

## Strength of Epoxy Polymers. I. Effect of Chemical Structure and Environmental Conditions

T. K. KWEI, *Bell Telephone Laboratories, Incorporated,  
Murray Hill, New Jersey 07971*

### Synopsis

The breaking times of two crosslinked epoxy polymers under constant stresses were found to decrease at high temperature and humidity. The effect of humidity is, in terms of Bueche's theory, to increase the jump frequency of the polymer segments and to reduce the number of polymer units in cooperative motion in a jump process. When two epoxy polymers with different segment mobilities are compared at a given temperature, the stress-breaking time relationship shifts toward longer times for the polymer with the higher transition temperature. The relation is also applicable in the presence of absorbed water molecules.

### Introduction

One of the recent advances in the understanding of the ultimate properties of amorphous polymers is the experimental and theoretical demonstration of the dependence of the ultimate strength and elongation on the viscoelasticity of the polymers.<sup>1-3</sup> It has been shown that the same equivalence of time and temperature applies to ultimate properties of polymers as one finds for viscoelastic properties. Review of this concept and its application to the study of elastomers was written by Halpin<sup>4</sup> recently. In contrast, highly crosslinked polymer networks which are outside the scope of rubber elasticity have been studied less extensively. Kaelble<sup>5</sup> measured the tensile strength and ultimate elongation of two epoxy polymers and fitted the data to the WLF equation in the appropriate temperature range. However, the measurement of breaking time  $t_b$  at constant stress, which is an alternate way of expressing ultimate properties and has the advantage of obtaining actual data at long times, has not been popular in the study of highly crosslinked polymers. Data in the transition region are especially scarce. We would like to report some preliminary results on the breaking times of two epoxy polymers in the transition regions. The effect of humidity on  $t_b$  will also be described.

As will be mentioned later, the fracture of these materials in our experiments is often accompanied by a highly localized deformation which is nevertheless very small in magnitude if the per cent deformation is calculated on the basis of the whole sample. The ultimate strain and the energetics of fracture are not easily measurable under these conditions. There-

fore, we have avoided the use of theories based on strain<sup>4,6,7</sup> or stored energy<sup>8</sup> in the treatment of our data. Instead, we resort to the simple theory by Bueche<sup>3</sup> which requires only a knowledge of two experimental quantities, stress and breaking time.

In Bueche's treatment,<sup>3</sup> the time to break  $t_b$  is related to the segment jump frequency  $\phi$ . In his model, the polymer chain passes through the cross-section of the sample at a number of places. At the beginning of the application of the stress, each segment that passes through the cross-section contributes to the support of the load. The number of load-bearing segments decreases with increasing time as a result of chain relaxation, i.e., the chain elongates and passes through the cross-section less frequently. The relaxation time is related to  $\phi$ . If all the segments are equally stressed and each can support a load  $F$ , the sample will break when the product of  $F$  and the number of load bearing segments is equal to the applied stress. It was also shown by Bueche that the time required for actual bond breakage is insignificant compared to the time consumed in the relaxation process leading to the break. The equation relating the stress  $\sigma$  to the breaking time  $t_b$  is:

$$\sigma = -(kT/V) \ln \phi t_b + \psi \quad (1)$$

where

$$\psi = (kT/V) \ln (2F^2/\pi^2\sigma^2V^{1/2}) \quad (2)$$

In the above equations,  $V$  is the volume of a segment,  $k$  is the Boltzmann constant, and the function  $V$  is nearly constant. (A segment as meant here may contain many repeating units which participate in the relaxation process as one statistical entity.) According to eq. (1), a plot of  $\sigma$  versus  $\ln t_b$  yields a straight line, from the slope of which  $V$  may be calculated. The intercept of the straight line on the abscissa is determined by  $\psi$  and  $\phi$ .

In this report, we would like to describe the results of our study of the breaking time of crosslinked epoxy polymers as a function of structure and environmental conditions, namely temperature and humidity. The experimental data are discussed in terms of Bueche's theory.

