

Tensile properties of novel polyarylate and aromatic polyamide resins

Masaharu Nishiwaki¹, Minoru Miwa¹, Akiyoshi Takeno¹, Teruyuki Yokoi¹,
Yoshihiro Kubota¹, Yoshihiro Sugi¹, Tohru Kishida², and Takayoshi Yamauchi²

¹ Department of Materials Science and Technology, Faculty of Engineering, Gifu University,
1-1 Yanagido, Gifu-shi, Gifu 501-1193, Japan

TEL&FAX: +81-58-293-2623, e-mail: miwa@apchem.gifu-u.ac.jp

² K. K. Nissei Kagaku Kogyosho, 2-18-110 Juhachijyo, Yodogawa-ku, Osaka 532-0001, Japan
Fax: +81-6-6396-4310

Thermosetting resins such as epoxy and unsaturated polyester resins have been used as matrix materials for composite materials. However, since these thermosetting resins are insoluble and infusible, it is difficult to reuse and recycle. In recent years, novel polyarylate and aromatic polyamide resins that dissolve in solvents and have heat-resistance were developed.

The tensile test for these resins was performed at temperatures of 20, 50, 100, 150, 200 and 250 °C, and strain rate of -2.0, -1.0, 0, 1.0/min, respectively. The tensile strength of polyarylate and aromatic polyamide resin was 57 MPa and 100 MPa, and tensile modulus was 1.6 GPa and 2.7 GPa at room temperature, respectively. These properties are almost the same as those of conventional thermosetting resins. For both resins, the tensile strength at all temperatures increases almost linearly with the increase in the logarithm of the strain rate. Moreover, the increasing tendency decreases with temperature. It was found that strain rate-temperature superposition holds for the tensile strength of both resins.

Key words: Polyarylate, Aromatic polyamide, Tensile strength, Tensile modulus, Strain rate-temperature superposition

1. INTRODUCTION

It is difficult to reprocess fiber reinforced plastics (FRP) wastes for material recycling in spite of many efforts, because polymers used as matrix materials for FRP are thermosetting resins such epoxy and unsaturated polyester resin, and reinforcing fiber and matrix resin strongly adhere at fiber-matrix resin interface. From these reasons, FRP wastes were usually crashed and grounded into granular or particle pieces, and slightly reclaimed as the plastic filler. The development of new type of recyclable FRP is urgent issues from the point of energy saving and recycling of materials.

In recent years, novel polyarylate and aromatic polyamide resins that dissolve in solvents and have heat-resistance were developed¹⁾. A polyarylate resin was synthesized by carbonylation-poly-condensation with 2,7-dibromo-9,10-dihydrophenanthrene and bisphenol-A¹⁻³⁾, while an aromatic polyamide resin by carbonylation-polycondensation with 2,7-dibromo-9,10-dihydro-phenanthrene and 4,4'-diaminodiphenyl-*em*ethane⁴⁾. These resins had the high heat-resistance above 350°C in the air atmosphere. These resins exhibited the dynamic viscoelastic behavior like typical amorphous polymer. Dynamic viscoelastic curve showed that the glass transition temperature were about 270 and 300 °C³⁾. Furthermore, these resins could be solved in organic solvents such as chloroform and *N,N*-dimethylacetamide. If these resins will be used as matrix, the recycling of composite materials may be

easy.

In this paper, we investigated the dependence of temperature and strain rate on the tensile strength of polyarylate and aromatic polyamide resins.

2. EXPERIMENTAL

2.1. Synthesis of polyarylate and aromatic polyamide resins

Resins used in this study were developed elsewhere¹⁻⁴⁾.

First, 2,7-dibromo-9,10-dihydrophenanthrene was prepared from 9,10-dihydrophenanthrene by known methods. Then, polyarylate was synthesized by palladium-catalyzed carbonylation-polycondensation of 2,7-dibromo-9,10-dihydrophenanthrene and bisphenol-A. This chemical structure is shown in Fig. 1. The weight average molecular weight (*M_w*), the number average molecular weight (*M_n*) and *M_w* / *M_n* determined by means of gel permeation chromatography on the basis of polystyrene calibration were 93,600, 46,200 and 2.03, respectively. This resin was thoroughly solved in chloroform or chlorobenzene.

