The Effect of Temperature on Mechanical Properties of Modified Polypropylene

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ABSTRACT

The mechanical behaviors of five modified polypropylene composites were investigated under the effect of various temperatures. Mechanical properties of polymer were carried out through uniaxial tensile tests for low and high temperatures respectively. The results showed that both yield stress and the elastic modulus of the material decrease with the increase of temperature. The properties are also significantly influenced by the addition and the additive quantity. The addition with glass fiber (GF) manifests higher properties than the other addition, and the modulus and yield stress increase with the increasing of the additive amount. Three models are chosen to fitting with the experiment values in order to understand the mechanical behavior of the polymer. By comparing the proposed simplified model with Gibson model, both are successfully validated by the excellent agreement between model prediction and experimental results.

KEYWORDS: *Modified polypropylene, Mechanical properties, Temperature effect*

1. INTRODUCTION

As the modification technology increasingly matures in the field of thermoplastic materials engineering applications, polypropylene exhibits raised interest as structural materials due to their excellent combination of mechanical properties, low production cost and weight in automotive industry [1-3]. However, modified polypropylene as such has to be reinforced to meet the high demands on stress

J. Polym. Mater. Vol. **35,** No. 1, 2018, 45-57

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and modulus in engineering applications. Major reinforcing elements such as: glass fibers and talc are often used for this purpose [4, 5]. The modified polypropylene has been attempted to achieve improvement mechanical properties, and barrier properties, while ensuring good process ability and insensitivity to moisture [6]. The mechanical properties of the modified polypropylene are quite a different under different loading conditions and effected by different addition [7, 8]. Consequently, an accurate understanding of the mechanical behavior under different loading modes is significantly important for scientific research and engineering structural design.

Several investigations have shown the importance of addition condition on filament structure and numerous studies have been conducted to elucidate the mechanical behavior of modified polypropylene under different loading modes [9-12]. Some studies have pointed out the temperature-dependent mechanical behavior of composites with polypropylene matrix and glass fiber [13], talc [14], and so-called all-polypropylene composites [15]. The yield stress and the elongation at break, for instance, are strongly influenced by the temperature [16, 17]. It was proved, that adding supplement to the blend decreased the value of melt flow index (MFI) and increased the strength and ductility parameters [18]. The values of yield stress at high strain rates and ambient temperature are much greater than that under low strain rates, and similar trend of marked temperature effect was observed on the yield properties [19]. Cady et al. studied the mechanical response of several polymers under dynamic loading at high temperatures [20]. The elastic modulus decreases with increasing temperature and have a significant change in transition region [21]. Several studies deal with the mathematical description of temperature-dependent mechanical properties for providing a reliable design database and extend existing composite material models about temperature dependency[22]. The yield energy is a linear function of temperature, extrapolating to zero near the melting point. The ratio of thermal to mechanical energy to produce yielding is about one third that for glassy polymers[23]. The influence of temperature on the rate of chemical reactions is almost always interpreted in terms of what is now known as the Arrhenius equation [24, 25]. Civan provides a formulation for the temperature dependence of the power needed to detach fine particles from a pore wall in the form of an empirical Arrhenius-type two-parameter asymptotic-exponential function [26]. Mahieux [27] firstly put forward a statistical model for describing the elastic modulus of polymer materials with temperature. Richeton [28] proposed a unified model for predicting of the elastic modulus with the influence by frequencies/strain rates and temperatures in order to describe the elastic property of polymers. However, the correlation coefficient is difficult to be determined directly through the test. Thus, the mechanical parameters of the material need to be directly described by the function of temperature, which will be studied in this paper.

The purpose of the present work is to thoroughly investigate the mechanical behavior of modified polypropylene under various temperatures. The results from the performed experiments may help to optimize the design of polypropylene based structures. By these experimental data, some relationship between temperature and

related mechanical properties are verified and transformed for conveniently application. The experimental data provide sufficient help in calibrating the relation to accurately predict the mechanical properties of modified polypropylene under various temperature conditions.

