DETERMINATION OF TIME-TEMPERATURE SHIFT FACTOR FOR LONG-TERM LIFE PREDICTION OF POLYMER COMPOSITES

K. Fukushima*, H. Cai**, M. Nakada*** and Y. Miyano***
* Graduate School, Kanazawa Institute of Technology
7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan
fukusima@venus.kanazawa-it.ac.jp
** School of Materials Science and Engineering, Xi'an Jiaotong University
28 Xianningxi Road, Xi’an, Shaanxi,710049, China
*** Materials System Research Laboratory, Kanazawa Institute of Technology
3-1 Yatsukaho, Hakusan, Ishikawa 924-0838, Japan

SUMMARY

The methodology for accurately determining the time-temperature shift factor used in the accelerated testing for the long-term life prediction of polymer composites is proposed in this paper.

Keywords: Polymer composites, Life prediction, Viscoelasticity, Time-temperature superposition principle

INTRODUCTION

In recent years materials that possess high specific strength and specific modulus were developed to fulfill the need for advanced lightweight structures. Fiber reinforced plastics (FRP) are materials that have these properties, and are being used in structures as primary as well as secondary load carrying members. Therefore, the development of a testing procedure to evaluate the lifetimes of materials in extreme service environments is becoming a high priority.

The stress-strain relation of polymer resin exhibits time and temperature dependence, called viscoelastic behavior, not only above the glass-transition temperature T_g but also below T_g. Thus, it can be presumed that the mechanical behavior of FRP also depends on time and temperature even below T_g which is within the normal operating-temperature range. These examples have been shown by Aboudi *et al.* [1], Gates [2], Rotem *et al* [3].

With service lifetimes measured in years, it is almost unthinkable to do real time testing under a variety of conditions. Accelerated testing methodologies for metals have been studied for some time. One of the most popular tools used to predict the fatigue life of metals is the S-N curve, which is based on the assumption that fatigue life depends on cycles, but not on time. Therefore, the cyclic loads can be applied at much higher frequencies than the actual loading to accelerate the fatigue test. Unlike metals, polymer composites are viscoelastic and their properties exhibit strong time and temperature dependencies as mentioned above. Since time plays an important role in the fatigue and creep of polymer composites, simply applying the S-N curve to polymer composites will not provide accurate prediction of the fatigue life.

We proposed the accelerated testing methodology (ATM) based on the time-temperature superposition principle (TTSP) for polymeric materials. This principle was originally developed for non-destructive material properties, but our recent studies have shown that it can also be applied to failure properties of composite materials [4-6]. In this case, elevated temperature states are used to accelerate the mechanical degradation, which occurs under loads over long period of time at lower temperature. We predicted the fatigue strengths of various kinds of FRP and structures under various types of loading methods using our methodology to discuss their applicability [7].

In this paper, the methodology for accurately determining the time-temperature shift factor used in ATM for the long-term life prediction of polymer composites is proposed and experimentally demonstrated.

ACCELERATED TESTING METHODOLOGY

Our ATM which rests on the three hypotheses, (A) same TTSP for all strengths, (B) linear cumulative damage law for monotonic loading, and (C) linear dependence of fatigue strength upon stress ratio. When these hypotheses are met, the fatigue strength under an arbitrary combination of frequency, stress ratio, and temperature can be determined based on the following test results: (a) master curve of strength under constant strain-rate (CSR) loading and (b) master curve of fatigue strength for zero stress ratio as shown in Fig. 1. The master curve of CSR strength is constructed from the test results at single strain-rate and various temperatures. On the other hand, the master curve of fatigue strength at zero stress ratio can be constructed from the test results at single frequency for various temperatures based on the hypothesis (A). The details of ATM can be obtained from our published paper [7].

