TIME DEPENDENT MECHANICAL PROPERTIES OF POLYMERS, THEORETICAL AND EXPERIMENTAL ANALYSIS OF THEIR RELATIONSHIPS

PHD DISSERTATION
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THESES

1. I have elaborated relations between real mechanical stimuli generated on a tensile test machine and the resulting material responses for linear viscoelastic materials.

   1.1 I have shown that in the case of constant deformation rate the following recursive and summation type relations exist between the measured $F_1(t)$ stress relaxation function at t_0 ($t_0 \geq 0$) upload time and the $F_2(t)$ tensile curve measured at constant crosshead speed:

   $$F_2(t) = F_1(t) + F_2(t - t_0), \quad t \geq t_0 > 0 \tag{T1.1}$$

   $$F_2(nt_o) = \sum_{i=1}^{n} F_1(it_0), \quad n \geq 1, \; t_0 > 0 \tag{T1.2}$$

   $F_1(t)$ can be calculated from $F_2(t)$ by rearranging (T1.1). The (T1.2) sum converges to the integral of $F_1(t)$ as $t_0 \to 0$.

   1.2 I have shown that in the case of constant force rate the following recursive and summation type relations exist between the measured $\varepsilon_3(t)$ creep function at t_0 ($t_0 \geq 0$) upload time and the $\varepsilon_4(t)$ tensile curve measured at constant force rate, $\dot{F}_0$:

   $$\varepsilon_4(t) = \varepsilon_3(t) + \varepsilon_4(t - t_0), \quad t \geq t_0 > 0 \tag{T1.3}$$

   $$\varepsilon_4(nt_o) = \sum_{i=1}^{n} \varepsilon_3(it_0), \quad n \geq 1, \; t_0 > 0 \tag{T1.4}$$

   $\varepsilon_3(t)$ can be calculated from $\varepsilon_4(t)$ by rearranging (T1.3). The (T1.4) sum converges to the integral of $\varepsilon_3(t)$ as $t_0 \to 0$.

2. For thermoplastic polyolefins having a crystallinity degree between 40-50% (T_g<0°C) I have shown that there is a linear relationship between the values of the tensile test curve as load levels, and the stress relaxation and creep curves measured at room temperature and at times not exceeding the double of the times corresponding to the ultimate tensile strength.

   2.1 In the case of Tipplen H543 F isotactic polypropylene (iPP) I have shown that the values at t=300 s of the stress relaxation curves measured at various load levels have shown closely similar shape to the tensile test curves measured at constant crosshead speed, demonstrated by the high goodness of fit (R^2=0.9975) value of the homogeneous linear relationship between them.

   2.2 In the case of Tipplen H543 F iPP I have shown that the values at t=73.6 s (the time at break) of the creep curves measured at various load levels have shown closely similar shape to the tensile test curves measured at constant force rate, demonstrated by the high goodness of fit (R^2=0.9991) value of the homogeneous linear relationship between them.

3. For thermoplastic polyolefins having a crystallinity degree between 40-50% (T_g<0°C) I have shown using experiments at room temperature below the load level corresponding to crazing, that the relationship between the $F_1(t)$ stress relaxation curve and the $F_2(t)$ constant crosshead speed tensile test curve can be approximated by consecutively applying a nonlinear viscoelastic (NLVE) and a linear viscoelsatic (LVE) mapping:

$$F_1(t) \overset{NLVE}{\rightarrow} F_{11}(t) \overset{LVE}{\rightarrow} F_{112}(t) \approx F_2(t) \quad \text{(T3.1)}$$

where the $F_{11}(t) \overset{LVE}{\rightarrow} F_{112}(t)$ LVE mapping is given by (T1.1):

$$F_{112}(t) = F_{11}(t) + F_{112}(t - t_0)\,,\ t \geq t_0 > 0 \quad \text{(T3.2)}$$

For the $F_1(t) \overset{NLVE}{\rightarrow} F_{11}(t)$ mapping I have elaborated two solutions.

