

Research note

Creep and Stress Relaxation Behavior of Polypropylene, Metallocene-Prepared Polyethylene and their Blends

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Abstract

Creep and stress relaxation of a polypropylene (PP)-based copolymer, a metallocene-prepared linear low density polyethylene (m-LLDPE) and their m-LLDPE/PP blends have been investigated. Struik and Nutting relationships were used for fitting the data obtained from the creep experiments. A relatively good agreement was found between the Struik model and the experimental data obtained from PP and the 50/50 blend, however, the results showed that the validity of the model is less for the m-LLDPE itself. A good correlation was also found for the Nutting relationship and the experimental data. Maxwell and Kohlrausch-Williams-Watts (KWW) equations were used to fit the data obtained from stress relaxation experiments. The results indicated that while the Maxwell model was not good enough to predict the stress relaxation time, KWW model could fit the data much better. Analysis of the data with KWW equation revealed that the relaxation time increased with m-LLDPE content, but not significantly. However, the factor that describes the width of relaxation time distribution reduced with m-LLDPE, showing that m-LLDPE had the broadest relaxation time distribution compared to that of PP and the blends.

Keywords: Metallocene-prepared Polyethylene, Polypropylene, Blend, Stress Relaxation, Creep

1. Introduction

Polymers are viscoelastic materials and exhibit time-dependent relaxations when subjected to stress or strain. While creep is a measure of increase in strain with time under a constant stress, stress relaxation is the reduction of stress with time under a constant strain. Therefore, creep and stress relaxation tests measure the dimensional stability of a polymer over time. Such tests are of great importance for engineers, particularly if a

polymer must be in service under stress and strain for long periods [1].

There are three major variables that affect the rate of creep and stress relaxation. These are molecular mobility, stress/strain level and time. Because increasing temperature generally increases molecular mobility, it is also a major factor. At very high stress/strain or temperature, creep/stress relaxation development is too fast to be qualified. Therefore, load and temperature should be

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suitably chosen for their studies in order that measurements can be made over a significant period of time [2].

Polypropylene (PP) and polyethylene (PE) are among the commodity polymers and the volume leader in the industrial field. The poor impact strength at low temperature and the low environmental properties of PP can be improved by blending PP with PE [3-4]. A secondary aim of studying the properties of PE/PP blends is to determine whether trace impurities are likely to be important in the recycling of plastics [3].

In recent years, catalysts based on metallocenes, which generally consist of a transition metal from Group 4b sandwiched between two cyclopentadienyl ring structures have been used to open up new areas for the production of polyolefines with controlled molecular weights, molecular weight distribution, comonomer displacements and variable densities [5].

Although many published literature exists on different polymers [6-10], no report was found to study the effect of introducing metallocene-catalyzed polyethylene on creep and stress relaxation behavior of PP. In our other published papers [11-21] we have extensively studied the isothermal crystallization kinetics, dynamic mechanical

properties, crystalline morphology, crystalline structure, thermal and mechanical properties, etc of a metallocene-prepared linear low density polyethylene (m-LLDPE), a random copolymer of PP with a few mole percent of ethylene and their blends. The aim of this work is to study the creep and stress relaxation behaviors of the m-LLDPE, PP and their blends so as to find whether the m-LLDPE added to the PP has any effect on the relaxation and retardation times. Nutting and Struik relationships for creep and Maxwell and Kohlrausch-Williams-Watts (KWW) functions for stress relaxation were used to establish which of them can be a better model to fit the creep and stress relaxation data.

2. Experimental

The m-LLDPE was supplied by Exxon Chemical Company (France) as an Exact grade 3009. ^{13}C NMR spectroscopy showed that it contains an average of 3.3 mol % n-hexene-1 comonomer content [22]. PP was supplied by Himont (Italy) as the grade Moplen EP (TP-176 AM). It was found to be a 5 mol % random copolymer of ethylene by FTIR spectroscopy. The other characteristics of the polymers are listed in Table 1.

Table 1. Specifications of the materials

Name	Mw (kg/mol)	Mn (kg/mol)	PDI	MFI (g/10min)	Density (g/cm ³)
m-LLDPE	102.0	40.7	2.5	1.5	0.923
PP (random copolymer)	365.0	101.0	3.6	1.8	0.902

In order to study the effect of m-LLDPE on creep and stress relaxation behavior of polypropylene random copolymer, three blends of m-LLDPE/PP with compositions of 10/90, 30/70 and 50/50 by weight were prepared using an APV 2000 twin screw compounder at $230 \pm 5^\circ\text{C}$ and 200 rpm screw speed. Square plaques (2 mm thick) of the blends were obtained by pressing the extruded pellets between polytetrafluoroethylene (PTFE) sheets in a hydraulic press at 210°C for 5 min. On molding, the sheets were directly quenched into water at room temperature.