### Experimental

4,4'-Bisglycidylphenyl-2,2'-propane (DER 332LC from Dow Chemical Co.), 1,6-hexanediamine (HMDA) from Eastman Organic Chemicals, and 2,2'-diaminodiethylamine (DETA) from Aldrich Chemical Co. and redistilled at 203–204°C. were used. Stoichiometric quantities of 4,4'-bisglycidylphenyl-2,2'-propane and each amine were mixed and allowed to polymerize slowly on standing. When the viscosity of the mixture reached a suitable level, films of 2–5 mils in thickness were drawn on tin foils by means of a Gardner gage. The films were allowed to stand in a desiccator for 24 hr. and then at 70°C. for 17 hr.

The procedure for the measurement of breaking time is as follows. A strip of film was fastened between two clamps. The upper clamp rested

on a rigid support. Prior to the experiment in dry air, the sample was conditioned at the desired temperature in an oven for at least 1 hr. When the experiment was carried out in an atmosphere of 100% R.H., the sample was placed in a covered bell jar which contained a bottle of water and was conditioned for at least one day to allow the attainment of sorption equilibrium of water vapor by the sample. A fixed weight was then attached to the lower clamp and the time to break was recorded.

The glass transition temperatures of the polymers were determined from dynamic mechanical properties by a torsional pendulum.<sup>9</sup> The temperatures of damping maxima are 52 and 76°C. for the HMDA and the DETA crosslinked polymers, respectively.

### Results and Discussion

In all our experiments, the fracture surfaces appeared to be sharp and straight by visual observation. In several cases, the length of the sample was checked periodically during the experiment. The extent of creep was invariably too small to be measured except perhaps at 80°C. for the HMDA polymer. When the fractured samples were reexamined, the cross-sectional areas at and near the fracture surfaces were found to have decreased by 5–20%. However, at a distance of about 1/20 in. from the fracture surface the cross-sectional area remained unchanged. It is likely that deformation occurs immediately before or during the macroscopic fracture propagation and is limited to a small area near the source of fracture. For the purpose of illustration, both the initial stress and the stress based on the final cross-sectional area at the fracture surface will be given for the HMDA polymer in this report.

The dependence of the breaking time on the applied stress for the HMDA polymer at several temperatures, with or without water vapor, is shown in Figure 1. Let us first describe the results in dry air. The plot at 24°C. has a relatively flat region at large stresses and short breaking times; it then shows a downward curvature as the breaking times become large at lower stresses. The flat region at 40°C. is less well defined than that at 24°C. and occurs at lower stress levels. At higher temperatures, the flat portions of the  $\sigma$  versus  $\log t_b$  plots seem to occur at  $t_b$  values considerably less than one minute and can not be located accurately by our experimental procedure. Within the ranges of  $t_b$  in our study, the relations between  $\sigma$  and  $\log t_b$  are linear at 50–60°C. At 80°C. the plot levels off with a slight concave curvature toward the  $\log t_b$  axis. It is apparent from Figure 1 that at any given  $t_b$  the ultimate stress decreases with increasing temperature. At each temperature, there appears to be a lower limit of stress, shown as a dotted line in Figure 1, below which the breaking time exceeds 500 hr. This lower limit of stress also decreases with increasing temperature.

Figure 2 shows the same data for the HMDA polymer in dry air replotted with stress values based on the final cross-sectional areas of the fracture surfaces. As mentioned previously, the final stresses are higher than

the initial stresses. In addition, the plot of final stress versus  $\log t_b$  is now substantially linear at 40°C., and the slope of the straight line is identical to those at 50 and 60°C. The use of final stress values appears to have some merit because these parallel lines can be shifted along the time axis to form a master curve which is also shown in Figure 2. The 50°C. line is

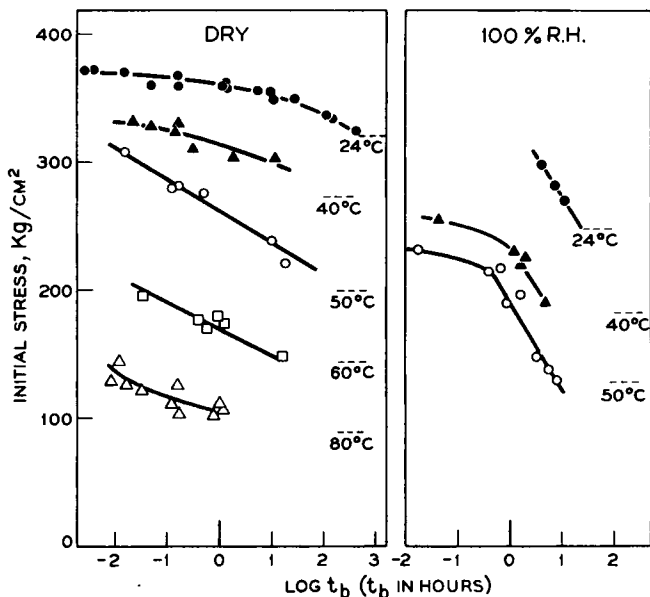


Fig. 1. Relationship between stress and breaking time of the HMDA-crosslinked epoxy polymer.