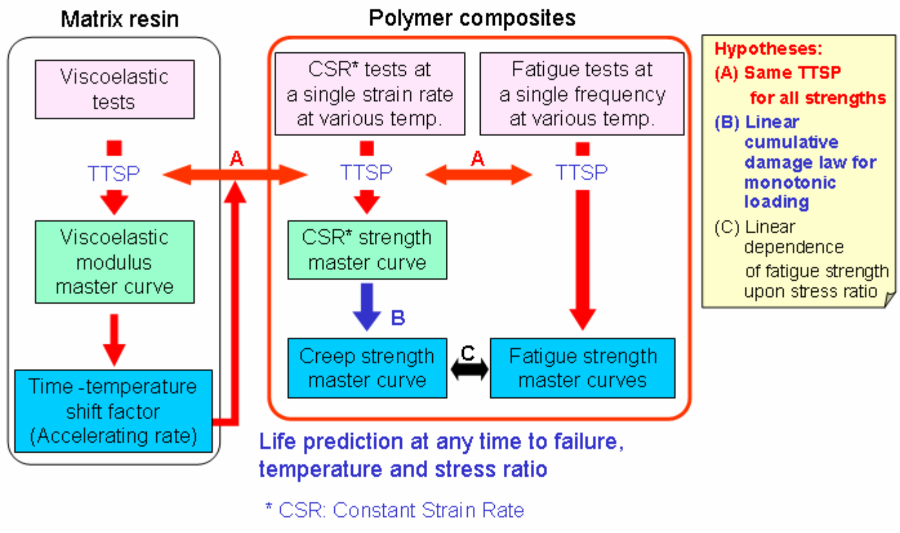


Figure 1 Accelerated testing methodology (ATM)

DETERMINATION OF TIME-TEMPERATURE SHIFT FACTOR

Inside of the frame of Fig. 2 shows the storage modulus E' versus time t (inverse of frequency) at various temperatures T (T_1~T_3) for matrix resin. The master curve of E' versus the reduced time t' was constructed by shifting E' at various constant temperatures along the log scale of t and the log scale of E'. The horizontal time-temperature shift factor $a_{T0}(T)$ and the vertical temperature shift factor $b_{T0}(T)$ at a reference temperature T_0 plotted in Fig. 3 are respectively defined by following equation.