The degree of crystallinities of the two polymers were measured using a Perkin-Elmer differential scanning calorimeter (model DSC-2) interfaced to a PC. The temperature scale of the DSC was calibrated from the melting points of tin, indium and stearic acid and the thermal response from the fusion enthalpy of indium which was taken to be 28.45 J/g. Taking the enthalpies of fusion of PP and m-LLDPE as 209 and 293 J/g [3], respectively, the degrees of crystallinity of PP and m-LLDPE were found to be $36 \pm 2\%$ and $40 \pm 2\%$, respectively.

Dumbbell shaped specimens were cut out from the molded sheets and creep and stress relaxation behavior were measured on an Instron Testing Machine (model 5566) at $23 \pm 1^\circ\text{C}$. The specimen gauge length was 25 mm and 4 mm wide. Creep experiments were carried out at 3 MPa constant stress, and strain was recorded as a function of time up to 15 hr. Stress relaxation experiments were carried out at 3% strain, and stress was recorded against time up to 15 min. These values were chosen from the linear section of the stress-strain curve of the materials. In

addition, the same dumb-bell shaped materials were tested at different strain rates in order to calculate the activation volumes of the two polymers. The averages of three determinations were taken for creep and five others for stress relaxation and activation volume measurements.

3. Results and discussion

3-1. Activation volume

The yielding behavior of polymers depends on the temperature and the strain rate adopted in the test. This behavior has been modeled by Eyring. In the high stress region where yielding occurs, the Eyring theory gives a relationship between strain rate and applied stress such that at the yield stress;

$$\left(\frac{\sigma_y}{T}\right) = \left(\frac{2}{V^*}\right) \left[\left(\frac{\Delta H}{T}\right) + 2.303R \log\left(\frac{\dot{\gamma}_y}{\dot{\gamma}_o}\right)\right] \quad (1)$$

where $\dot{\gamma}_y$ is the strain rate at yield, $\dot{\gamma}_o$ is a constant, R is the gas constant, V^* is the activation volume, ΔH is the height of energy barrier, σ_y is the yield stress and T is the temperature [23-24].

A plot of σ_y/T versus $\log \dot{\gamma}_y$ for m-LLDPE and PP is shown in Fig. 1. The activation volumes were calculated from the slope of the linear plots to be $34 \pm 5 \text{ nm}^3$ for m-LLDPE and $7 \pm 1 \text{ nm}^3$ for PP. The crystallographic studies on the two materials have revealed that the unit cell volume of m-LLDPE and PP each contain 4 methylene and 12 propylene units and the volume of the unit cells are 0.094 nm^3 and 0.94 nm^3 , respectively [25]. Hence, V^* for m-LLDPE is

a volume equivalent to approximately 1450 ± 210 CH₂ units and 90 ± 15 propylene units for PP.

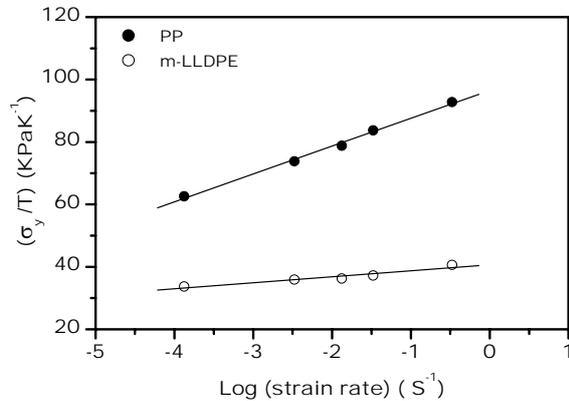


Figure 1. Eyring plot of σ_y/T against log (strain rate) for m-LLDPE and PP

Haward and Thackray [26] have stated that the activation volume is the volume of the polymer segment involved in polymer flow. However, Bowden [27-28] has suggested that the activation volume, although having dimension of volume, has no physical significance. He has proposed that the quantity of activation volume multiplied by stress is the work done when a mobile segment jumps from its previous position to the present position.

Zhou [28] has studied LLDPE/HDPE blends and found that the activation volume decreased with increasing HDPE content. He suggested that since increasing HDPE content increases the degree of crystallinity of the blends and movement of the segments is limited, and the segmental volume involved in deformation is reduced, the measured activation volume supports Haward's definition of activation volume.