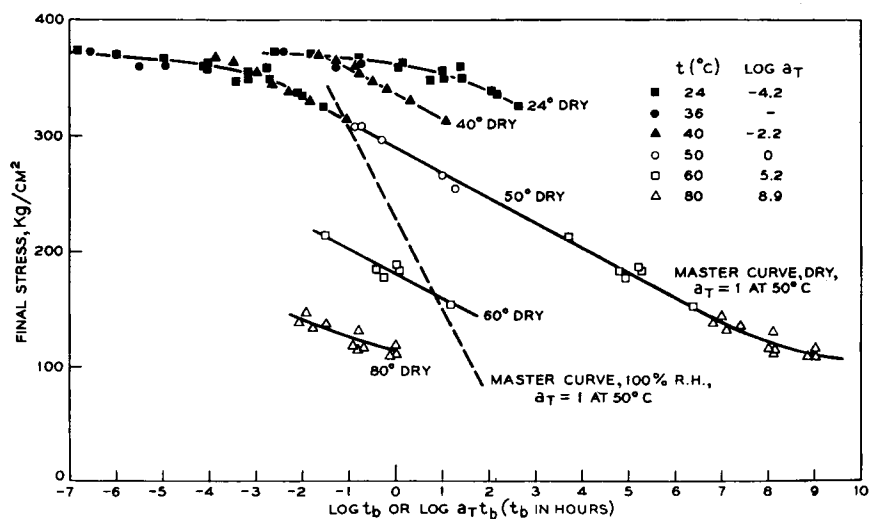


Fig. 2. Master curves of  $\sigma$ - $\log t_b$  plots of the HMDA polymer.

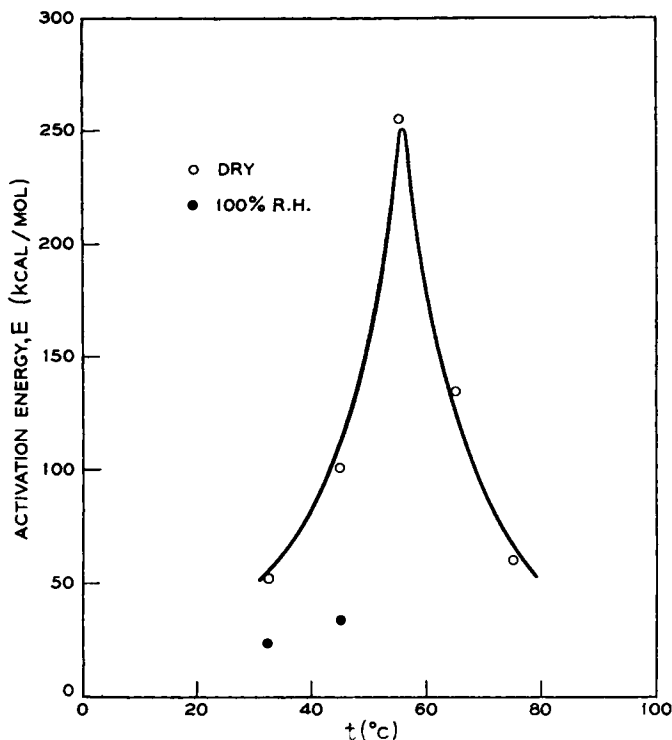


Fig. 3. Apparent activation energies of fracture of the HMDA polymer.

used as reference, i.e., the shift factor  $a_T$  is unity at 50°C. which is approximately the glass transition temperature of the polymer.