3.1 I have shown that that for the investigated Tipplen H543 F iPP the following nonlinear function can be applied as the $F_1(t) \rightarrow F_{11}(t)$ outer mapping:

$$F_{11}(t) = F_{11}(t_o) - a(\varepsilon_0)\left[F_1(t_0) - F_1(t)\right]^{b(\varepsilon_0)} e^{c(\varepsilon_0)[F_1(t_0) - F_1(t)]} \quad \text{(T3.3)}$$

where a, b, c are constants depending on the ε_0 load level. The high goodness of fit values ($R^2 \geq$ 0.9986 in the ε_0=0.08% and ε_0=1.0% initial deformation level range) of the approximated and measured curves demonstrate close correlation.

3.2 I have shown that that for the investigated Tipplen H543 F iPP the following nonlinear functions, defined by the monotonically increasing $h(t)$ function, can be used for the $F_1(t) \rightarrow F_{11}(t)$ inner mapping having the following variable transformation form:

$$F_{11}(t) = F_0 - b\left[F_0 - F_1\left(h(t)\right)\right] \quad \text{(T3.4)}$$

where F_0=$F(t_0)$ and b>0 are constants and

$$h1(t_1) = a\left(\frac{t_1 - t_0}{t_B - t_1}\right)^C + t_0 = a\left(\frac{\dfrac{t_1 - t_0}{t_B - t_0}}{1 - \dfrac{t_1 - t_0}{t_B - t_0}}\right)^C + t_0 \qquad \dot{h}(t_0) > 0 \text{ if } c = 1 \quad \text{(T3.5)}$$

$$h3(t_1) = a\,\frac{t_1 - t_0}{t_B - t_1}\left[1 + \left(\frac{t_1 - t_0}{t_D - t_0}\right)^C\right] + t_0,\ c > 0 \quad \text{(T3.6)}$$

$$h5(t_1) = a\,\mathrm{tg}\,\frac{\pi(t_1 - t_0)}{2(t_B - t_0)} + t_0\,, \quad t_0 < t_1 < t_B \quad \text{(T3.7)}$$

$$h6(t_1) = a(t_1 - t_0)^k e^{\frac{c}{1-\frac{t_1-t_0}{t_B-t_0}}} + t_0\,, \quad \dot{h}(t_0) > 0 \text{ if } k = 1 \tag{T3.8}$$

The high goodness of fit values ($h1$: R^2=0.9984, $h3$: R^2=0.9920, $h5$: R^2=0.9932 and $h6$: R^2=0.9994, at ε_0=0.08% initial deformation level) of the approximated and measured curves demonstrate close correlation.

4. For thermoplastic polyolefins having a crystallinity degree between 40-50% (T_g<0°C) I have shown using experiments at room temperature below the load level corresponding to crazing, that the relationship between the $\varepsilon_3(t)$ creep curves measured at various load levels and the $\varepsilon_4(t)$ constant force rate tensile test curve can be approximated by consecutively applying a nonlinear viscoelastic and a linear viscoelsatic mapping:

$$\varepsilon_3(t) \overset{NLVE}{\rightarrow} \varepsilon_{33}(t) \overset{LVE}{\rightarrow} \varepsilon_{334}(t) \approx \varepsilon_4(t) \tag{T4.1}$$

The $\varepsilon_{33}(t) \overset{LVE}{\rightarrow} \varepsilon_{334}(t)$ LVE mapping is given by (T1.3):

$$\varepsilon_{334}(t) = \varepsilon_{33}(t) + \varepsilon_{334}(t - t_0)\,,\ t \geq t_0 > 0 \tag{T4.2}$$

4.1 I have shown that for the investigated Tipplen H543 F iPP the following function can be applied as the $\varepsilon_3(t) \rightarrow \varepsilon_4(t)$ outer mapping:

$$\varepsilon_4(t) = \int_{t0}^{t} h_4(x)dx + \dot{\varepsilon}(t - t_0) \tag{T4.3}$$

