Macromol. Symp. **2007**, 247, 28–34 DOI: 10.1002/masy.200750104

The Thermoviscoelastic Constitutive Equation of PP and PA Blends and Its Rate Temperature Equivalency at High Strain Rates

Shi Shaoqiu, Yu Bing, Wang Lili*

Summary: By using Instron 1342 testing system and an improved SHPB technique, PP/PA blends are tested at a wide range of strain rates from 10^{-4} up to 10^{3} s^{-1} and at a temperature range of 25–80 °C. Their mechanical responses are shown to be sensitive both to the strain rate and temperature. Based on the experimental data of 113 blends at a wide range of strain rates from 10^{-4} up to 10^{3} s^{-1} and at a temperature range of 25–80 °C, it is shown that the mechanical behavior of this PP/PA blends can be described with ZWT thermoviscoelastic constitutive equation. The corresponding thermoviscoelastic parameters for 113 blends are obtained. The predicted theoretical results coincide quite well with the experimental data.The experimental results also reveal that the rate/time-temperature equivalence relation is shown for PP/PA blends. Raising the temperature is equivalent to the increasing of time (the decreasing of strain rate). Conversely, decreasing the temperature is equivalent to the decreasing of time (the increasing of strain rate). Through introducing a dimensionless parameter $Z = \frac{\dot{\varepsilon}\eta_0}{E}\exp\left(\frac{A}{kT}\right)$, two characteristic parameters: strain rate $\dot{\varepsilon}$ and temperature T are put together to this unified parameter Z. From experimental results, A/k is fitted, A/k = 8.595 °C, and a unified curve characterizing the rate/time –temperature equivalence relation is obtained.

Keywords: polymer blends; rate/time-temperature equivalence; thermoviscoelastic response

Introduction

The equivalent relation between rate/time-dependency and temperature dependency for polymer materials are important research problems, to which many research workers both in the fields of mechanics and materials science have focused their attention. A number of studies of thermo-viscoelastic constitutive relations and the related temperature rate/time equivalence have been made.

For linear viscoelastic materials, it has been found[1] that by introducing the so-called "shift factor" *a(T)* and the related "reduced time"

$$\tau = \frac{t}{a_T} \tag{1}$$

a group of relaxation moduli $G\ (T,\ t)$ or creep compliances $J\ (T,\ t)$ at different temperature T may be reduced to a unified function $G_{TR}(T,\ t)$ or $J_{TR}(T,\ t)$ at a reference temperature TR with a single argument τ. A material with such a character is called thermo-rheologically simple material.[2] Morland and Lee[3] proposed an integral-form constitutive equation for thermo-rheologically simple material, although limited to small viscoelastic deformation. Lians,[4] Ting,[5] McGuirr and Lianis,[6] and Morgan and Ward[7] have conducted some further research works theoretically or

---

Faculty of Engineering, Ningbo University, 315211, P.R.China
E-mail: shishaoqiu@nbu.edu.cn

experimentally in the range of non-linear viscoelastic deformation, but the main condition concerned was under low strain rates, such as in quasi-static testes or creep testes. However the research works related to non-linear viscoelastic solids, especially to polymer blends and under high strain rates were less published due to the complexity of problem. In this paper PP/PA blends are tested at a wide range of strain rates from 10^{-4} up to 10^{3} s^{-1} and at a temperature range of 25–80 °C. A ZWT thermo-viscoelastic constitutive equation is used to describe its mechanical behavior. The temperature-rate/time equivalence for non-linear viscoelastic polymer blends at high strain rates is studied on the basis of the experimental results at high strain rates and the ZWT model.