The apparent activation energy  $E$  of the molecular process responsible for the fracture may be calculated from the temperature dependence of the shift factor by eq. (3):

$$E = R d \ln a_T / d(1/T) \quad (3)$$

The variation of the apparent energy of activation with temperature for the HMDA polymer in dry air is shown in Figure 3. Both the shape of the  $E-T$  curve and the magnitude of the activation energies are similar to those found by Bueche<sup>10</sup> in his study of breaking time and viscous flow of poly-(methyl methacrylate) and by McLoughlin and Tobolsky<sup>11</sup> in the study of stress relaxation of the same polymer. A maximum in the  $E-T$  curve is found at about 55°C., near the transition temperature of 52°C. The occurrence of the maximum was attributed by Bueche to the rapid change in the local liquid structure near the transition temperature.<sup>10</sup>

The shape of the master curve for the HMDA polymer in dry air, as shown in Figure 2, resembles those of the stress relaxation curves with a box distribution.<sup>12</sup> The central portion of the master curve is a straight line connecting two plateau regions at high and low stress levels, respectively,

which are separated by a time scale of more than ten decades. Using Tobolsky's notation, one may write an expression for the ultimate strength data:

$$\sigma = \int_{-\infty}^{\infty} H \exp \{ -t/\tau \} d \ln \tau \quad (4)$$

where  $H$  is the distribution of relaxation times  $\tau$ . In the linear portion of the curve,

$$-d\sigma/d \log t = 2.3H = 21.5 \text{ kg./cm.}^2 \quad (5)$$

where  $2.3H$  is the height of the box distribution. It would be of future interest to measure the stress relaxation of the same polymer and compare its distribution function with the above calculation derived from ultimate strength data.

We now return to eq. (1) by Bueche for the analysis of  $t_b$ . From the slope of the linear plot of  $\sigma$  versus  $\log t_b$  the quantity  $V$ , which is volume of the segment in the relaxation process, is obtained as  $3830 \text{ \AA.}^3$  or  $(15.7 \text{ \AA.})^3$  for the HMDA polymer in dry air. This is to be compared with Bueche's value<sup>5</sup> of  $(13 \text{ \AA.})^3$  for polystyrene and polymethacrylate. It is understandable that, in our highly crosslinked polymer, the cooperative motion of many more units may be required in the relaxation process and the volume of the segment is correspondingly larger.

At 100% R.H., the HMDA samples break at lower stresses (Fig. 1). At the same stress levels, the breaking times are often shorter by two orders of magnitude. The lower stress limit below which the breaking time becomes inordinately large is also reduced. The apparent activation energies are  $1/2$  to  $1/3$  as large (Fig. 3). The slope of the  $\sigma$  versus  $\log t_b$  plot is much steeper, and the quantity  $V$  is  $1435 \text{ \AA.}^3$  or  $(11.3 \text{ \AA.})^3$ , only about 38% of the value in dry air. The decrease in the value of  $V$  implies that the number of units moving cooperatively as a segment is less and hence the mobility of the polymer chain increases in the presence of absorbed water molecules. This is also consistent with the lower activation energies found for the wet conditions.

The jump frequency  $\phi$  at a given temperature may be calculated by inserting appropriate values of  $\sigma$ ,  $t_b$ ,  $V$ , and  $F$  (taken as  $5 \times 10^{-4}$  dyne by Bueche) in eq. (1). The calculated value of  $\phi_w$  is many orders of magnitude larger than  $\phi_d$ , where the subscripts  $w$  and  $d$  denote wet and dry conditions, respectively. Although caution must be exercised in dealing with the absolute value of  $\phi$  owing to the nature of the approximations inherent in the simplified model, it seems instructive to compare the ratio of the two  $\phi$  values. The ratio at  $50^\circ\text{C.}$  is:

$$\log \phi_w / \phi_d = 8.2 \quad (6)$$

The increase in  $\phi$  under wet conditions is again consistent with the decreases in  $E$  and  $V$ . It is suggested that water molecules may interact with the hydroxyl groups which are engaged in interchain hydrogen bonding in

the epoxy polymer. The disruption of the interchain hydrogen bonding may conceivably impart greater degree of mobility to the polymer chain.

