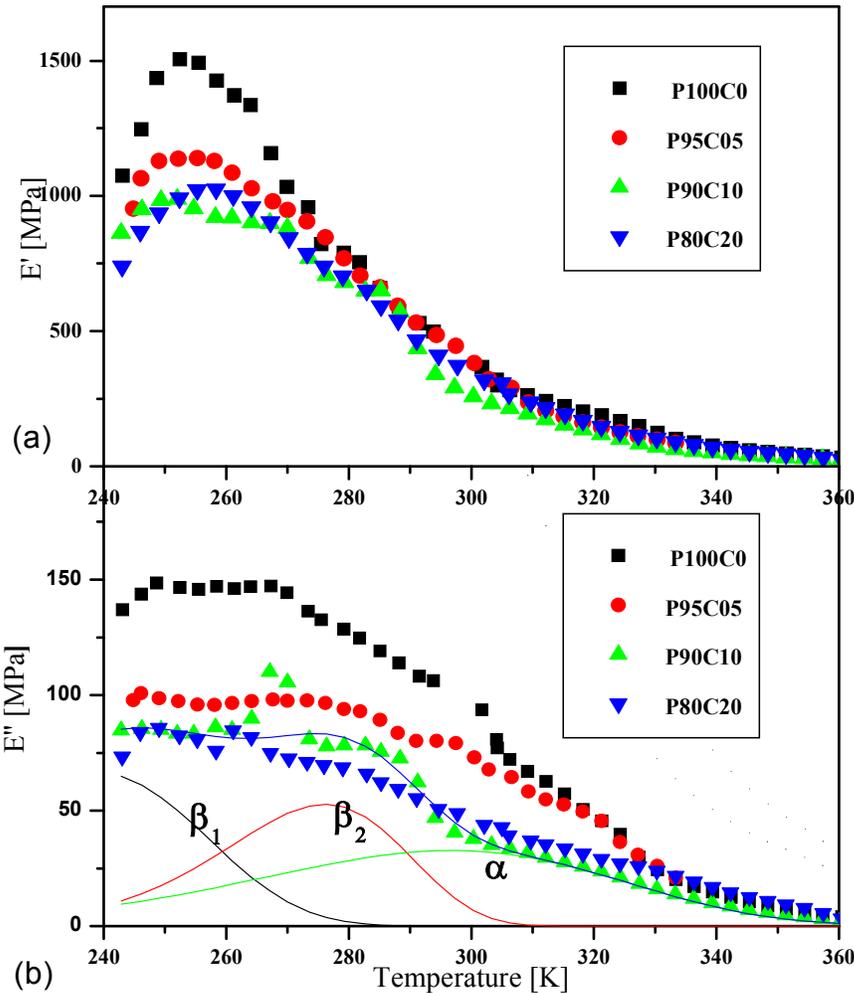
Figure 2 (a): Storage modulus as a function of temperature for RLDPE-CEL blends at 1 Hz. (b): loss modulus as a function of temperature for RLDPE-CEL blends at 1 Hz. Solid lines are fit lines according to equation 1

It can be observed that the storage moduli of the blends were lower than those of the corresponding pure RLDPE. The blends also display three transitions as pure sample. E' decreased with CEL intake showing that the blend stores less energy on impact. T_α does not change with C intake meaning it does not change the free volume. Also T_β does not change with C intake due to lamellar stresses.

3.3   Creep Analysis
3.3.1   Time-temperature Superposition
By selecting as the reference the curve for 30 °C, and then shifting all other isothermal curves of the creep modulus versus time obtained at 40 °C, 50 °C and 60 °C with respect to time, the curves of creep modulus versus

