

Impression Recovery of Amorphous Polymers

FUQIAN YANG, SHENGLIANG ZHANG, and JAMES C.M. LI

Materials Science Program, Department of Mechanical Engineering,
University of Rochester, Rochester, NY 14627

The impression made by a loaded cylindrical flat-end punch on a polymer surface was observed to disappear with time at the same temperature after the load was removed. The depth-time relation appeared to obey second order kinetics. The temperature dependence of the rate constant shows two consecutive processes with activation energies, 906 kJ/mole (between 143 and 147°C) and 91 kJ/mole (between 150 and 160°C) for PC (T_g is at about 146°C) and 440 kJ/mole (between 104 and 110°C) and 95 kJ/mole (between 115 and 140°C) for PMMA (T_g is at about 112°C). These activation energies are probably associated with the motion and annihilation of conformational or structural defects of opposite signs. This kind of shape memory phenomena may be general for all amorphous polymers.

Key words: Creep, dimensional recovery, dimensional stability, impression recovery, indentation recovery, PC, PMMA, polymer

INTRODUCTION

The application of chemical kinetics to the recovery of crystalline materials is well known. Examples include the annealing of quenched-in vacancies in gold¹ by the use of first order kinetics and the annihilation of dislocation dipoles² in LiF by using second order kinetics. The second order kinetics were also applied to the recovery of stored energy after deformation³ and to the rate of recrystallization with simultaneous recovery.⁴⁻⁸ Li⁹ reported some annealing experiments on the recovery of shear strain in the coarse shear bands in polystyrene and found second order kinetics applicable in the later part of recovery. It was also found that second order kinetics are valid for the recovery of strain, volume and stored energy for certain polymers.¹⁰⁻¹³

Recently impression and indentation techniques have been used to measure a wide variety of material properties, such as creep resistance,¹⁴⁻¹⁶ stress relaxation,^{17,18} Young's modulus,¹⁹ dimensional recovery,^{10,20}

and even fatigue behavior.²¹ It is the purpose of this note to report the study of impression recovery of PMMA and PC. The dependence of the impression depth on time was recorded and analyzed by second order kinetics. The difference between this study and the usual recovery studies is that most recovery experiments have been done at a temperature higher than the deformation temperature. Since this appears to be the first time that recovery is carried out at the same temperature as the deformation temperature, two common polymers, PC and PMMA are used just to make sure that this phenomenon is not unique for just one polymer.

Impression Recovery of PC

Impression recovery test was performed on PC samples of $15 \times 15 \times 5$ mm³ by using the Rheometric Solid Analyzer (RSA II, Rheometrics, Inc., Piscataway, NJ) and a flat-end cylindrical punch of 0.5 mm diameter. Figure 1 shows the time dependence of the impression depth during loading and unloading at the same temperature. Based on the second order kinetics of the recovery processes,^{10,20} the time depen-

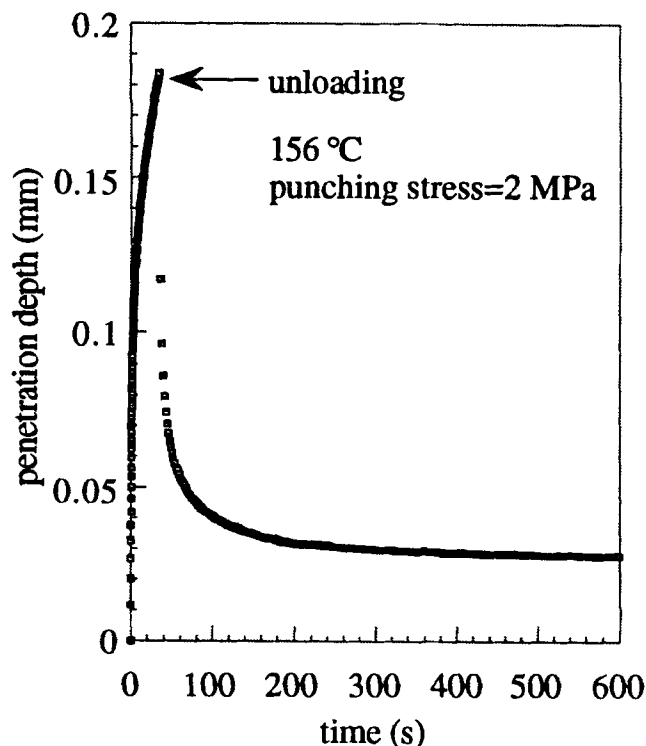


Fig. 1. The variation of impression depth during loading and unloading for PC at 156°C.