According to the theory of transport in liquids by Cohen and Turnbull,<sup>13</sup> the jump frequency may be formulated in terms of the free volume concept as follows:

$$\phi = B \exp \left\{ -v^*/v_f \right\} \quad (7)$$

where  $v_f$  is the average free volume of the liquid molecule,  $v^*$  is the critical amount of free volume associated with the transport process to permit the molecule to jump to a new position, and  $B$  is a proportionality constant. An increase in  $\phi$  can result from changes in both  $v^*/v_f$  and  $B$ . It is of interest to estimate the relative contribution of these two terms to the increase in  $\phi$  under wet conditions. The ratio  $v^*/v_f$  may be viewed as a measure of the number of molecules participating in the cooperative motion and its physical meaning is perhaps the same as Bueche's  $V$  divided by the volume of a polymer repeating unit,  $v_u$ . The two parameters  $V$  and  $\phi$  in Bueche's equation are therefore interrelated in this sense.

For vinyl polymers, the values of  $v_u$  are often in the neighborhood of 100–150 Å.<sup>3</sup> In the epoxy polymer it is somewhat difficult to define a repeating unit. If the value of  $v_u$  is taken as 150 Å.<sup>3</sup> for the HMDA polymer and the term  $v/v_u$  is equated to  $v^*/v_f$ , then the difference in the value of  $v^*/v_f$  in the dry and the wet conditions may be obtained as:

$$(v^*/v_f)_d - (v^*/v_f)_w = (V_d/v_u) - (V_w/v_u) = 15 \quad (8)$$

We may now express the ratio  $\phi_w/\phi_d$  in the notation of Cohen and Turnbull:

$$\log \frac{\phi_w}{\phi_d} = \log \frac{B_w}{B_d} + \frac{1}{2.3} \left[ \left( \frac{v^*}{v_f} \right)_d - \left( \frac{v^*}{v_f} \right)_w \right] \quad (9)$$

The term  $\log \phi_w/\phi_d$  is about 8.2 according to eq. (6) and the term  $(1/2.3) [(v^*/v_f)_d - (v^*/v_f)_w]$  is about 6.5 according to eq. (8). Hence the quantity  $\log (B_w/B_d)$  has a value of about 1.7. It appears that the major contribution to the difference in  $\phi_w$  and  $\phi_d$  lies in the fact that the critical free volume  $v^*$  for transport, or the number of cooperative units participating in the jump process, is smaller in the presence of water molecules.

A direct consequence of eq. (1) is that it predicts a large value of  $t_b$ , at a given stress, for a polymer of restricted mobility or low jump frequency  $\phi$ . Conversely, for a given value of  $t_b$ , the less mobile polymer chain is able to sustain a higher stress. To demonstrate the dependence of  $t_b$  on chemical structure, we prepared the DETA polymer. The rigidity of this network is reflected in its high shear moduli<sup>9</sup> and its glass transition temperature of 76°C., in comparison with 52°C. for the HMDA polymer. The results of our experiments with the DETA polymer are shown in Figure 4. The  $\sigma$ - $\log t_b$  plots show very gentle slopes at 40 and 50°C. in dry air. They differ markedly with the HMDA curves at the same two temperatures but are similar to the flat portion of the 24°C. curve of the

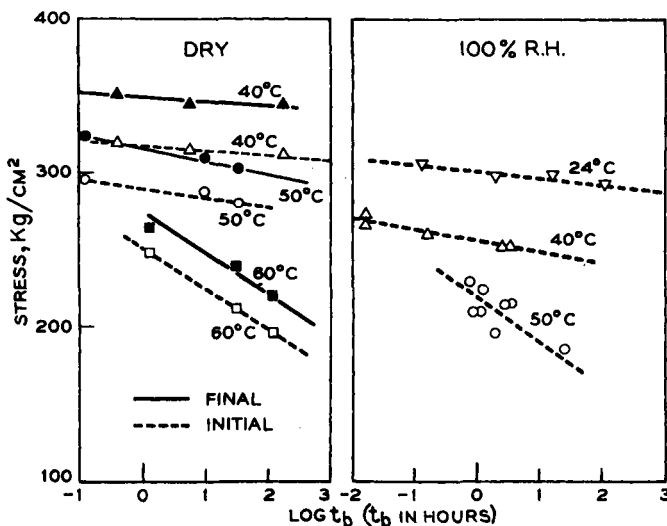


Fig. 4. Stress-breaking time relationships of the DETA-crosslinked epoxy polymer.

latter polymer. The ultimate strengths at very short times are approximately the same for both polymers at these two temperatures; but the DETA polymer retains higher strength at long times, especially at 50°C. The difference in strength is more pronounced at 60°C, which is below the  $T_g$  of the DETA polymer but above the transition temperature of the HMDA polymer. The slope of the stress-time plot for the DETA polymer at 60°C., however, is almost the same as that of the linear portion of the master curve for the HMDA polymer. Thus, the two polymers have nearly the same value of  $V$  as the transition is approached.