$$\log a_{T0}(T) = \log t - \log t' \tag{1}$$

$$\log b_{T0}(T) = \log D_C(t,T) - \log D_C(t',T_0) \tag{2}$$

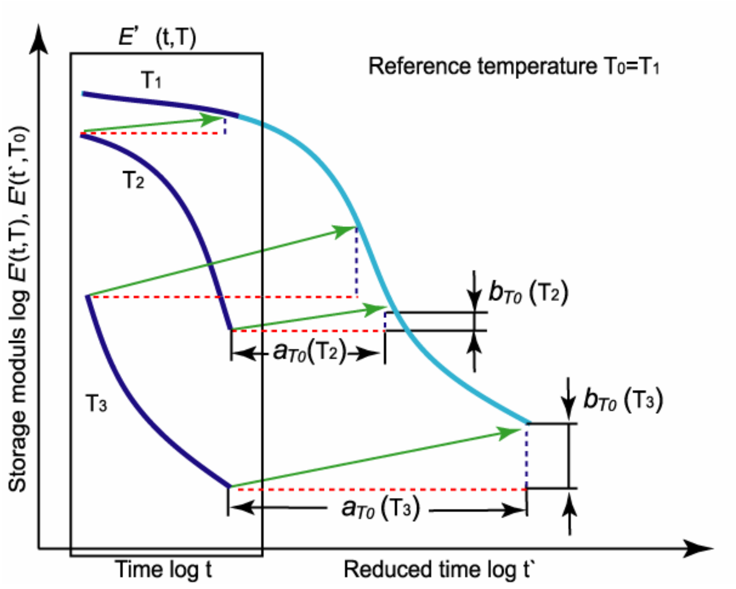


Figure 2 Master curve of storage modulus

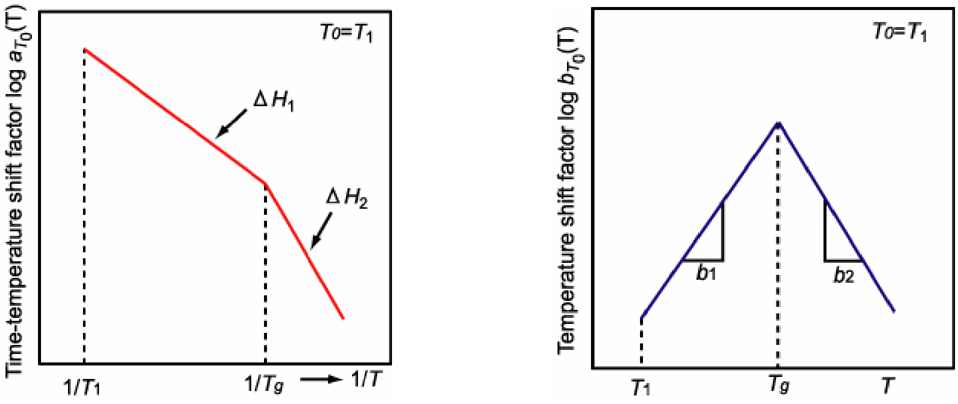


Figure 3 Time-temperature shift factor $a_{T0}(T)$ and temperature shift factor $b_{T0}(T)$

To determine accurately the time-temperature shift factor in TTSP, we propose the following steps:

(1) To evaluate the influence of physical aging on the viscoelastic modulus of matrix resin during the accelerated testing,

(2) To determine the post curing conditions of specimen based on (1),

(3) To measure the viscoelastic modulus at various times and temperatures for specimens which are cured at conditions obtained in (2),

(4) To construct the master curve of viscoelastic modulus using the measured data in (3) without personal errors.

At the time of master curve creation, the automatic shift program was used. For example shown in Fig. 4, the auto-shift will shift the creep compliance curve measured at T_2 horizontally and vertically to that at T_1 with a_{To} and b_{To}, respectively, to minimize the sum of the deviations ($\Sigma\Delta y_i$) from the fitted curve $y = a_2'x^2+a_1'x+a_0'$. The fitting parameters a_2, a_1, and a_0 are finally determined after shifting.

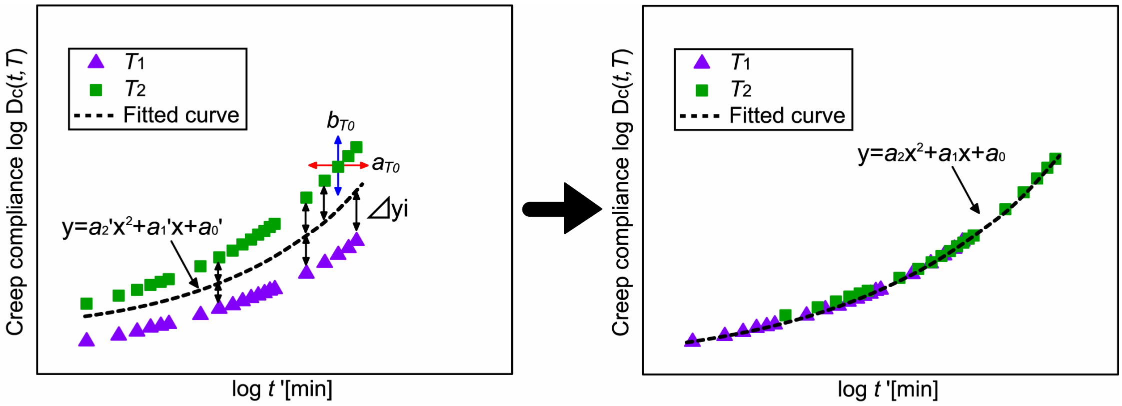


Figure 4 Principle of automatic shift

EXPERIMENTS

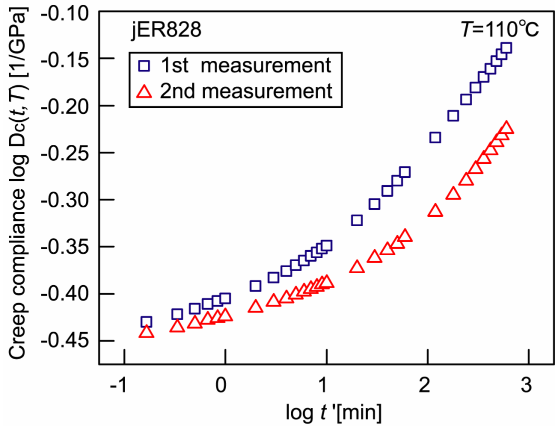
Preparation of Specimens

The epoxy resin used in this study consists of deglycidyl ether of bis-phenol A (jER828), metylnadic anhydride, and 2-ethyl-4-methyl-imidazole as shown in Table 1. Epoxy resin was cured by casting with a cure schedule of 70°C for 12 hours, 150°C for 4 hours, 190°C for 2 hours followed by a slow cooling at 0.5°C per minute. By these heat treatments, the specimens were stabilized chemically during the accelerated testing. The specific volume of polymer resins consists of the occupied volume and the free volume [8]. The occupied volume is the volume occupied by molecular chains and the free volume is the space which permits movement of molecular chains. The free volume decreases moderately and the thermodynamic equilibrium state is approached with the passage of time. This behavior is called physical aging.