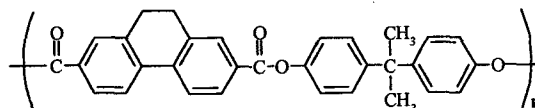


Fig. 1. Chemical structure of polyarylate resin.

Aromatic polyamide was synthesized by palladium-catalyzed carbonylation-polycondensation of 2,7-dibromo-9,10-dihydrophenanthrene and 4,4'-diaminodiphenylmethane. This chemical structure is shown in Fig. 2. M_w , M_n and M_w/M_n were 73,900, 37,900 and 1.95, respectively. This resin was thoroughly solved in *N,N*-dimethylacetamide.

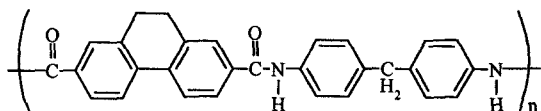


Fig. 2. Chemical structure of aromatic polyamide resin.

Heat-resistant temperature of various resins⁶⁾ are shown in Fig. 3. Heat-resistant temperature of novel polyarylate and aromatic polyamide resins are higher than those of thermosetting resins such as epoxy and unsaturated polyester resins and are almost the same as those of U-polymer and PEEK resins. But, these are lower than that of polyimide resin.

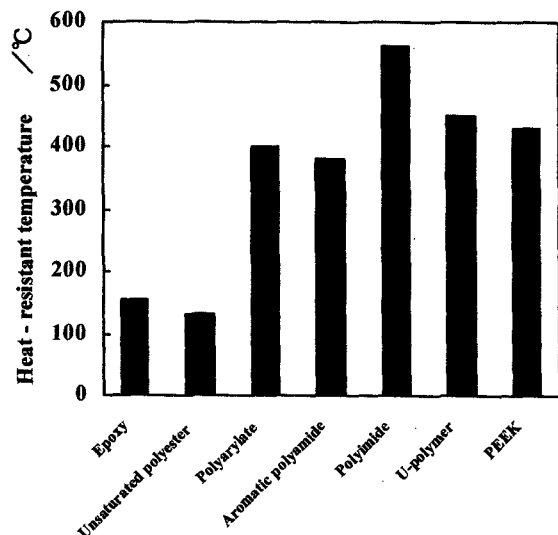


Fig. 3. Heat-resistant temperature of various resins

2.2. Specimen preparation

The films of the polyarylate and aromatic polyamide resins were prepared by casting method.

First, polyarylate (5 wt% in concentration) was mixed into the chloroform solution. Next, the mixed solution was cast into a desired mold and then dried for one day in the atmosphere. The mold was set in the oven and heated from room temperature to 55 °C in 17 h, and then continued drying for 30 min. in a vacuum. Then, it was heated to 90 °C in 5 h and continued drying for 1 h. Finally, it was allowed to cool to room temperature at a cooling rate of 5 °C/h. Using polymer films prepared in this manner, test specimens were cut into 20 μm in thickness, 10 mm in width and 50 mm in length.

Aromatic polyamide (10 wt% in concentration) was mixed into the *N,N*-dimethylacetamide solution. Next, the mixed solution was cast into a desired mold. The

mold was set in the oven and heated from room temperature to 55 °C in 17 h, and then continued drying for 30 min. in a vacuum. Then, it was heated to 90 °C in 5 h and continued drying for 1 h. Finally, it was allowed to cool to room temperature at a cooling rate of 5 °C/h. Using polymer films prepared in this manner, test specimens were cut into 30 μm in thickness, 10 mm in width and 50 mm in length.

2.3. Tensile test

In order to investigate the strain rate and temperature dependence of the tensile properties of polyarylate and aromatic polyamide resins, each specimen was subjected to a tensile test at the temperatures of 20, 50, 100, 150, 200 and 250 °C and at strain rates of -2.0, -1.0, 0, 1.0/min, respectively with the aid of a Tensilon UTM-I-2500 (Orientec). Gauge length was set 30 mm. More than five specimens were tested for each test condition.