2. EXPERIMENTS AND MATERIALS

2.1 Material and specimen

The material used in the present study was reinforced polypropylene (PP) with different additives as follow: The PP+EPDM-T20 used in this study was a commercial product from Lyindellbasell, Holland. It is mixed polypropylene material with the addition of 20% talc and EPDM rubber. The melt flow index (MFI at 230!) and density of PP+EPDM-M14 were 20 g/min and 1.05 g/cm^3, respectively. The PP+EPDM-T15 was supplied by Shanghai Pret Composites, China. The addition was 15% talc and EPDM rubber. MFI and density of PP+EPDM-T15 were 14 g/min and 1.02 g/cm^3, respectively. The PP+EPDM-M14 was supplied by Lotte Chemical, Korea. It is mixed polypropylene material with the addition of 15% mica powder and EPDM rubber. MFI of PP+EPDM-M14 was 25 g/min, and the density was 0.9 g/cm^3. The PPLGF20 was supplied by Sabic Innovative Plastics, Saidu. It is mixed polypropylene material with the addition of 20% long glass fiber. MFI and density of PPLGF20 were 16 g/min and 1.14 g/cm^3, respectively. The PPSGF20 was supplied by Borealis, Austria. It is mixed polypropylene material with the addition of 20% short glass fiber. MFI and density of PPSGF20 were 15 g/min and 1.12 g/cm^3, respectively.

Samples were dumbbell-shaped specimens fabricated by injection molding according to ISO527-1A and processed by Yanfeng Jingqiao automotive trim systems.

2.2 Experimental setup

All tensile tests were performed on the universal testing machine (Z020, Zwick/Roell, Germany). A high temperature heating furnace and a cryogenic liquid nitrogen tank were assembled to adjust the ambient temperature. A plurality of thermocouple elements were used in the furnace for real-time temperature measurement to ensure that the sample was tested at the specified temperature. In order to obtain the uniaxial tensile strain of the material accurately, the strain data was obtained by using a non-contact video extensometer. During the testing, the temperature gradually increased, the samples were preheated at least 30 min in the heating chamber, then placed for 10 min on the test machine before loading to ensure that the preheat treatment would not affect the mechanical properties [29]. In this study, the performed tests incorporated quasi-static uniaxial tensile for different testing temperatures (-30°C, -10°C, 23°C, 60°C, 80°C and 110°C). The velocity of machine chuck was 2 mm/min and the frequency of the video extensometer 20 frames per second (fps). The strain change with time during the testing can be accurately measured. At least three samples were tested in the experiment.

3. RESULTS AND ANALYSIS

3.1 Experimental results

The experimental data for the stress-strain curves of the aforementioned polypropylene samples at different temperatures ranging from -30°C to 110°C are shown in Fig. 1 for all-PP composites. As expected, variation of the test temperature shows a remarkable effect on the tensile behavior of the all-PP composites with enhanced tensile tendency when the temperature increased. This effect can be recognized as the effect of temperature on the mobility of the macromolecular chains which are determined by the properties of the materials and the additions. The necking phenomenon can be clearly observed in the test. Also, the elastic phase and the yield-like behavior can be found in the stress-strain curves. The yield stress is generally defined as the true stress at the peak point on the stress-strain curves. With temperature increasing, the values of yield stress and elastic

modulus decreased apparently and the highest values are observed for the lowest temperature.

The tensile properties of material are influenced by their physical structure, which is controlled by the additions. Common fibers can produced by a commercial spin line have tensile stress up to 3-5 GPa, yield stress up to 60 MPa [30]. From the results it is clear that PPLGF20 and PPSGF20 show higher yield stress and elastic modulus than the other materials at all the temperatures. This could be explained from the difference in the composite morphology, namely crystallinity and void content as well as the reinforcement architecture.

For the material of PP-T15, PP-T20 and PP-M14, an obvious stress drop occurs following a plastic flow platform when the stress reaches the peak point at low temperature. However, it is not really occurring at high temperature. Under constant temperature conditions, the values of the mechanical properties for the material (PP-T15, PP-T20, PP-M14) are similarly close and located on the same order of magnitude (Table. 1). According to Albano et al. [31], a decrease in yield stress and elastic modulus is observed when the addition of the talc increases. Data in Table. 1 also highlight the effect of addition on the mechanical properties of all-PP composites.