Experimental Method and Results

In this study a new type of reinforced PP/PA blends with a compatibilizer: grafted thermoplastic elastomer, TPE-g (ethylene-octylene elastomer grafted with maleic anhydride/semi-crystalline poly-olefins, grafted percentage 1%) (code number 113) is used. The weight ratio is: PP/PA/TPE-g = 49/30/21. All materials used were dried in ovens for 8 h, at 80°C. Then cylindrical specimens in diameter of 12 mm and length of 6 mm were prepared from injection mold at 210 °C. The quasi-static compressive tests under strain rates of 10^{-4}, 10^{-2} s^{-1} were performed in Instron1342 Servo-hyduaulic testing system. The controlled testing temperatures of specimens are: 25 °C 40 °C 60 °C and 80 °C respectively. The dynamical impact testes under the high strain rate up to 10^{3} s^{-1} and at a temperature range of 25–80 °C were performed in an improved SHPB apparatus with diameter of 14.5 mm at Ningbo University. For considering the low-impedance of polymer blends, the aluminum incident and transmit bars are used and the pulse shaper is attached at the end of the incident bar to guarantee the stress equilibrium and uniform deformation of specimens.

The experimental quasi-static true stress-true strain curves of 113 at different temperatures are shown in Fig. 1. The experimental true stress-true strain curves of 113 at 25 °C under different high strain rates are shown in Fig. 2. The experimental true stress-true strain curves of 113 under high strain rates (850 s^{-1}, 2000 s^{-1}) at different temperatures are shown in Fig. 3, Fig. 4. All these experimental results indicate that the mechanical response of

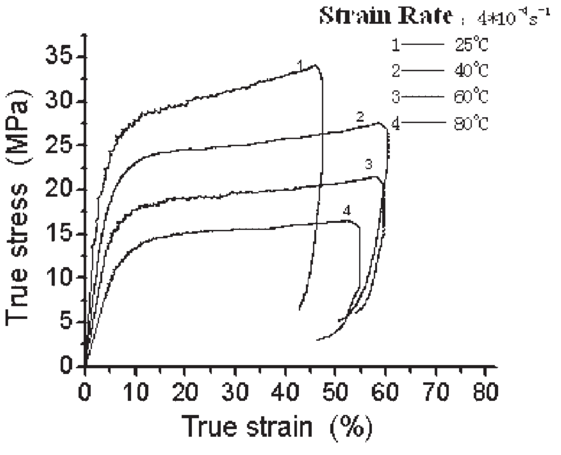

Figure 1.
The comparison of quasi-static true stress-true strain curves of 113 at different temperatures.

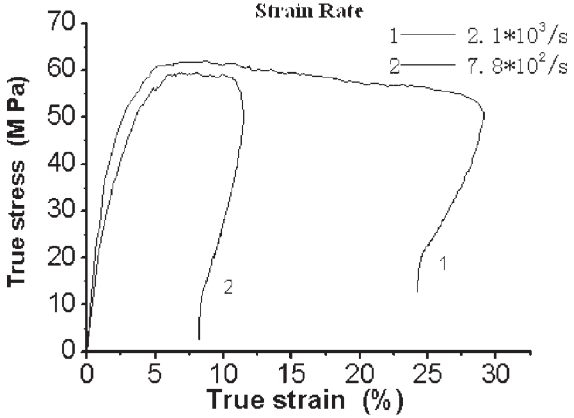

Figure 2.
The comparison of true stress-true strain curves of 113 at 25 °C under different high strain rates.

113 is sensitive both to the strain rate and temperature.

Non-linear thermoviscoelastic constitutive equation of PP/PA blends

According to the experimental results for many kinds of polymers at strain-rates from 10^{-4} to 10^{3} s^{-1} and at strain up to 7–8%, Zhu, Wang and their co-works found that the dynamic behavior for all the tested polymers can be well described by the following Zhu-Wang-Tang (ZWT) non-linear viscoelastic constitutive equation,[5]

$$\sigma = \sigma_E(\varepsilon) + E_1 \int_0^t \dot{\varepsilon}(\tau) \exp\left(-\frac{t-\tau}{\theta_1}\right) d\tau + E_2 \int_0^t \dot{\varepsilon}(\tau) \exp\left(-\frac{t-\tau}{\theta_2}\right) d\tau \tag{2a}$$

$$\sigma_E = E_0\varepsilon + \alpha\varepsilon^2 + \beta\varepsilon^3 \tag{2b}$$