The $h_4(t)$ function can be approximated by the following nonlinear equation:

$$\hat{h}_4(t) = \frac{a\left(\frac{G_3(t)}{G_{30}}\right)^n}{\left(1 - \frac{G_3(t)}{G_{30}}\right)^m} \tag{T4.4}$$

where a, n m and G_{30} are variable parameters and $G_3(t)$ is calculated from the measured creep curve (ε_3) according to the following expression:

$$G_3(t) = \int_{t0}^{t} \varepsilon_3(x)dx \tag{T4.5}$$

The high goodness of fit values ($R^2 \geq 0.9978$ in the F_0=100 N and F_0=400 N initial load level range) of the approximated and measured curves demonstrate close correlation.

4.2 I have shown that for the investigated Tipplen H543 F iPP the following nonlinear functions, defined by the monotonically increasing $h(t)$ function, can be used for the $\varepsilon_3(t) \rightarrow \varepsilon_{33}(t)$ inner mapping having the following variable transformation form:

$$\varepsilon_{33}(t) = \varepsilon_0 + b[\varepsilon_3(h(t)) - \varepsilon_0] \tag{T4.6}$$

where $\varepsilon_0=\varepsilon(t_0)$, b>0 are constants and the $h(t)$ functions are identical with equations (T3.5-T3.8). The high goodness of fit values (($h1$: R^2=0.9989, $h3$: R^2=0.8257, $h5$: R^2=0.9981 and $h6$: R^2=0.9773 at F_0=100 N initial load level) of the approximated and measured curves demonstrate close correlation.

5. For thermoplastic polyolefins having a crystallinity degree between 40-50% (T_g<0°C) I have shown using experiments at room temperature below the load level corresponding to crazing, that the relationship between the $\varepsilon_4(t)$ constant force rate tensile test curve and the $\varepsilon_3(t)$ creep curves measured at various load levels can be approximated by consecutively applying a linear viscoelastic and a nonlinear viscoelsatic mapping:

$$\varepsilon_4(t) \underset{S_4}{\overset{LVE}{\longrightarrow}} \varepsilon_{43}(t) \underset{S_{43}}{\overset{NLVE}{\longrightarrow}} \bar{\varepsilon}_{433}(t) \xrightarrow{Lin.transzf.} \varepsilon_{433}(t) \approx \varepsilon_3(t) \tag{T5.1}$$

The $\varepsilon_4(t) \underset{S_4}{\overset{LVE}{\longrightarrow}} \varepsilon_{43}(t)$ LVE mapping is given as:

$$\varepsilon_{43}(t) = S_4\left[\varepsilon_4(t)\right] = \varepsilon_4(t) - \varepsilon_4(t-t_0), t \geq t_0 \tag{T5.2}$$

I have shown that for the investigated Tipplen H543 F iPP the following relationship can be applied as the $\varepsilon_{43}(t) \underset{S_{43}}{\overset{NLVE}{\longrightarrow}} \bar{\varepsilon}_{433}(t)$ inner variable transformation mapping:

$$\bar{\varepsilon}_{433}(t) = \varepsilon_{43}(h^{-1}(t)),\ t_0 \leq t \leq t_{s3} \tag{T5.3}$$

from which $$\varepsilon_{433}(t) = \varepsilon_0 + b_{433}\left(\varepsilon_{43}(h^{-1}(t)) - \varepsilon_0\right) \tag{T5.4}$$

and $$h^{-1}(t) == h6^{-1}(t) = t_0 + (t_B - t_0)\left(\frac{\ln(1+\frac{t-t_0}{t_a})}{c+\ln(1+\frac{t-t_0}{t_a})}\right) \tag{T5.5}$$

The high goodness of fit values (R^2≥0.9962 in the F_0=100 N – F_0=400 N initial load level range) of the approximated and measured creep curves demonstrate close correlation.