3-2. Creep

The empirical equation discussed by Struik which takes the form [29-32];

$$D(t) = D_0 \exp(t/\tau_d)^\gamma \quad (2)$$

has been suggested for describing low-strain creep behavior of polymers. Where $D(t)$ is the tensile creep compliance at time t , D_0 is the instantaneous compliance at $t = 0$, τ_d is the mean retardation time for the creep mechanism and γ is the distribution factor. Value for the exponent γ can range from 0 to 1, although in practice values of 0.33 are commonly suggested for glassy amorphous polymers. This equation is consistent with the stress relaxation function proposed by Kohlrausch [33-34].

Fig. 2 shows the creep compliance of m-LLDPE, PP and the 50/50 blend as a function of log time. The different D_0 values indicate that these materials have different initial creep compliances. Using Eqn (2), quantitative analysis was made by plotting $\ln(\ln(D(t)/D_0))$ versus $\ln t$ (see Fig. 3). A linear relationship was observed in the creep compliance with $\ln t$ after the initial part of the experiment. This usually took a few minutes. Read [35-36] has attributed this to the presence of different relaxation processes associated with the α and β -relaxations. The α -relaxation is the main relaxation and occurs over a longer time than the β -relaxation. However, separation of these two processes is usually very difficult because they overlap.

Average values for the parameters of Struik equation were found from the slope and intercept at $\ln t = 0$, which gave a distribution

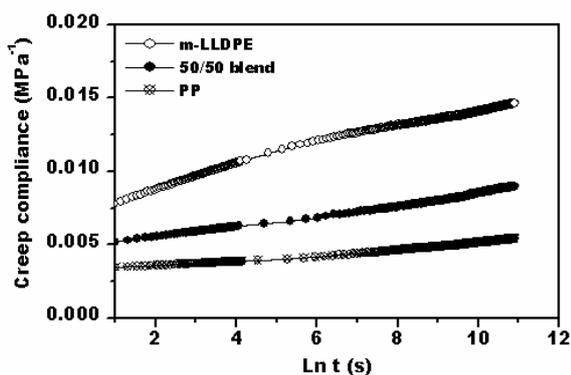


Figure 2. Creep compliance against log t for m-LLDPE, PP and their 50/50 blend.

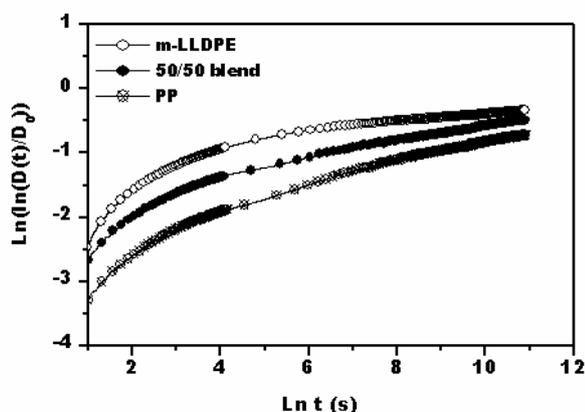


Figure 3. The relationship between $\ln(\ln(D(t)/D_0))$ and $\ln t$.

factor, γ , and $-\gamma \ln t$, respectively. Relatively good agreement between experimental data and straight lines were obtained for PP and 50/50 blend, however, the amount of linearity was decreased for m-LLDPE itself. Moreover, it was found that the γ values were not about 0.33 as proposed by Struik [29,31,37] and other authors [38], but varied for each material. These results were in agreement with the results reported by Lu [2] for amorphous, unoriented and semicrystalline, oriented PET. The results of creep analysis based on Struik equation are summarised in Table 2. As it can be seen, the retardation time is the highest for m-LLDPE.

However, the γ value was decreased with increasing of m-LLDPE.

Table 2. Parameters for m-LLDPE, PP and 50/50 blend using Struik's equation

Material	$\tau_d \pm 20\%$ (hr)	γ	R
m-LLDPE	1900	0.07 ± 0.02	0.968
50/50 blend	450	0.11 ± 0.01	0.996
PP	1200	0.17 ± 0.02	0.994

There is a stress level at which strain at time t , $\varepsilon(t)$, is no longer directly proportional to the applied stress. One way of describing this nonlinear behavior in uniaxial tensile creep, especially for high modulus/low creep polymers is a power-law relation such as the Nutting equation [1];

$$\varepsilon(t) = K \sigma^\alpha t^n \tag{3}$$

where K , α and n are constants at a given temperature and σ is stress. The constant α is equal to or greater than 1.0. Although Eqn(3) represents most experimental data reasonably accurately, it has little theoretical justification. In the linear region, $\alpha = 1$ and the Nutting equation implies that $\log D(t)$ is linear against $\log t$.