The difference in the properties of the two polymers is even more apparent under wet conditions (Fig. 4). Within the time scale of our experiment, the  $\sigma-t_b$  plots of the DETA polymer remain flat at 24 and 40°C. A pronounced increase in the steepness of the plot occurs at 50°C., although the slope still seems to be less than those of the HMDA curves. At each of the three temperatures, the  $t_b$  values for the DETA polymer at low stresses are larger by more than two decades of time than the corresponding values for the HMDA polymer.

### Conclusions

The effect of humidity on the breaking time of an epoxy polymer is, in Bueche's terminology, to increase the jump frequency  $\phi$  of the polymer segments and to reduce the number of polymer units moving cooperatively in a jump process.

When the properties of two epoxy polymers with different segmental mobilities are compared at a given temperature, the  $\sigma-t_b$  relationship shifts toward longer times for the polymer with the higher  $T_g$ . At a given  $t_b$ , the stress-temperature relationship of the high  $T_g$  polymer shifts to lower



temperatures. This is merely a statement of the time-temperature equivalence principle. It also appears to be valid in the presence of water molecules.

### References

1. F. Bueche, *J. Appl. Phys.*, **28**, 784 (1957).
2. F. Bueche, *J. Appl. Phys.*, **29**, 1231 (1958).
3. F. Bueche, *Physical Properties of Polymers*, Interscience, New York, 1962, Chap. 11.
4. J. C. Halpin, *Rubber Chem. Technol.*, **38**, 263, 1007 (1965).
5. D. H. Kaelble, *J. Appl. Polymer Sci.*, **9**, 1213 (1965).
6. B. D. Coleman and A. G. Knox, *Textile Res. J.*, **27**, 393 (1957).
7. L. H. Tung, *J. Polymer Sci. A*, **3**, 1045 (1965).
8. H. W. Greensmith, *J. Appl. Polymer Sci.*, **8**, 1113 (1964).
9. T. K. Kwei, *J. Polymer Sci.*, in press.
10. F. Bueche, *J. Appl. Phys.*, **26**, 738 (1955).
11. J. McLoughlin and A. V. Tobolsky, *J. Polymer Sci.*, **8**, 543 (1952).
12. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960.
13. M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).

### Résumé

Les temps de rupture de deux polymères époxy pontés sous tension constante ont diminué avec une température croissante et à l'humidité. L'effet de l'humidité est, sur la base de la théorie de Bueche, d'augmenter la fréquence du saut des segments polymériques et de diminuer le nombre d'unités polymériques dans le mouvement coopératif dans ce saut. Lorsque deux polymères époxy avec des mobilités segmentaires différentes sont comparés à une température déterminée, le rapport tension-temps de rupture glisse vers les durées plus grandes pour le polymère qui a la température de transition la plus élevée. Le rapport est également applicable à la présence de molécule d'eau absorbée.

### Zusammenfassung

Die Bruchdauer von zwei vernetzten Epoxypolymeren unter konstanter Spannung nimmt bei hoher Temperatur und Feuchtigkeit ab. Der Einfluss der Feuchtigkeit besteht nach der Theorie von Bueche in einer Erhöhung der Sprunghäufigkeit der Polymersegmente und in einer Herabsetzung der Zahl der Polymerbausteine, die sich bei einem Sprungvorgang in kooperativer Bewegung befinden. Beim Vergleich zweier Epoxypolymerer mit verschiedener Segmentbeweglichkeit bei einer gegebenen Temperatur verschiebt sich die Spannungs-Bruchdauerbeziehung für das Polymere mit der höheren Umwandlungstemperatur zu längeren Dauern. Die Beziehung kann auch bei Gegenwart absorbierter Wassermoleküle angewendet werden.

Received May 9, 1966

Prod. No. 1405