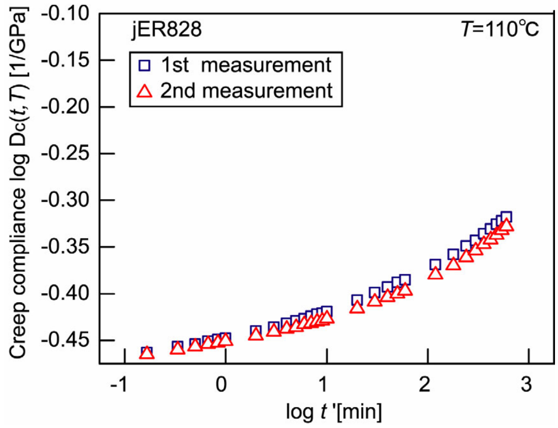
If physical aging of resin progresses during the accelerated testing, the viscoelastic property of resin will be influenced. In this study, specimens were put into the constant temperature chamber under 120°C for 50 hours after curing to conduct physical aging before the accelerated testing. We confirmed that the creep compliance of epoxy resin without aging treatment (120°C for 50 hours) which measured in 2nd times decreases remarkably during the creep test at 110 °C as shown in Fig. 5 (a). On the other hand, the creep compliance of epoxy resin with aging treatment which measured in 2nd times decreases scarcely during the creep test at 110 °C as shown in Fig. 5 (b).

Table 1 Molding condition for epoxy resin

Composition	
Epoxy resin : jER828	100
Hardener : MHAC-P	103.6
Cure accelerator : 2E4MZ	1
Cure schedule	
70℃×12h+150℃×4h+190℃×2h	



(a) Measured by using specimen without aging treatment



(b) Measured by using specimen with aging treatment

Figure 5 Creep compliance of epoxy resin

Viscoelastic Test

The creep compliance and storage modulus of epoxy resin were obtained as the viscoelastic modulus. The creep compliance was obtained by the creep test machine which can measure the viscoelastic deformation precisely. Three point bending creep tests for epoxy resin were carried out under various temperatures using an creep testing machine with temperature chamber. The creep compliance D_c was calculated from the deflection δ at the center of specimen using the following equation.

$$D_C = \frac{4bh^3\delta}{P_0 L^3} \tag{3}$$

where P_0 is dead load which is decided as the strain at the center of the specimen less than 1%. L is the span (50mm), and b and h are the width (25mm) and the thickness (3.0mm) of specimen, respectively.

The storage modulus was obtained by the dynamic mechanical analyzer (DMA) which can evaluate easily the storage modulus in wide ranges of temperature and frequency. The strain amplitude of 0.06% by the sinusoidal wave with frequency range of 0.01-10Hz was applied to specimen. The width, thickness and length of specimen are 6.4mm, 1.6mm, and 44.5mm, respectively. The span is 38mm.

RESULTS AND DISCUSSION

The left sides of Figs. 6 and 7 show the creep compliance D_c and the storage modulus E' versus time t at various temperatures T of epoxy resin. The master curves of D_c and E' versus the reduced time t' were constructed by shifting D_c and E' at various constant temperatures along the log scale of t and the log scale of D_c and E' as shown in the right sides of Figs. 6 and 7. Since D_c and E' at various temperatures can be superimposed smoothly, TTSP is applicable for D_c and E'.