Fig. 4 shows the variation of $\log(\varepsilon(t)/\sigma)$ against $\log t$ for the 50/50 blend. The results obtained from fitting the Nutting relationship are also listed in Table 3. The constant n , which can vary from 0 for a perfectly elastic material to 1.0 for a Newtonian fluid, were about 0.05 ± 0.01 for

all the materials studied. This is consistent with the fact that the materials behave elastically.

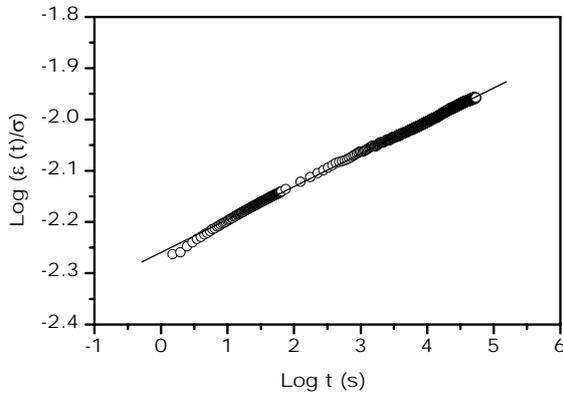


Figure 4. Validity of Nutting equation for 50/50 blend.

Table 3. The values of the Nutting parameters

Material	K (GPa ⁻¹ s ⁿ)	n	R
m-LLDPE	8.80±0.35	0.054±0.003	0.999
50/50 blend	5.20±0.30	0.060±0.005	0.992
PP	3.20±0.35	0.047±0.002	0.986

3-3. Stress relaxation

Fig. 5 shows the variation of stress with time for m-LLDPE, PP and their three blends. The Maxwell model which takes the form [39]:

$$\sigma(t) = \sigma_0 e^{-(t/\tau_r)} \quad (4)$$

was considered to simulate the stress relaxation experiment. Where $\sigma(t)$ is the stress at time t , σ_0 is the stress at $t = 0$ and τ_r is the relaxation time. Rearranging the equation and taking logarithms yield;

$$\ln\left(\frac{\sigma_0}{\sigma(t)}\right) = \left(\frac{1}{\tau_r}\right)t \quad (5)$$

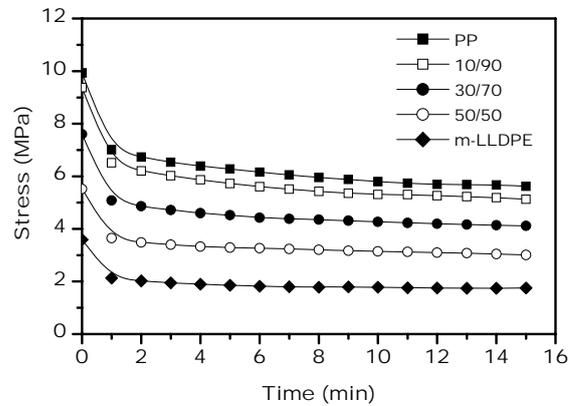


Figure 5. Stress relaxation curves for m-LLDPE, PP and the blends.

A plot of $\ln\left(\frac{\sigma_0}{\sigma(t)}\right)$ versus time is a straight

line of slope $\frac{1}{\tau_r}$. This is shown in Fig. 6. As

can be seen from the plot, the Maxwell model does not fit the experimental data, and a second model, the Kohlrausch-Williams-Watts (KWW) relaxation function was used. This model had been used successfully to explain different relaxation phenomena in the glassy state [22,40].

$$\phi_t = \frac{E(t)}{E_0} = \frac{\sigma(t)}{\sigma_0} = e^{-\left(\frac{t}{\tau_r}\right)^\beta} \quad (6)$$

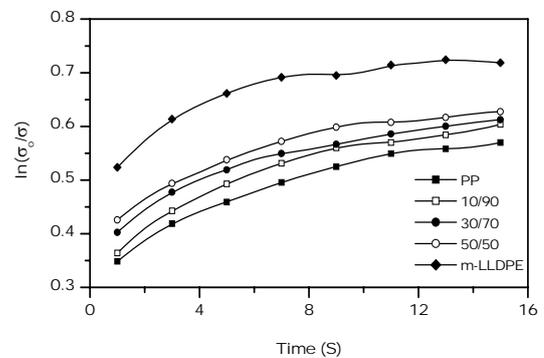


Figure 6. Maxwell equation for m-LLDPE, PP and the blends.