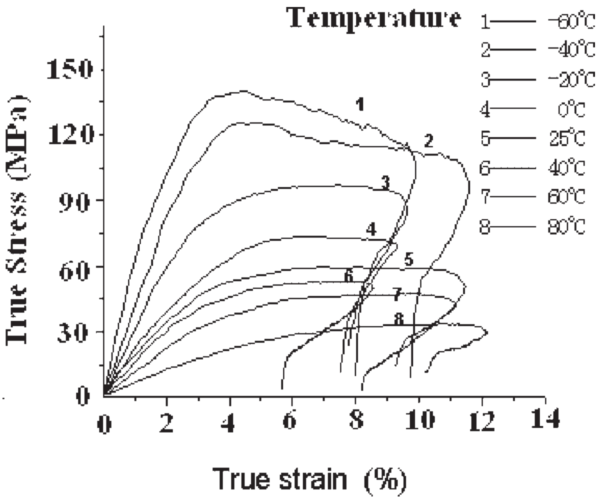

Figure 3.
The comparison of true stress-true strain curves of 113 under high strain rate (850 s^{-1}) at different temperatures.

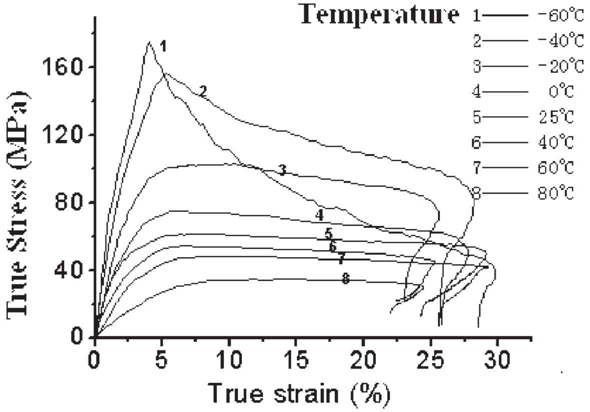

Figure 4.
The comparison of true stress-true strain curves of 113 under high strain rate (2000 s^{-1}) at different temperatures.

where the first term $\sigma_E(\varepsilon)$ in Eq. (2a) describes the nonlinear elastic equilibrium response, E_0, α, β in Eq. (2b) are the corresponding elastic constants; the next integral term in Eq. (2a) describes the viscoelastic response for low strain rates, E_1,θ_1 are the elastic constant and relaxation time, respectively, of the corresponding Maxwell element I; and the last integral term describes the viscoelastic response for high strain rates, E_2,θ_2 are the elastic constant and relaxation time, respectively, of the corresponding Maxwell element II. The corresponding rheological model is shown in Fig. 5.

From the experimental results of Fig. 3 and Fig. 4, it is clear that all the viscoelastic stress-strain curves at different temperatures display a similar character and the strain rate sensitivity $\lambda(=\partial\sigma/\partial\log\dot{\varepsilon})$ increases with decreasing temperature. Thus it is not unreasonable to assume that E_0, α, β, E_1,θ_1, E_2 and θ_2 in ZWT equation are all the function of temperature T. Then Eq. (2) can be generalized to the following

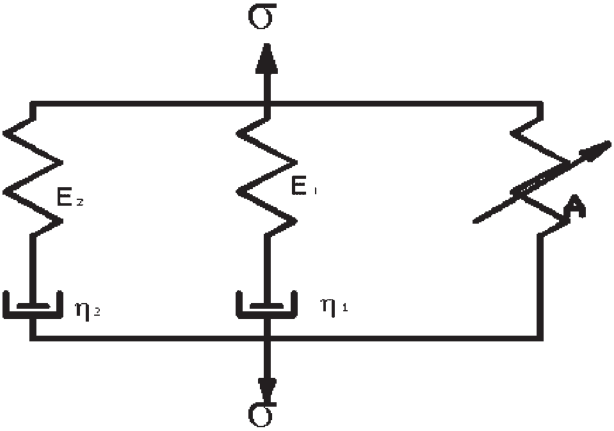

Figure 5.
The rheological model corresponding to ZWT equation.