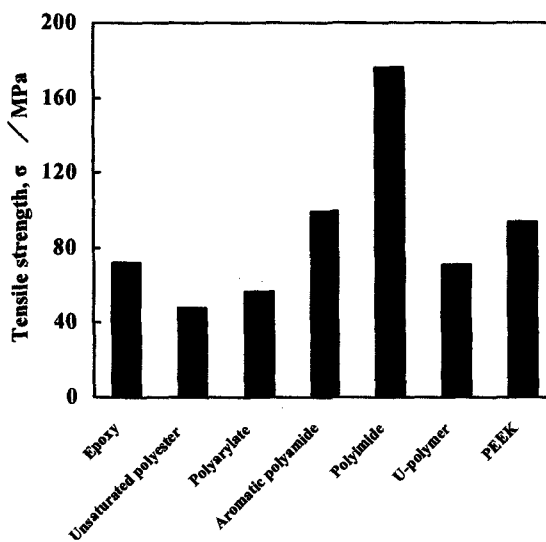


Fig. 4. Tensile strength of various resins

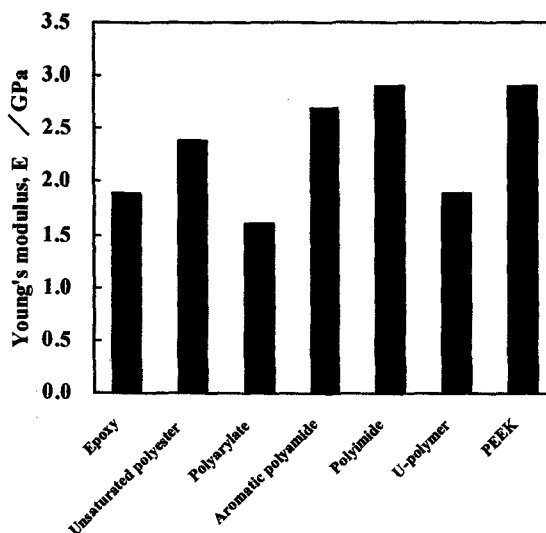


Fig. 5. Young's modulus of various resins.

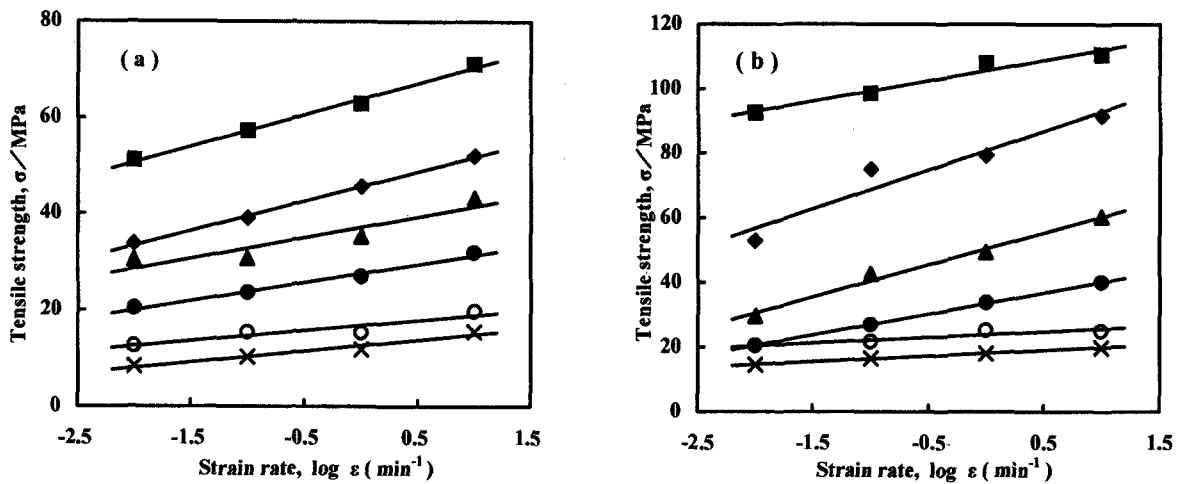


Fig. 6. Relation between strain rate and tensile strength at various temperatures. (a) Polyarylate resin, (b) aromatic polyamide resin. ■, 20 °C; ◆, 50 °C; ▲, 100 °C; ●, 150 °C; ○, 200 °C; ×, 250 °C.