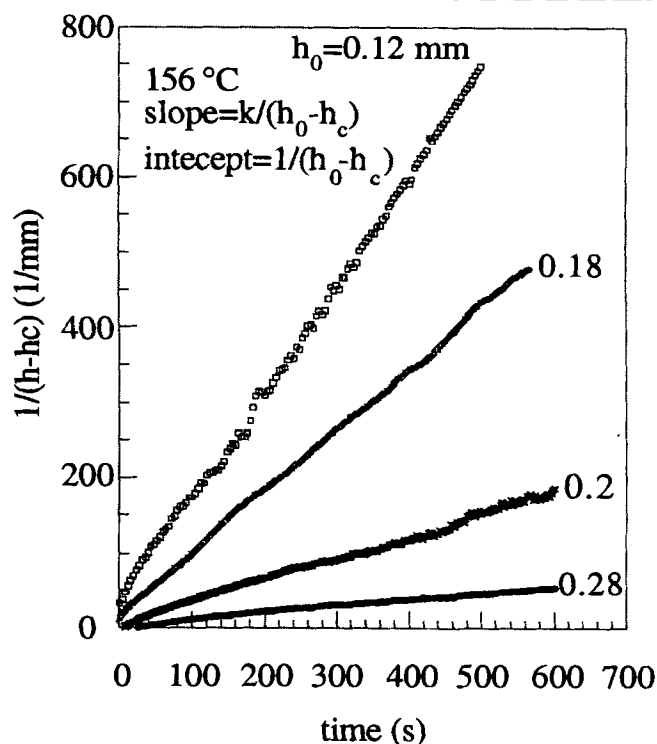


Fig. 2. Time dependence of the reciprocal of recoverable depth for PC at 156°C.

dence of the impression depth can be expressed as follows

$$(h - h_c)^{-1} = (1 + kt)(h_0 - h_c)^{-1} \quad (1)$$

where h is the depth at any time t during recovery, k

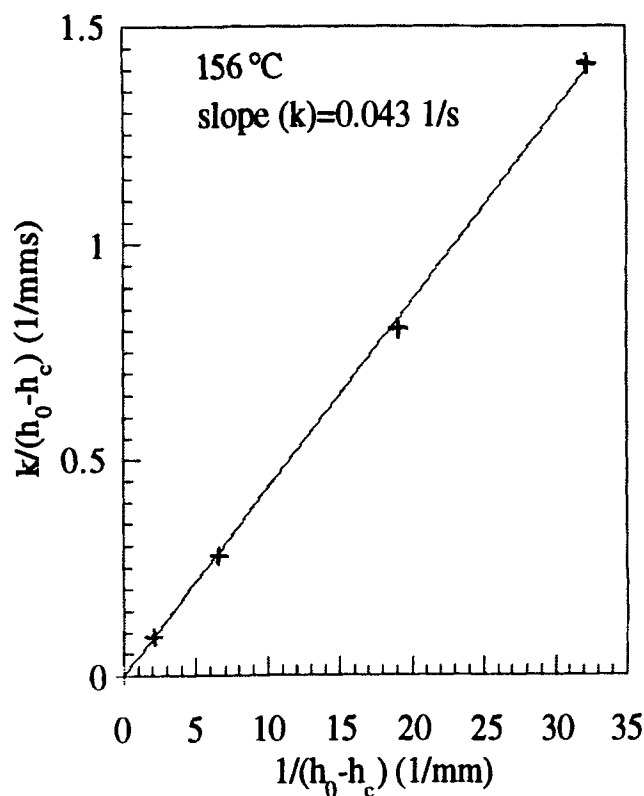


Fig. 3. Evaluation of the second order rate constant for the impression recovery of PC at 156°C.

is the second order rate constant which is independent of the initial impression depth h_0 at the time of unloading before recovery, and h_c is a constant obtained by trial and error which is the residual depth that cannot be recovered. The relation between the reciprocal of recoverable depth and time is plotted in Fig. 2 for a range of initial depths between 0.12 and 0.28 mm, which confirms the validity of Eq. (1) at each initial depth. Figure 3 shows that the second order rate constant is independent of the initial depth.

Based on second order kinetics, the temperature dependence of the second order rate constant is plotted in Fig. 4. by using the Arrhenius equation, the activation enthalpy of the recovery process can be calculated from the slope of the curve at each temperature,

$$\Delta H = -R \frac{d \ln k}{d(1/T)} \quad (2)$$

where ΔH is the activation enthalpy of the recovery process, R is the gas constant, and T is the recovery temperature. From Fig. 4, it is seen that the activation enthalpy is 906 kJ/mol between 143 and 147°C and 91 kJ/mol between 150 and 160°C. The curve is the best fit for $1/k$ by using $1/k_1$ plus $1/k_2$ as required for consecutive processes²² such as shown in Fig. 4.