TABLE. 1. Values of the elastic modulus and the yield stress for 5 PP material at constant temperature

Properties			Composites		
	PP+EPDM-T15	PP+EPDM-T20	PP+EPDM-M14	PPLGF20	PPSGF20
Elastic Modulus/ MPa	16.60	17.49	15.89	37.77	60.59
Yield Stress/ MPa	1384.83	1483.52	1702.49	2394.70	3178.10

The addition of GF (glass fiber) has sharply increased the yield stress and elastic modulus. A similar trend to that of the tensile stress and elastic modulus was again observed that the related enhancement manifests prominent effects in PPSGF20 than PPLGF20. Elongation at break, on the other hand, increases with increasing temperature for the material of PPSGF20, but no apparent rule for a considerably elongation to break was found. This suggests that different kinds of modified polypropylene have great variability in their mechanical properties which can be documented as a standard to choose material in engineering design.

3.2 Effect of temperature on mechanical property

Examination of the data revealed that the mechanical properties changed with temperature. Thus, the results show the necessity to describe the elastic properties and the stress as a function of temperature:

$$E_i = E_i(T),\ \sigma_{Y_i} = \sigma_{Y_i}(T) \qquad (1)$$

Various relationships have been proposed for modelling the variation of mechanical properties of polymers or composites with temperature. The influence of temperature on the properties is almost always interpreted in terms of what