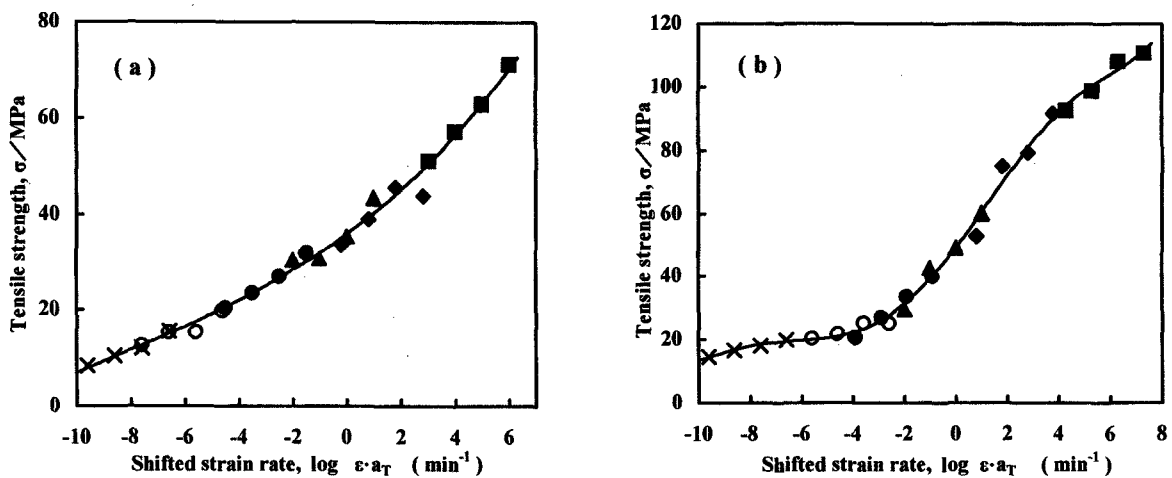


Fig. 7. Master curve of tensile strength plotted against shifted strain rate. Reference temperature is 100 °C. (a) Polyarylate resin, (b) aromatic polyamide resin. ■, 20 °C; ◆, 50 °C; ▲, 100 °C; ●, 150 °C; ○, 200 °C; ×, 250 °C.

3. RESULTS AND DISCUSSION

Tensile strength and Young's modulus of various resins are shown in Figs. 4 and 5. Tensile strength and Young's modulus of polyimide, U-polymer and PEEK resins are data in elsewhere⁷⁾.

As shown in Fig. 4, the tensile strength of novel polyarylate and aromatic polyamide resins are almost the same as those of thermosetting resins such as epoxy and unsaturated polyester resins and are almost the same as those of U-polymer and PEEK resins. But, these are lower than that of polyimide resin.

As shown in Fig. 5, Young's modulus of polyarylate and aromatic polyamide resins are almost the same as those of another resins. These novel resins may be fully expected as matrix materials.

Fig. 6 shows the relationship between strain rate $\dot{\epsilon}$ and tensile strength σ at various temperatures for novel polyarylate and aromatic polyamide resins. For both resins, the tensile strength at all temperatures increases almost linearly with the increases in the logarithm of the

strain rate. Moreover, the increasing tendency decreases with temperature.

Data in Fig. 6 have been shifted along the logarithm of the strain rate axis to obtain master curves of the tensile strength, as shown in Fig. 7. In Fig. 7, the reference temperature is 100 °C. Although a slight deviation exists in both cases, data can be reduced into a single master curve, implying that the strain rate-temperature superposition holds for the tensile strength of polyarylate and aromatic polyamide resins.

The relationship between the logarithm of the shift factor in order to obtain these master curves and the reciprocal of absolute temperature is shown in Fig. 8. Although there is an inflexion at temperatures in the region of 200 °C for aromatic polyamide resin, the logarithm of the shift factor increases almost linearly with an increase in the reciprocal of absolute temperature. For both resins, it is thus recognized that a temperature dependence of Arrhenius type holds on the shift factor. Apparent activation energy ΔH