time   at   reference   temperature   are   generated   as   shown   in   Fig   3.
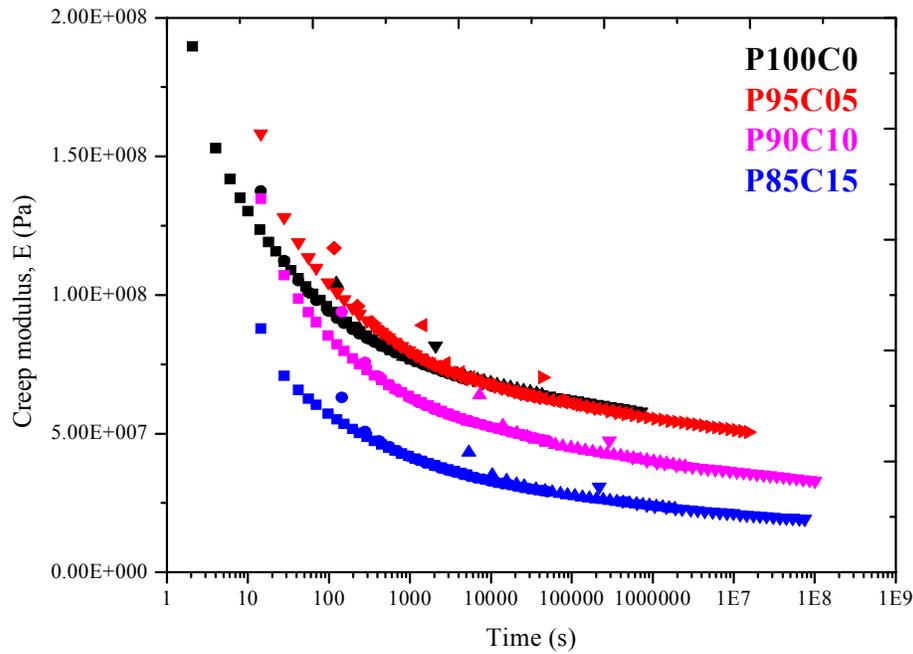
Figure 3: Creep modulus master curves for all blends at 30, 40, 50 and 60 °C.

The creep modulus, E, versus time curves are shifted to lower values with an increase of the CEL. At longer times viscous flow occurs and the materials exhibit a relatively low creep modulus. The results can be explained as follows: Under constant load, CEL undergoes molecular relaxation and rearrangement. The process involved in molecular rearrangement become more pronounced with time and are faster at higher temperatures. They are time and temperature dependent. The experimental data for the shift factors, a_T were tested with WLF model equation 2 (Ward and Hadley, 1993) and shown in Figure 4.

$$\log \frac{\tau(T)}{\tau(T_g)} = -\frac{C_1(T - T_g)}{C_2 + T - T_g}$$ .... (2)

where $\tau(T)/\tau(T_g)$ = the shift factor relative to the reference temperature, T_g, C_1 & C_2 are empirically determined constants and T_g is a glass transition temperature.
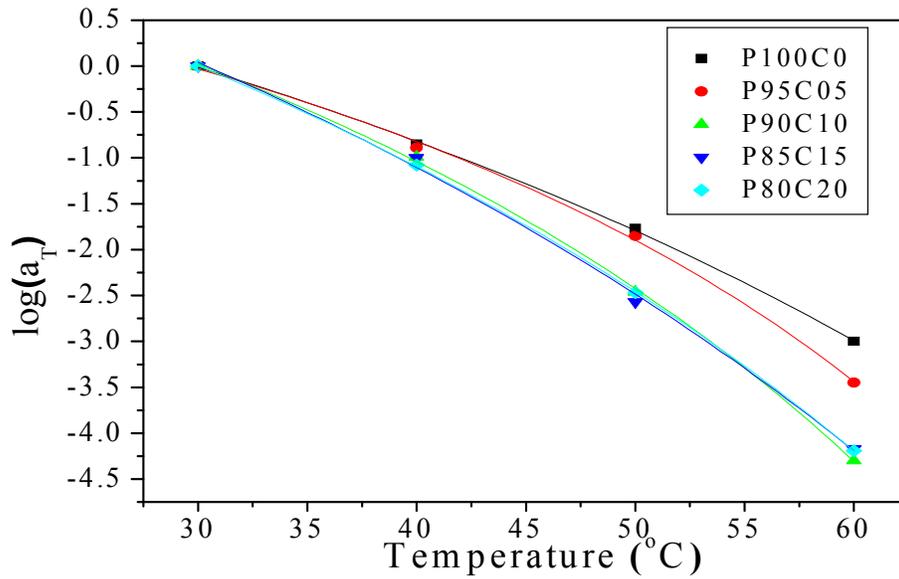
Figure 4: Activation plot for creep modulus. Solid lines are fits according to equation 2

The results show good agreement with the WLF model. The shift factors decrease with CEL loading. The activation plot also shows that creep is dependent on free volume since the graph is not a straight line. Deformation of the blends depends on large chain segments. The fitted parameters are shown in the Table 1.