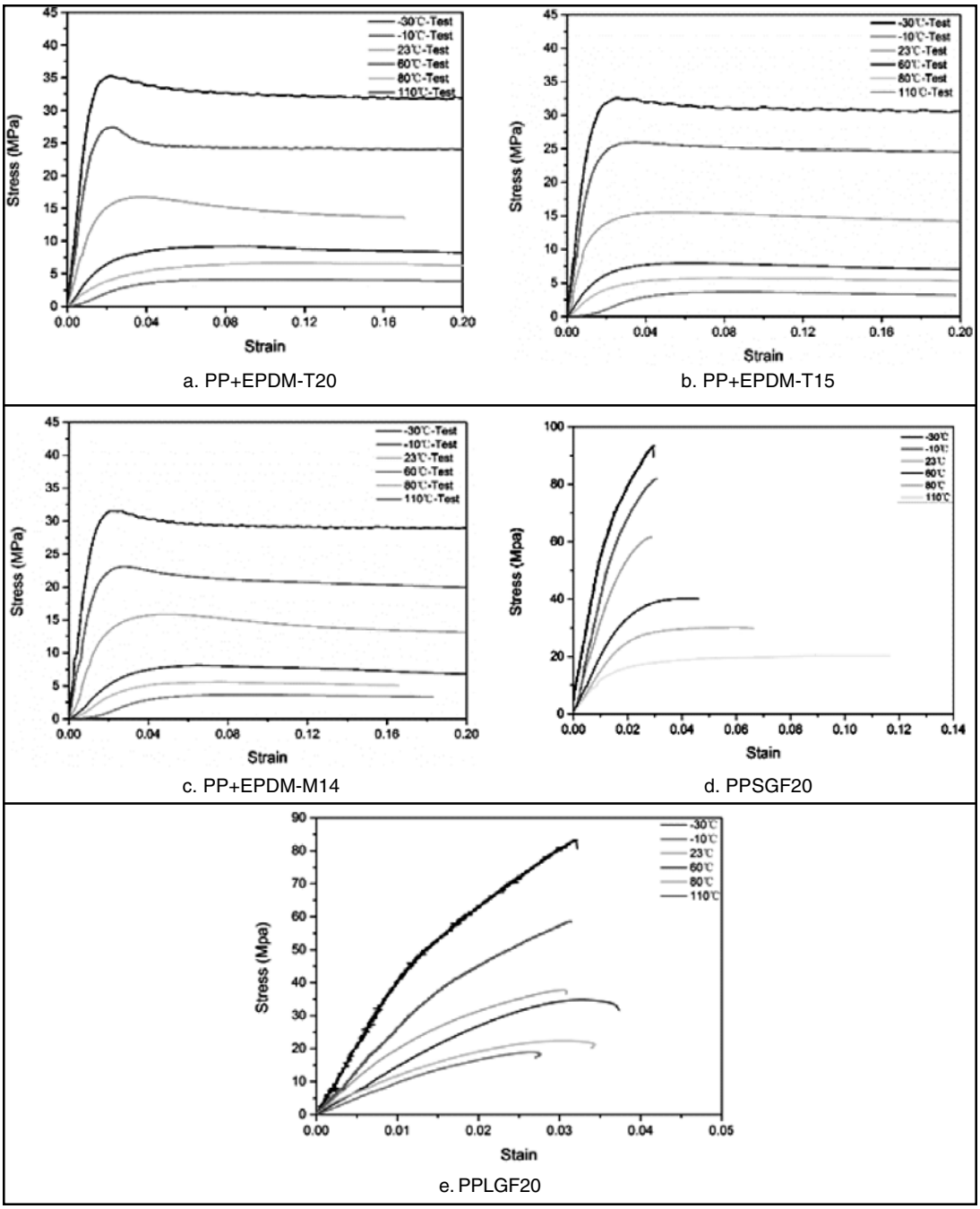


Fig. 1. Typical stress-strain curves of the PP composites at different temperatures

is now known as the Arrhenius equation. According to this, Ha and Springer [32] proposed a non-linear power relationship between property values and temperature:

$$P(T) = P_0(T_0)\left(\frac{T_r - T}{T_r - T_0}\right)^n \quad (2)$$

where, *P(T)* is the property under consideration (stress, modulus, or initial Paisson's ratio) at temperature T, and P_0 is the value of the property at the reference temperature T_0 which can be chosen at room temperature. T_r is a reference temperature, and n is a constant with a value between 0 and 1. The T_r and n values obtained by a least square by fitting Eq. 2 to the data. An exponential model has been proposed by Wade et al. [33]:

$$P(T) = P_0 exp\left(\frac{A}{BT}\right) \quad (3)$$

where, P_o is the reference value, A and B are material parameters determined by test data. For combining Eq. 2 and Eq. 3, the model of Wade can be extended to give, the parameters has the same meaning as Eq. 2

$$P(T) = P_0 exp\left(C\left(\frac{T_r - T}{T_r - T_0}\right)^n\right) \quad (4)$$

In this optic, an empirical relationship with a hyperbolic function for modeling the changes of the mechanical property values within the transition regions was proposed by Gibson et al. [34]:

$$P(T) = P_1 + 0.5(P_1 - P_2)\big(1 + tanh\big(c_1(T - T_1)\big)\big) - 0.5(P_2 - P_3) * \big(1 + tanh\big(c_2(T - T_2)\big)\big) \quad (5)$$

This approach takes into account the significant influence of the transition regions on mechanical property values. T_1 and T_2 are the respective transition temperatures. P_1, P_2 and P_3 present the property values below lower transition, between the transitions and above the upper transition, respectively. C_1 and C_2 are model parameters for adjusting the breadths of transition ranges. It can be seen that seven constants are needed to fully describe the behavior.

Additionally, a multi-linear model which seem also accurate with respect to the changing material properties is proposed here using a simple linear function by Hutchison [35],

$$P(T) = P_0(1 - \beta(T - T_r)) \quad (6)$$

Taking into account the measured data of yield stress and elastic modulus, the test data of PP+EPDM-T20 was chosen to verify the representational models above (Eq. 2, Eq. 5 and Eq. 6) by the least squares method. The values of the elastic modulus and yield stress are listed in Table 2. The comparison of the fitting results with the measured models of the elastic modulus and yield stress are shown in Fig. 2 and Table 3, respectively.

In general, the yield stress and elastic modulus are momentously affected by the temperature enhancement. The yield stress of PP-EMDM-T20 is reduced about 31% and 49% respectively from -10°C to 23°C and 23°C to 60°C. Surprisingly, the elastic modulus is decreasing about 31% and 71% across the same temperature range. In the investigated temperature area, the values of modulus drop from 1483MPa to 320MPa. This phenomenon

TABLE. 2. Values of the elastic modulus and the yield stress

Temperature/ °C	Elastic Modulus/MPa	Yield Stress/MPa
-30	3748.42	31.55
-10	2148.24	23.07
23	1483.52	15.89
60	320.60	8.09
80	239.54	5.59
110	126.40	3.66

results from the glass transition due to the different coefficients of thermal expansion. Here, motion of the macromolecules in the amorphous regions increase significantly.

Gibson's model represents the temperature dependence more accurately but Ha/Springer's and Hutchison's models have the advantage of less number of parameters. On account of the characteristics of the power function, Eq. 2 can not reflect the variation of the yield strain at all temperature ranges. It is also clearly observed in Fig. 3b that Ha/Springer model is not suitable for the whole temperature ranges but only for a small region.