Table 1.
The material parameters in ZWT equation at different temperatures

T (°C)	E_0 (GPa)	α (GPa)	β (GPa)	E_1 (GPa)	θ_1 (s)	E_2 (GPa)	θ_2 (μs)	$\eta=\theta\times$ E (pa · s)
80	0.45	−10.51	86.94	0.12	2.41	0.81	5.67	4567
60	0.61	−8.40	52.60	0.16	14.06	0.82	6.03	4913
40	0.62	−6.39	28.03	0.24	23.91	0.83	6.34	5276
25	0.67	−3.32	−18.14	0.30	34.04	0.86	6.82	5872

nonlinear thermo-viscoelastic constitutive equation:

$$\sigma = \sigma_E(T,\varepsilon) + E_1(T)\int_0^t \dot{\varepsilon}\exp\left(-\frac{t-\tau}{\theta_1(T)}\right)d\tau + E_2(T)\int_0^t \dot{\varepsilon}\exp\left(-\frac{t-\tau}{\theta_2(T)}\right)d\tau \qquad (3a)$$

$$\sigma_E(T,\varepsilon) = E_0(T)\varepsilon + \alpha(T)\varepsilon^2 + \beta(T)\varepsilon^3 \qquad (3b)$$

From the experimental data the material parameters at different temperatures in equation (2) can be determined by the best least-squares fit. These material parameters of 113 blends are listed in Table 1.

The typical ZWT model prediction at 40 °C is shown in Fig. 6. It coincides quite well with the experimental data.

Under the impact loading with time scale from 1 to 10^2 μs, the low frequency Maxwell element with the relaxation time θ_1 of 1 to 10^2 s has no enough time for relaxation. Then the low frequency Maxwell element is reduced to a single spring element with the elastic constant E_1, and correspondingly, the nonlinear thermo-viscoelastic ZWT Eq. (3) is reduced to

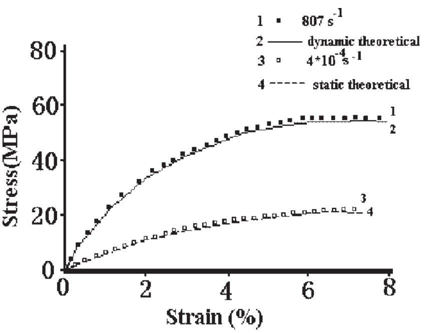

Figure 6.
The comparison between the ZWT equation prediction and the experimental result.

$$\sigma(T,\varepsilon) = \sigma_0(T,\varepsilon) + E_2(T)\int_0^t \dot{\varepsilon}(\tau)\exp\left(-\frac{t-\tau}{\theta_2(T)}\right)d\tau \qquad (4a)$$

$$\begin{aligned}\sigma_{eff}(T,\varepsilon) &= [E_0(T)+E_1(T)]\varepsilon + \alpha(T)\varepsilon^2 + \beta(T)\varepsilon^3 \\ &= E_a(T)\varepsilon + \alpha(T)\varepsilon^2 + \beta(T)\varepsilon^3 \qquad (4b)\end{aligned}$$

Rheologically, Eq. (4) corresponds to a simple three-elements thermo-rheological model, consisting of a nonlinear spring and a Maxwell element sensitive to the temperature.

For convenience of further discussion, Eq. (4a) can be re-writthen into the following form.

$$\sigma - \sigma_{eff}(T,\varepsilon) = E_2(T)\int_0^t \dot{\varepsilon}\exp\left(-\frac{t-\tau}{\theta_2(T)}\right)d\tau \qquad (4c)$$

where $[\sigma - \sigma_{eff}]$ may be called "the over stress", in similar to the case in the viscoplastic theory.