where $\phi(t)$ is the relaxation function, $E(t)$ and E_0 are the modulus at time t and at $t=0$, respectively. Chow and Prest [41] have shown that the relaxation phenomena explained by KWW equation are controlled by continuous relaxation spectra. The β value is inversely related to the breadth of the relaxation spectrum and $0 < \beta < 1$. The higher the value of β , the narrower the spectrum and, in the extreme case of $\beta=1$ (Maxwell model), there is only one relaxation process. Rearrangement of KWW equation and taking logarithm yields:

$$\ln\left(\ln\left(\frac{\sigma_0}{\sigma(t)}\right)\right) = \beta(\ln t - \ln \tau_r) \quad (7)$$

Variation of $\ln\left(\ln\left(\frac{\sigma_0}{\sigma(t)}\right)\right)$ versus $\ln t$ is shown in Fig. 7. From the plot it can be concluded that this model can fit the data much better than the Maxwell model.

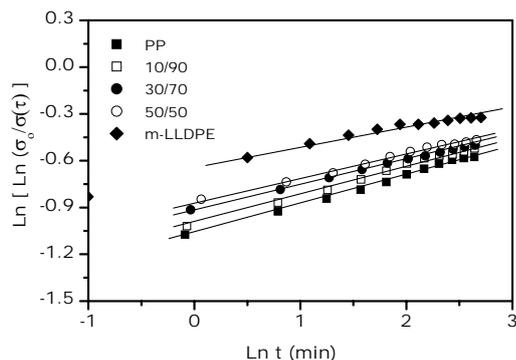


Figure 7. KWW equation for stress relaxation of m-LLDPE, PP and the blends.

Fig. 8 shows the variation of stress relaxation time with m-LLDPE content in the blends. As can be seen, the average relaxation time increases with m-LLDPE content, however,

this increase is not significant and remains within the experimental error. The variation of β against the m-LLDPE content is shown in Fig. 9. Decreasing the β value represents that m-LLDPE has the broadest relaxation time distribution compared with that of PP and the blends.

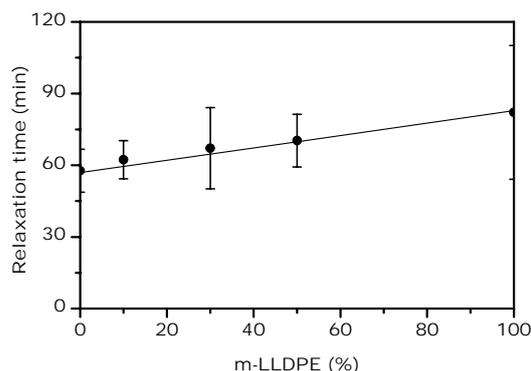


Figure 8. Variation of relaxation time with m-LLDPE composition in the blends.

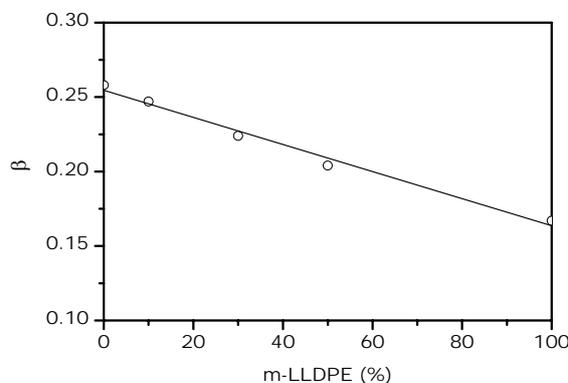


Figure 9. Effect of m-LLDPE content on β value in stress relaxation.

4. Conclusions

Creep and stress relaxation behavior of m-LLDPE, PP random copolymer and their blends were studied. It was found that Struik equation fit the data relatively well for PP and 50/50 blend, however, the degree of precision was reduced for evaluating the m-

LLDPE behavior. Assuming $\alpha=1$, Nutting relationship fitted the creep data well and the constant n was found to be about 0.05 ± 0.01 for all the materials studied. This was consistent with the elastic behavior of the materials. The results obtained from fitting the Maxwell and KWW relationships into the data obtained from the stress relaxation experiments revealed that the Maxwell model was not good enough to predict the stress relaxation time. However, the KWW model could fit the data much better. The relaxation times calculated from KWW equation increased with m-LLDPE content but more or less remained within the experimental errors for all the materials studied. However, the width of relaxation time distribution increased with m-LLDPE content, showing that the m-LLDPE had the broadest relaxation time distribution compared to that of PP and the blends.

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