By comparing with fitting results of the three models (Gibson's, Ha/Springer's and Hutchison's), the Gibson's model describes temperature-dependency for the entire temperature range and the model parameters have a physical relevance. However, the Hutchison approach enables the modelling of the ultimate slight decrease of elastic modulus and yield stress. In general, Gibson relationship is sufficiently accurate to describe the mechanical properties depending on temperature.

3.3 Simplification of Gibson's model

A wealth of parameters exists in Gibson's model, the parameters are determined by a mass of data and it is not suitable for engineering application. So the following equation has been obtained after some simplification by the Gibson's model for providing convenient calculation and applicable forecasting method for the thermoplastic materials.

$$P(T) = a * tanh\left(\frac{T+b}{c}\right) + d \qquad (7)$$

where: a, b, c and d are temperature-independent parameters determined by the material properties. It can be found that the simplified model has good fitting degree with the experimental values as same as the Gibson model which are shown in Fig. 3 and Table 4.

The experimental results show that the tension behavior of polypropylene is sensitive to temperature. The values of yield stress and elastic modulus decrease dramatically with increasing of the temperature. This phenomenon can be effectively described by the Eq. 7.

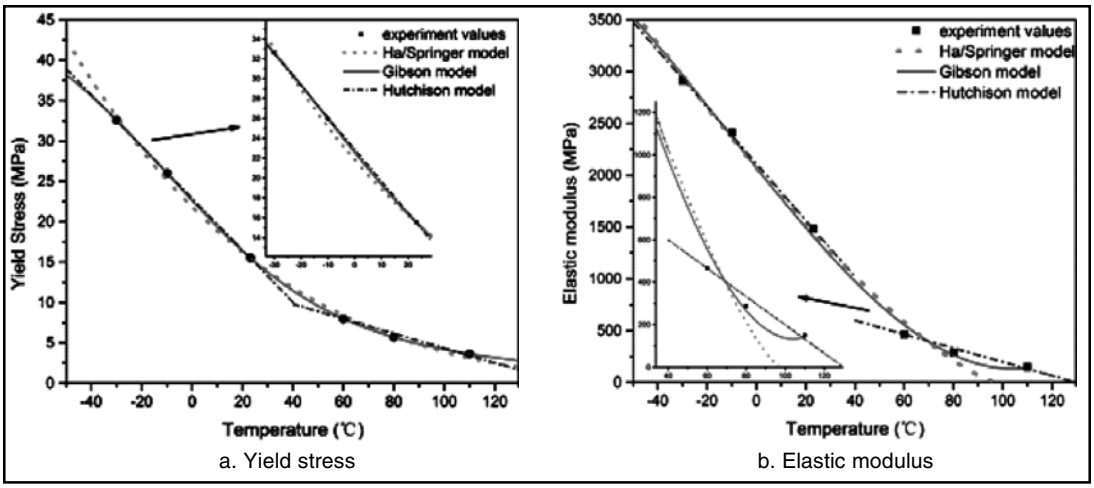


Fig. 2. Comparison of the fitting results with the measured models

The measured values of the elastic modulus and yield stress with all-PP composites (PP+EPDM-T20, PP+EPDM-M14, PPLSG20, PPSGF20) at -30°C, -10°C, 23°C, 60°C and 110°C are chosen to fitting by the least square method. Meanwhile, the values at 80°C are calculated by the model with the fitting parameters and compared with the experiment data. The fitting line shows good agreement with the experimental data as shown in Fig. 4.

In this way, a functional formula within a certain temperature range is established by the relationship and the mechanical properties at a certain temperature can be obtained. The error between the predicted values by the simplified function (Eq. 7) and experimental values was utilized to evaluate the prediction accuracy of values, which is defined as Eq. 8:

$$error = \frac{V_E - V_P}{V_E} \quad (8)$$

TABLE. 3. The fitting results of the model with the values of the elastic modulus and the yield stress