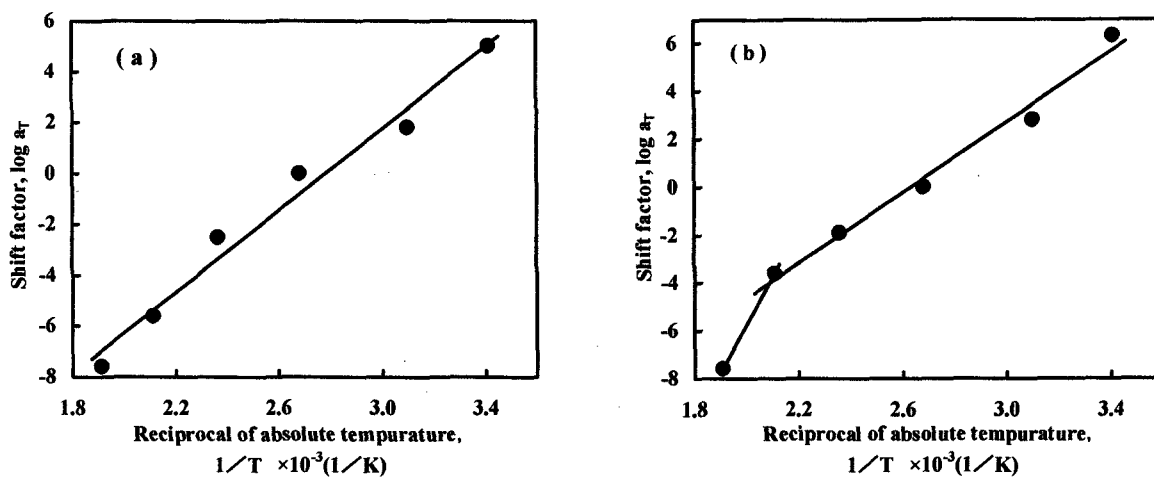


Fig.8. Shift factors with the reciprocal of temperature. (a) Polyarylate resin, (b) aromatic polyamide resin.

Table I. Activation energy, ΔH (kcal/mol).

Resin	Low temperature region	High temperature region
Polyarylate resin	144 (20 ~ 250 °C)	
Aromatic polyamide resin	141 (20 ~ 200 °C)	383 (200 ~ 250 °C)
Epoxy resin	363 (20 ~ 60 °C)	680 (60 ~ 80 °C)
Unsaturated polyester resin	434 (20 ~ 80 °C)	

obtained from the gradient of the straight line, which was obtained by a least squares method, is shown in Table I. For comparison, apparent activation energy for epoxy and unsaturated polyester resins⁸⁾ is shown in Table I. Apparent activation energy ΔH of polyarylate and aromatic polyamide resins are smaller than those of epoxy and unsaturated polyester resins. The inflection point for the aromatic polyamide resin may be caused by the secondary dispersion⁵⁾.

4. CONCLUSIONS

Tensile properties for polyarylate and aromatic polyamide resins were discussed.

The tensile strength of novel polyarylate and aromatic polyamide resins was 57 MPa and 100 MPa at room temperature, respectively. These properties are almost the same as those of conventional unsaturated polyester and epoxy resins. For both resins, the tensile strength at all temperatures increases almost linearly with the increase in the logarithm of the strain rate. Moreover, the increasing tendency decreases with temperature. It is found that a strain rate-temperature superposition holds for the tensile strength of both resins.

Novel polyarylate and aromatic polyamide resins have higher heat stability and mechanical properties being almost the same as ones of the conventional matrix. Thus, these resins are expected as recyclable matrix resins for FRP.

REFERENCES

- [1] Y. Kubota, K. Takeuchi, T. Hanaoka, and Y. Sugi, *Catal. Today*, **31**, 27 (1996).
- [2] Y. Kubota, K. Takeuchi, T. Hanaoka, and Y. Sugi, *Bull. Chem. Soc. Jap.*, **67**, 563-571 (1994).
- [3] Y. Sugi, K. Takeuchi, T. Hanaoka, S. Takagi, and Y. Doi, *Sekiyu Gakkaishi*, **37**, 70 (1994).
- [4] Y. Sugi, Y. Kubota, and S. Nakada, *Mater. Trans.*, **43**, 326 (2002).
- [5] Y. Ishigure, T. Yamauchi, Y. Kubota, Y. Sugi, M. Miwa, and M. Niikawa, *J. Adv. Sci.*, **13**, 398 (2001).
- [6] N. Ogata et al., "Koubunshi Shinsozai Binran", Ed by Koubunshi-gakkai, Syubidou Co. Ltd. Press, Tokyo (1989) pp.530-545.
- [7] K. Ishikawa et al., "Saishin Koubunshizairyō Gijutsusouran", Ed by Saishin Koubunshizairyō Gijutsusouran Hensei-iinkai, Bikousya Co. Ltd. Press, Tokyo (1988) p.458.
- [8] M. Minoru, N. Ohsawa, and K. Sato, *Sen'i Gakkaishi*, **41**, 78 (1985).

(Received October 10, 2003; Accepted October 31, 2003)