Temperature-Rate/Time Equivalence for PP/PA Blends at High Strain Rate

By introducing the following non-dimensional relaxation time

$$a(T) = \frac{\theta(T)}{\theta_R(T)} = \frac{\eta(T)E_R}{\eta_R E(T)} \qquad (5)$$

where θ_R, E_R and η_R are the relaxation time, elastic constant and the viscosity coefficient at reference temperature, respectively and in similar to Eq. (1), defining "the reduced time" τ as

$$\tau = \frac{t}{a_T} \tag{6}$$

Eq. (4c) can be rewritten as

$$\begin{aligned}\overline{\sigma}_\tau &= \frac{\sigma - \sigma_{eff}(T, \varepsilon(\tau))}{E_2(T)} \\ &= \int_0^\tau \left[-\frac{\tau - \tau'}{\theta_R}\right] \frac{d\varepsilon}{d\tau'} d\tau' \end{aligned} \tag{7}$$

It means that if the thermo-viscoelastic response of polymers is described by the non-dimensional "over stress" $\overline{\sigma}_\tau$, then the only independent variable is "the reduced time" τ, instead of two independent variables, T and t, in Eq. (4). In other words, the $\overline{\sigma}_\tau - \tau$ curves at different temperatures are coincident with each other, if their strain-history with regard to the reduced time $\varepsilon(\tau)$ are same. Thus Eq. (7) characterizes "the rate/time-temperature equivalence" for polymers at high strain rates and large deformation.

Moreover, if we introduce the following non-dimensional parameter

$$Z = \dot{\varepsilon}\theta_2(T) \tag{8}$$

"the reduced strain rate" $d\varepsilon/d\tau$ is then related to Z by the following equation

$$\frac{d\varepsilon}{d\tau} = a\frac{d\varepsilon}{dt} = \frac{\dot{\varepsilon}\theta(T)}{\theta_R} = \frac{Z}{\theta_R} \tag{9}$$

So, the non-dimensional parameter Z is physically just corresponding to "the reduced strain rate", $d\varepsilon/d\tau$., since θ_R is a given constant.

For tests at $T=$ const. and $\dot{\varepsilon}=$ const. as in our experiments mentioned above, Eq. (7) becomes

$$\frac{\overline{\sigma}_\tau}{Z} = 1 - \exp\left(-\frac{\varepsilon}{Z}\right) \tag{10}$$

It means that the description of rate-dependence and temperature-dependence of overstress -strain relation can be unified in terms of single parameter Z. In other words, Z characterizes the quantitative equivalence between $\dot{\varepsilon}$- equivalence and T- equivalence. For example, when T increases $\theta(T) = \eta(T)/E(T)$ decreases in general, and consequently Z decreases if $\dot{\varepsilon}=$ const.; this is equivalent to decrease the strain rate if $T=$ const.. Graphically, it corresponds to a shift of overstress-strain rate curve along the positive strain-rate axis.

According to Eq. (10), all the experimental data in regard to the $\dot{\varepsilon} - T$ equivalent parameter Z shall lie on the unified single curve of $\overline{\sigma}_\tau/Z$ versus ε/Z, regard less of the strain-rate or temperature. The

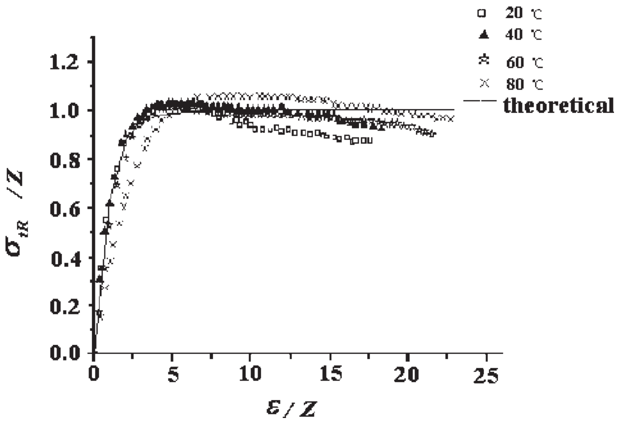

Figure 7.
The unified curve of versus*e/Z* for 113 blends at various temperatures.

comparison of such a theoretical prediction and experimental data of 113 is shown in Fig. 7. Taking account of that the experiments under high strain rates are nearly of adiabatic process while the theoretical prediction is for an isothermal process, the agreement between the prediction and experiments is good enough to reflect the rate-temperature equivalence.