Properties	Model	Parameters	PP+EPDM-T20
			<23°C >23°C
Elastic modulus	Ha/Springer	P_0(MPa); T_r(°C); T_0(°C); n	1483; 97.6; 23; 1.3
	Gibson	P_1(MPa); P_2(MPa); P_3(MPa); T_1(°C); T_2(°C); c_1; c_2	101910; 852870; -973257; 0.003; -0.0003; -10; 80
Yield stress	Hutchison	P_0(MPa); T_r(°C)	1483; 23; 0.02 465; 60; 0.14
	Ha/Springer	P_0(MPa); T_r(°C); T_0(°C); n	15.5; 318; 23; 4.5
	Gibson	P_1(MPa); P_2(MPa); P_3(MPa); T_1(°C); T_2(°C); c_1; c_2	54.3; 11.8; -5.9; 0.015; 0.002; -10; 80
	Hutchison	P_0(MPa); T_r(°C); β	15.5; 23; 0.02 8; 60; 0.01

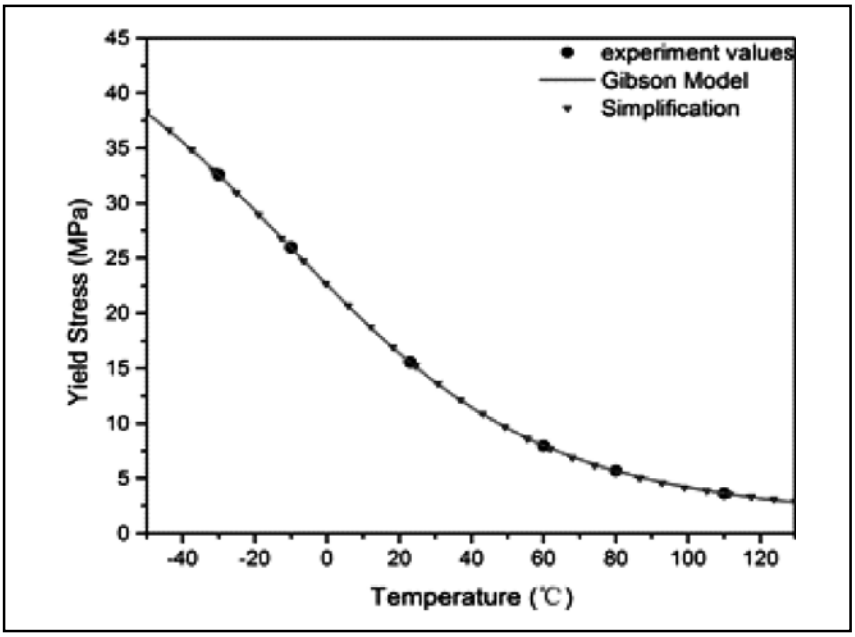


Fig. 3. Fitting results of the simplified model

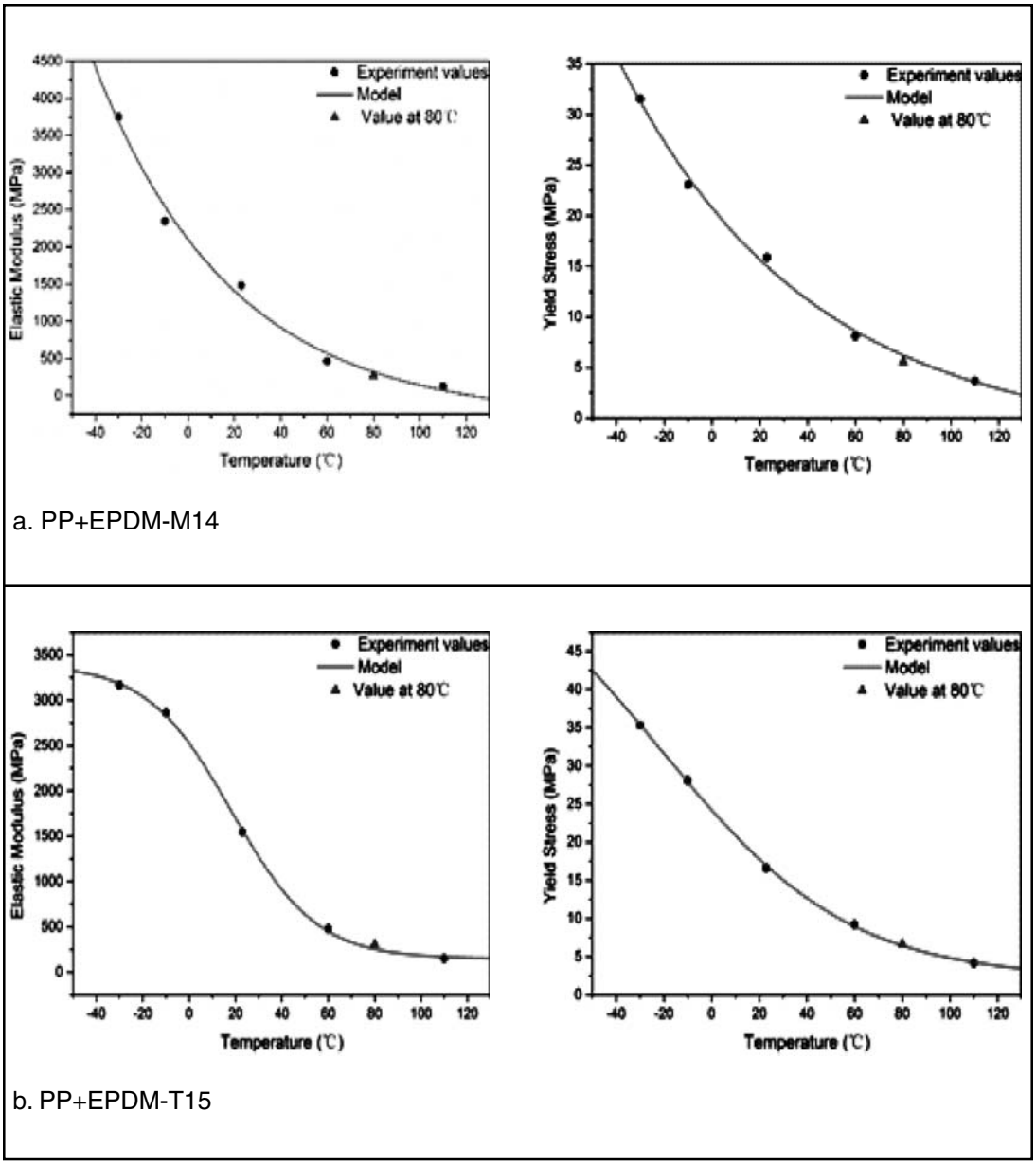
TABLE 4. R-Square of the Gibson and the simplified model

Properties	Model	Adj. R-Square
Yield stress	Gibson	0.99999
	Simplified model	0.99997

where, V_E and V_P are the experimental and predicted values, respectively. The error at 80°C for four PP composites is listed in Table 5. It is seen that the largest error is less than 10%. Hence, the model is validated to have the ability of accurately predicting the mechanical properties of the other four PP composites at a range temperature.

4. CONCLUSION

The stress-strain response and temperature-dependent mechanical properties of five polypropylene composites are analyzed and verified by tensile test in this paper. The experimental results show that the tension behavior of polypropylene is sensitive to temperature and the values of yield stress and elastic modulus decrease dramatically with increasing of the temperature. It was also observed that the values of yield stress and elastic modulus can be effected by the addition of the talc, which the values increase by increasing the addition. The composites with glass fiber (PPLSF20, PPSGF20) have higher elastic modulus and yield stress than the composites with talc and mica. Meanwhile,