3.4   Diffusion

The results for water uptake of RLDPE-CEL samples are shown in Figure 5.
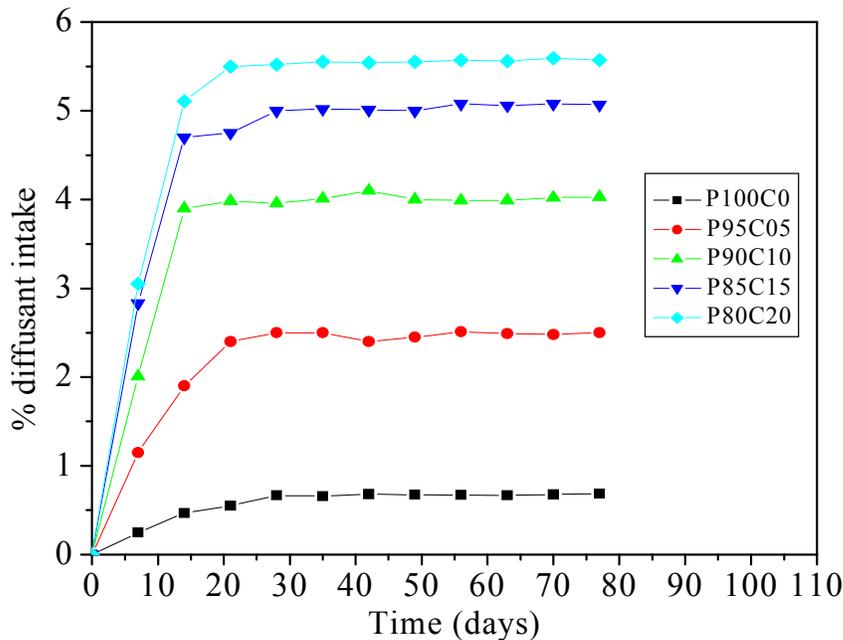
Figure 5: Variation of percentage weight of RLDPE-CEL blends with time

RLDPE exhibited reasonably good water resistance compared to RLDPE-CEL blends. In the first 7 days, the pure RLDPE absorbed only 0.27 % of water; however, the RLDPE-CEL of 95:5 blends absorbed 1.3 % of water in the first week. The water absorption slowly increased over a period of the 28 days, by which time the blends containing 0, 5, 10, 15 and 20 % CEL absorbed 0.5, 2.5, 4.0, 5.0 and 5.5 % of water, respectively. Water intake increased with time and CEL loading meaning the OH groups in CEL provided hydrophilic environment thus more water was absorbed.

3.5 Diffusion Coefficient

CEL affects the water diffusion rate into the blends significantly because the water molecules get into the cellulose through cellulose- matrix interface. To understand this effect, diffusivity, D of water in the RLDPE-CEL blends specimens was determined by use of Fick's equation 3 (David *et al.,* 1996, Devi *et al.,*1997 and Ramazan *et al.,* 2007).

$$\frac{M}{M_{max}} = 4\left[\sqrt{\frac{Dt}{\pi h^2}}\right] \quad .... \text{ (3)}$$