As $\theta(T) = \eta(T)/E(T)$ and $E_2(T)$ is nearly a constant (from Table 1. it's about 0.83 GPa), so the temperature dependence of relaxation time $\theta(T)$ is just determined by the temperature dependence of the viscosity coefficient $\eta\ (T)$. If $\eta\ (T)$ follows Arrhenius equation:

$$\eta(T) = \eta_0 \exp\left(\frac{A}{KT}\right) \tag{11}$$

where $\eta_0 = 4189$ pa · s, A/K = 8.595 °C

The Z-parameter reduces to Zener-Hollomaon Parameter $Z = \frac{\dot{\varepsilon}\eta_0}{E}\exp\left(\frac{A}{KT}\right)$, which is well known in the research of rate-temperature equivalence in metals.

Conclusions

(1) By using Instron 1342 testing system and an improved SHPB technique, PP/PA blends are tested at a wide range of strain rates from 10^{-4} up to 10^{3} s^{-1} and at a temperature range of 25–80 °C. Their mechanical responses are shown to be sensitive both to the strain rate and temperature. Based on the experimental data of 113 blends, it is shown that the mechanical behavior of this PP/PA blends can be described with ZWT thermoviscoelastic constitutive equation. The Corresponding thermoviscoelastic parameters for 113 blends are obtained. The predicted theoretical results coincide quite well with the experimental data.

(2) The time-temperature equivalence relation is shown for PP/PA blends. Raising the temperature is equivalent to the increasing of time (the decreasing of strain rate). Conversely, decreasing the temperature is equivalent to the decreasing of time (the increasing of strain rate).

(3) Through introducing a dimensionless parameter $Z = \frac{\dot{\varepsilon}\eta_0}{E}\exp\left(\frac{A}{KT}\right)$, two characteristic parameters: strain rate $\dot{\varepsilon}$ and temperature T are put together to this unified parameter Z. From experimental results, A/k is fitted, A/k = 8.595 °C, and a unified curve characterizing the time–temperature equivalence relation is obtained

[1] J. D. Ferry, Viscoelastic Properties of Polymers, Wiley, New York, 1980.

[2] F. Schwarzl and A. J. Staverman, J. Appl. Phys., v23 **1952**, 838.

[3] L. W. Morland, E. H. Lee, Stress Analysis for Linear Viscoelastic Materials with Temperature Variation, Journal of Rheology, 1960, Volume 4, Issue 1, March, pp. 233–263.

[4] G. Lianis, Proc, 5 th Int. Cong. Rheol., v.14 **1969**, 313.

[5] E. C. Ting, Trans. Soc. Rheo., v.14 **1970**, 297.

[6] C.W. McGurirt and G. Lianis, Int. J. Engng. Sci., v.79 **1969**, 579.

[7] C. J. Morgan and I.M. Ward, J. Mech. Phys Solids, v.19 **1971**, 165.

[8] Zhu Zhaoxiang, Xu Daben, Wang Lili, Thermo-Viscoelastic Constitutive Equation and Time-temperature Equivalence of Epoxy Resin at high strain rates, Journal of Ningbo University, v.1 **1988**, No., 58–68.

[9] Shi Shaoqiu, Gansu and Wang Lili, The Thermo-Viscoelastic Mechanical Behavior of Aeronautical PMMA under Impact Loading, Journal of Ningbo University, v.1 **1988**, No., 58–68.

[10] Wang Lili, Zhu Xixiong, Shi Shaoqiu, An Impact Dynamics Investigation on some Problems in Bird Strike on Windshields of High Speed Aircraft, *Acta Aeronautica et Astronautica Sinica*, v.5 **1992**, No.3, 205–213.