a. PP+EPDM-M14

b. PP+EPDM-T15

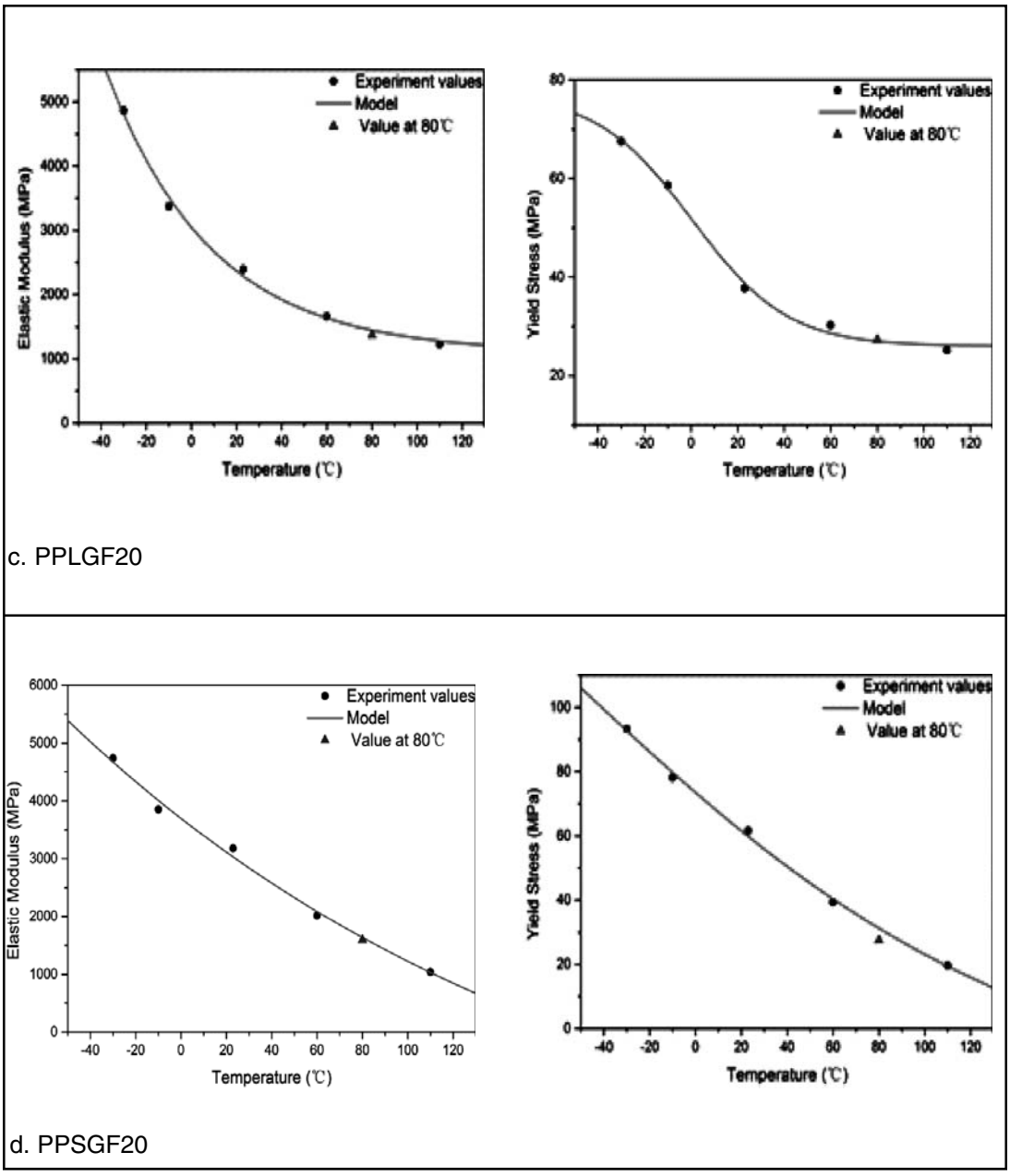


Fig. 4. Fitting results for all-PP material by the simplified model

TABLE. 5. The error at 80°C for four PP composites

Materials	Properties	Experiment values (MPa)	Predicted values (MPa)	Error (%)
PP+EPDM-T15	Elastic modulus	304.77	282.41	7.34
	Yield stress	6.65	6.41	3.66
PP+EPDM-M14	Elastic modulus	275.54	298.07	-8.99
	Yield stress	5.59	6.10	-9.11
PPLGF20	Elastic modulus	1368.60	1441.21	-5.31
	Yield stress	27.32	26.97	1.28
PPSGF20	Elastic modulus	1594.10	1627.79	-2.11
	Yield stress	27.52	30.18	-9.67

the short glass fiber shows fairly strong mechanical properties than the long glass fiber which may be caused by the physical structure of glass fiber.

Based on the experimental investigation, the models describing the relationship of the temperature-dependent properties, summarized in our previous work, were inter-compared by fitting with the experiment data. The Gibson model is able to accurately reflect the relationship between temperature and mechanical properties. By some simplification, a hyperbolic-liked model was proposed and verified by the experiment values. The R-squared is precise and the prediction has less error with the tensile experimental results. In addition, the prediction model is demonstrated to have ability to accurately predict the mechanical behavior from low to high temperature. This method can reduce the difficulty of the test and the test cycle, and provide the applicable forecasting method for the engineering application of the thermoplastic materials.

Acknowledgement

This work is supported by the Research Program of Shanghai Science and Technology Committee (NO.14DZ1204203).

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Received: 18-01-2018

Accepted: 09-03-2018