where M is the amount of diffusant taken up by the sheet in a time *t* and *h* is the thickness of the sample. M/M_{max} was plotted against $t^{\frac{1}{2}}$ as shown in Figure 6.
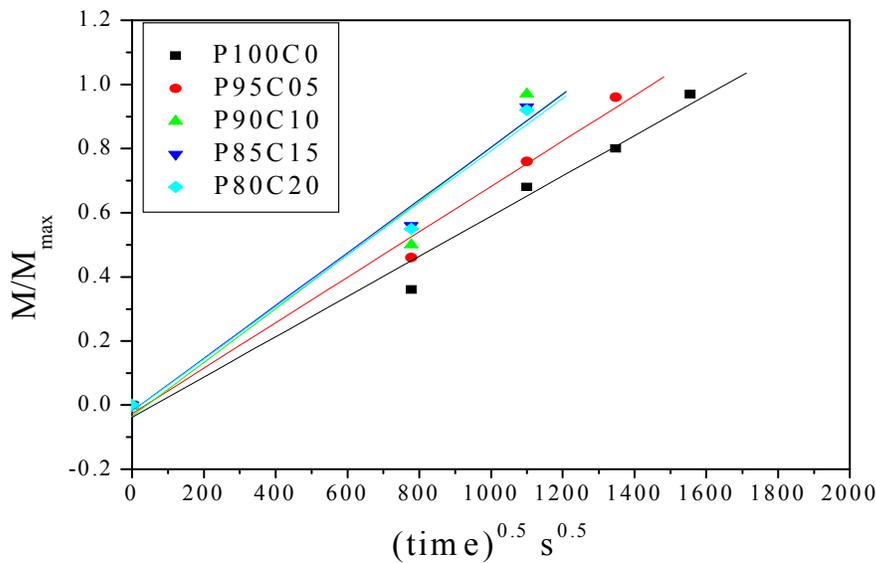
Figure 6: The effect of CEL concentration on the diffusion coefficient (D) of RLDPE blends at room temperature

The diffusivity was determined from the initial slope of the plot in Figure 6. The Table 2 shows values of diffusivity, D of blends with different percentages of CEL concentration. Diffusivity increases with CEL loading due to highly polar OH groups in the matrix enabling hydrogen bonding with water molecules hence increased water uptake. The water molecules could saturate the surface of the RLDPE-CEL composites easily and also penetrate into the blend through voids, resulting in higher water absorption in a short exposure time. The value of diffusion coefficient of RLDPE is in agreement with the one reported by Me´tayer *et al.* (1999). Diffusivity increases with increase in CEL concentration in the blend.

3.6 Thermal Stability of Blends

Thermal stability of RLDPE–CEL blends for different application is necessary in determining their temperature range of use and combustibility of compositions. Figure 7 presents the TGA experimental data for RLDPE–CEL blends.
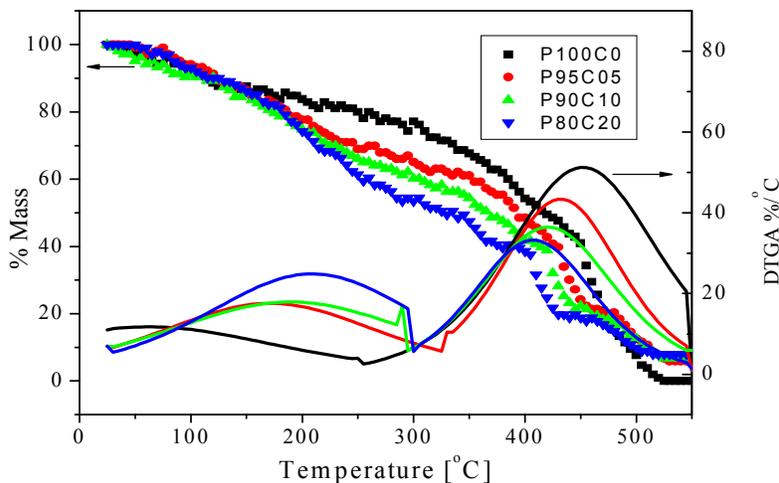
Figure 7: Thermogravimetric and derivative thermogravimetric curves of RLDPE blends

RLDPE/CEL blends shows two- step degradation. The first stage is characterized by random scission /branching and breakage of glucosidic linkage in CEL while the second stage is due to decomposition of RLDPE. The peak decomposition temperature for the first stage increases with increasing CEL intake due to increase in glucosidic linkages. On the other hand, peak decomposition temperature for the second stage decreases with increasing CEL intake due to decrease in RLDPE backbone which shows a decrease in thermal stability. Also the ash content increased with increase with CEL showing presence of less toxic byproducts of RLDPE. The mass loss of RLDPE started at 25 ºC and continued very slowly at temperature below 530 ºC. Above 530 ºC, the quantity of RLDPE residue was very low (equal 0.01%) due to further breakdown into gaseous products at higher temperature. This finding seems to be in agreement with Behjat *et al.* (2009).