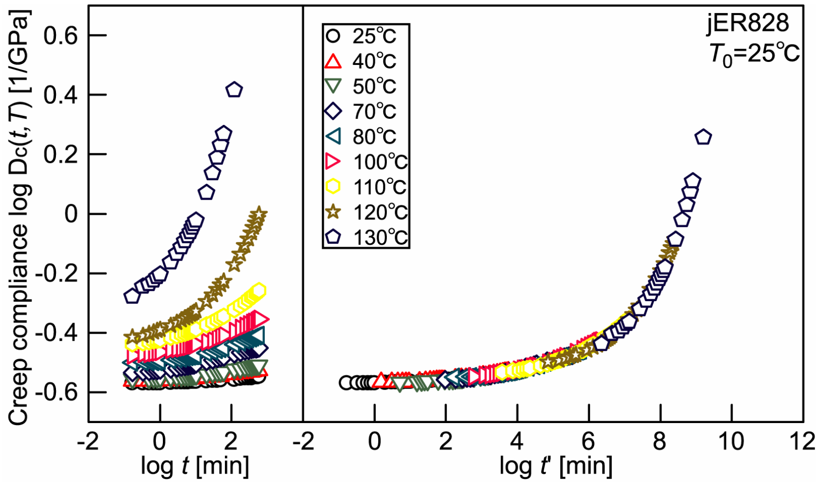


Figure 6 Master curve of creep compliance of epoxy resin

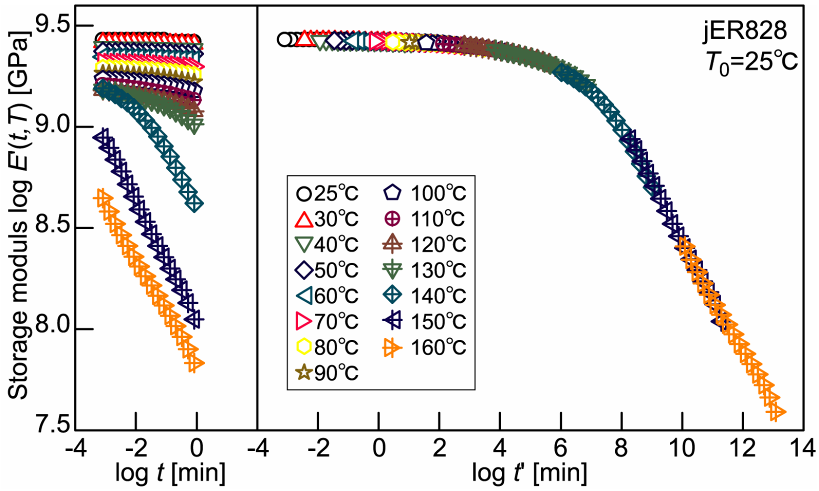
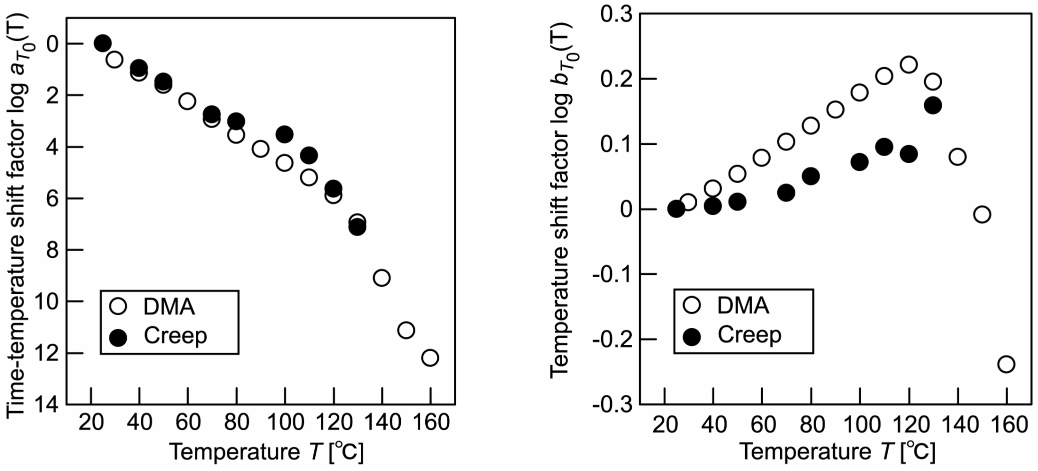


Figure 7 Master curve of storage modulus of epoxy resin

Figure 8 shows the time-temperature shift factor a_{T_0} and the temperature shift factor b_{T_0} those obtained from the master curves of D_c and E', respectively. The a_{T_0} obtained from DMA and creep test agree well with each other, while the b_{T_0} do not agree with each other. The difference in the b_{T_0} from DMA and creep test was caused by the loading method.