3.7 Kinetic Analysis of RLDPE-CEL Blends for Thermal Degradation

The values of activation energy of thermal degradation were obtained from the slopes of the two parts of the graphs using Broido's equation 4 (Broido, 1969).

$$\ln(\ln\frac{1}{x}) = \frac{-E}{RT} + \ln\frac{RZT_m^2}{E_a\beta} \qquad \text{for n=1}……………………………………… (4)$$

Z is the frequency factor and T_m is the temperature of the maximum reaction rate. Fig 8 shows the activation plots and kinetic parameters of thermal degradation of RLDPE- CEL blends.
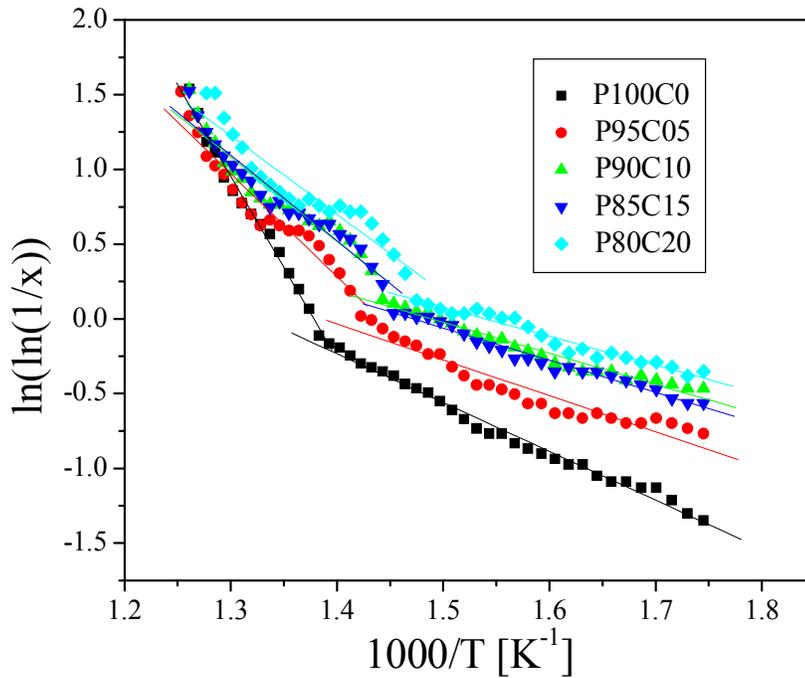
Figure 8: Activation plots and kinetic parameters of thermal degradation of RLDPE-CEL blends. Solid lines are fits according to equation 4

The activation energy E_{a1} for pure RLDPE was 27.4 kJ/mol and it reduced with CEL loading. The activation energy E_{a2} for pure RLDPE was 101.4 kJ/mol and was found to reduce with CEL intake (Table 3).

Table 1: WLF activation parameters of RLDPE- CEL blends

% CEL	C_1	C_2	T_O
0	-9	-117	29.8
5	-5	-76.7	29.6
10	-8	-85	30.2
15	-12	-115	30.4
20	-10	-104	30.1

Table 2: Diffusion values of RLDPE- CEL blends

% CEL	D (cm^2/s)
0	6.04×10^{-10}
5	7.26×10^{-10}
10	9.55×10^{-10}
15	1.06×10^{-9}
20	1.05×10^{-9}

Table 3: Kinetic parameters of thermal degradation of RLDPE-CEL blend

% CEL	E_{a1} (kJ/mol)	E_{a2} (kJ/mol)
0	27.4	101.4
5	19.9	57.3
10	17.5	46.5
15	18.3	47.4
20	15.8	44.0

Table 4: Full degradation times of RLDPE-CEL blend

% CEL	Full deg time(yrs)
0	1459
5	8
10	7.6
15	5
20	3.5

Since $E_{a1} < E_{a2}$; CEL decomposes at lower temperature than RLDPE. E_{a2} decreases with CEL loading due to decrease in thermal stability.