(a) Time-temperature shift factor $a_{T_0}(T)$

(b) Temperature shift factor $b_{T_0}(T)$

Figure 8 Shift factors obtained from master curves of D_c and E'.

The master curves of compliance obtained from DMA and the creep test are shown in Fig. 9, where the compliance from DMA is the inverse of E'. The master curves from DMA and creep test do not agree with each other, however those shapes are almost same. From these results, it can be considered that the time-temperature shift factor is obtained accurately and easily by using DMA.

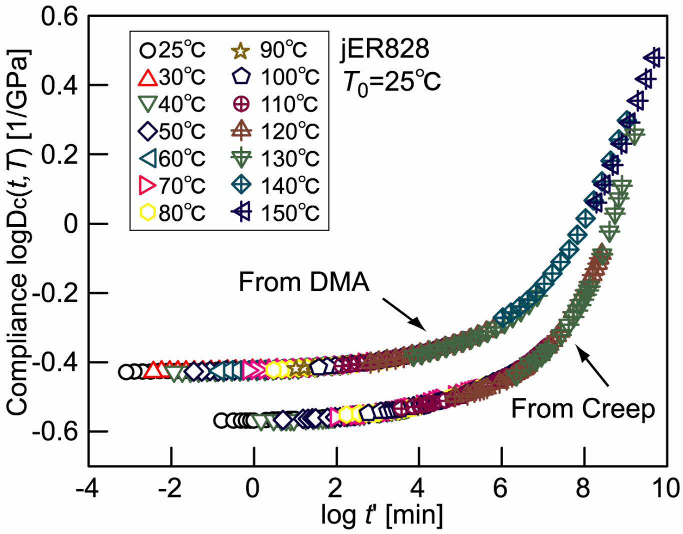


Figure 9 D_c of creep test and DMA

CONCLUSION

This paper is concerned with the accurate determination of the time-temperature shift factor used in the accelerated testing for the long-term life prediction of polymer composites. Aging treatment is performed to the specimen before the accelerated testing, and the specimen is stabilized physically. The dynamic viscoelastic test and creep test were performed as the accelerated testing to measure the storage modulus and the creep compliance, respectively. The master curves of the storage modulus and the creep compliance were constructed by the automatic shift program and the time-temperature shift factor is determined without personal errors. From the comparisons of both test results, it can be considered that the time-temperature shift factor is obtained accurately and easily by the dynamic viscoelastic test.

REFERENCES

1. Aboudi, J. and Cederbaum, G., Analysis of Viscoelastic Laminated Composite Plates, Composite Structures, 12 (1989) 243-256.Sullivan, J., Creep and Physical Aging of Composites, Composite Science and Technology, 39 (1990) 207-232.
2. Gates, T., Experimental Characterization of Nonlinear, Rate Dependent Behavior in Advanced Polymer Matrix Composites, Experimental Mechanics, 32 (1992) 68-73.
3. Rotem, A. and Nelson, H. G., Fatigue Behavior of Graphite-Epoxy Laminates at Elevated Temperatures, Fatigue of Fibrous Composite Materials, ASTM STP 723 (1981) 152-173.
4. Miyano, Y., Kanemitsu, M., Kunio, T. and Kuhn, H., Role of Matrix Resin on Fracture Strengths of Unidirectional CFRP, Journal of Composite Materials, 20 (1986) 520-538.

5. Miyano, Y., McMurray, M. K., Kitade, N., Nakada, M. and Mohri, M., Role of Matrix Resin on the Flexural Static Behavior of Unidirectional Pitch-based Carbon Fiber Laminates, Advanced Composite Materials, 4 (1994) 87-99.
6. Miyano, Y., McMurray, M. K., Enyama, J. and Nakada, M., Loading Rate and Temperature Dependence on Flexural Fatigue Behavior of a Satin Woven CFRP Laminate, Journal of Composite Materials, 28 (1994) 1250-1260.
7. Miyano, Y., and Nakada, M., Cai, H., “Formulation of long-term creep and fatigue strengths of polymer composites based on accelerated testing methodology”, Journal of Composite Materials, Vol.42, pp.1897-1919 (2008).
8. J. D. Ferry, "Viscoelastic Properties of Polymers", 218, John Wiley & Sons, Inc., 1961.