3.8 Biodegradation

Figure 9 shows use of regression lines to obtain the lifespan of blends of the RLDPE-CEL blends buried in the alluvial soil. The rate of biodegradation increases with increase in cellulose content in RLDPE matrix. Full degradation times were obtained from the regression lines and given in Table 4.
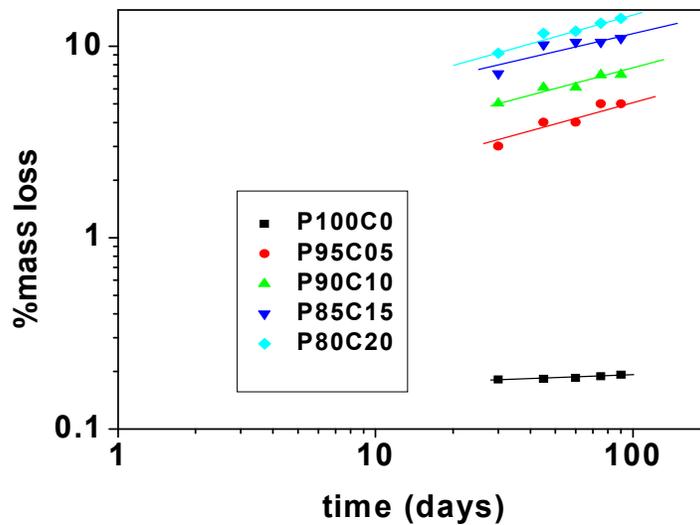
Figure 9: Percentage mass loss as a function of time for the RLDPE-CEL blends buried in the alluvial soil. Solid lines are fits according to $y = mx + c$.

This result shows close agreement with the analysis performed by Peanasky *et a1.* (1991). According to these authors, microbial invasion took place from the top and bottom surfaces of the polymer films. Availability of highly polar hydroxyl groups in CEL increases hydrophilicity hence making the blend more compatible with microorganisms. Small oligomers may diffuse into the organism and get assimilated. The ultimate products of degradation are CO_2, H_2O and biomass under aerobic conditions. Anaerobic microorganisms can also degrade these polymers under anoxic conditions. The primary products then are CO_2, H_2O, CH_4 and biomass under methanogenic condition or H_2S, CO_2 and H_2O under sulfidogenic condition. The environmental conditions decide the group of microorganisms involved. Ultimate degradation of pure RLDPE takes 1459 years (Kawai *et al.,* 2002).

4.0   Conclusions

Based on this study, there is an effective conclusion that CEL strongly affected the physical and mechanical properties of RLDPE-CEL blends. Three relaxation processes were detected using DMA. The intensity of the moduli decreased with CEL loading. No transition temperature, T_α and T_β shifts were observed. The WLF model was able to characterize creep property of the blends for long-term prediction purposes and showed that deformation depends on free volume. CEL decreases resistance to creep. The kinetics of water absorption of the RLDPE-CEL blends conforms to Fick's law of diffusion. The D values range from 6.04×10^{-10} cm/s^2 for pure RLDPE to 1.05×10^{-9} cm/s^2 for P80C20. This shows that the uptake of water increases with CEL loading. RLDPE-CEL blends are therefore promising permeable membranes.

Thermal properties of RLDPE-CEL blends showed two stage degradation due to RLDPE (decomposition of its low and high molecular weight fragments) and CEL (cross-linking and unzipping of the CEL chain).   The activation energy for thermal degradation was found to range from 27.4 kJ/mol for pure RLDPE to 15.8 kJ/mol for P80C20 during the first step of degradation and 101.4 kJ/mol to 44.0 kJ/mol for P80C20. The full biodegradation times of pure RLDPE and P80C20 were found to be 1459 years and 3.6 years respectively. Addition of CEL increased the biodegradability characteristics of RLDPE wherein microbes assimilate the CEL particles and leave the RLDPE matrix alone with the weaken bonding of polymer chains. The breakdown of the RLDPE chains down into small particles with a large surface area follows. RLDPE-CEL blends are therefore promising non environmental plastic pollutants.

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