A comparison of the activation enthalpy data of creep of PC,²³ the recovery data are on the high side of T_g and the creep data are on the low side. As shown by Chiang and Li²⁴ the activation enthalpy appears to have a maximum value at around the glass transition. More measurements are needed to cover a wider

temperature range.

A possible mechanism for second order kinetics is the motion and annihilation of defects such as the excess volumes²⁰ of opposite signs introduced during the impression deformation. The high activation energy at low temperatures and low activation energy at high temperatures indicate two consecutive processes,²² one after the other in order to effect the dimensional recovery. Since complex motions of atoms and atomic groups may be involved in annihilating excess volumes of opposite signs and perhaps other conformational defects of opposite signs, the activation energies may be larger than the usual single atomic processes.

Figure 5 shows the measurement of glass transition temperature by using the temperature sweep of impression test at constant impression depth. It is seen that the applied load decreased with increasing temperature. The glass transition temperature is about 146°C, which is close to 147°C as shown in Fig. 4. This suggests that the recovery mechanism below T_g is different from that above T_g . However, they take place simultaneously but consecutively during recovery.

To see whether the recovery of dimension is due to surface tension, a groove of a depth more than the impression depth used was carefully cut out on the sample surface. Then the sample was annealed at the maximum experimental temperature of 170°C for 1 h (much longer than the recovery testing time). There is no change of the groove depth so the surface tension has no effect on the inelastic recovery of PC below 170°C.

Impression Recovery of PMMA

The same test was conducted on another common polymer, PMMA. Samples of $25 \times 25 \times 7 \text{ mm}^3$ were impression tested by using the same method as described in the previous section. The time dependence of the impression depth during loading and unloading at the same temperature is similar to Fig. 1. The relation between the reciprocal of recoverable depth and time is similar to Fig. 2 for a range of initial depths between 0.12 and 0.28 mm. The second order rate constant is also independent of the initial depth so Eq. (1) is applicable to PMMA also.

The temperature dependence of the second order rate constant shows as in PC two consecutive processes with the activation enthalpies of 440 kJ/mole between 104 and 110°C and 95 kJ/mole between 115 and 140°C. The transition temperature is at about 113°C which is comparable to the glass temperature T_g (about 112°C) measured by a temperature sweep in the impression test at constant displacement similar to Fig. 5 for PC. Conventional creep tests²³ showed an activation enthalpy of 420 kJ/mole at around 97°C and a data point of 440 kJ/mol at 104°C would be consistent with the trend for the temperature effect in creep. However, as pointed out by Chiang and Li,²⁴ the activation enthalpy for creep has a maximum at about the glass transition temperature. What observed here

in recovery is on the branch of decreasing activation enthalpy with increasing temperature.

DISCUSSION

Instead of second order kinetics, a simple spring-

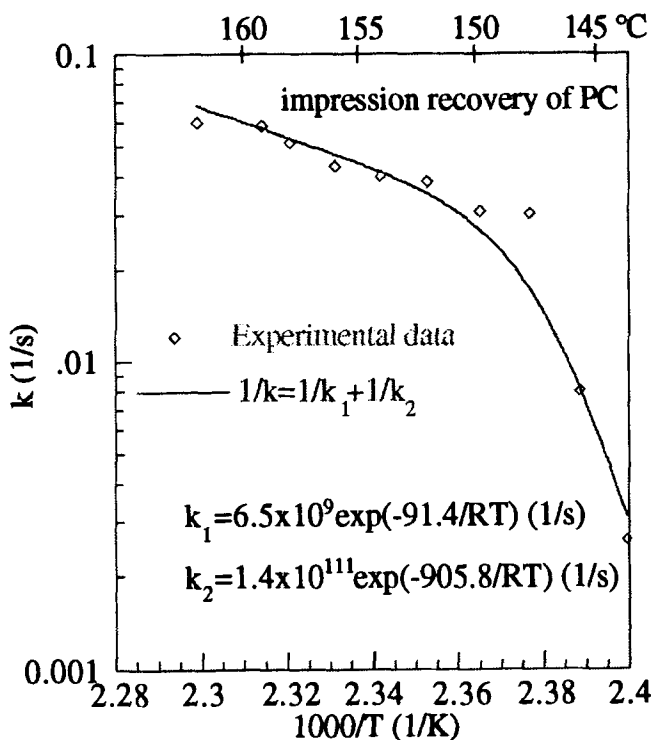


Fig. 4. Temperature dependence of the rate constant.

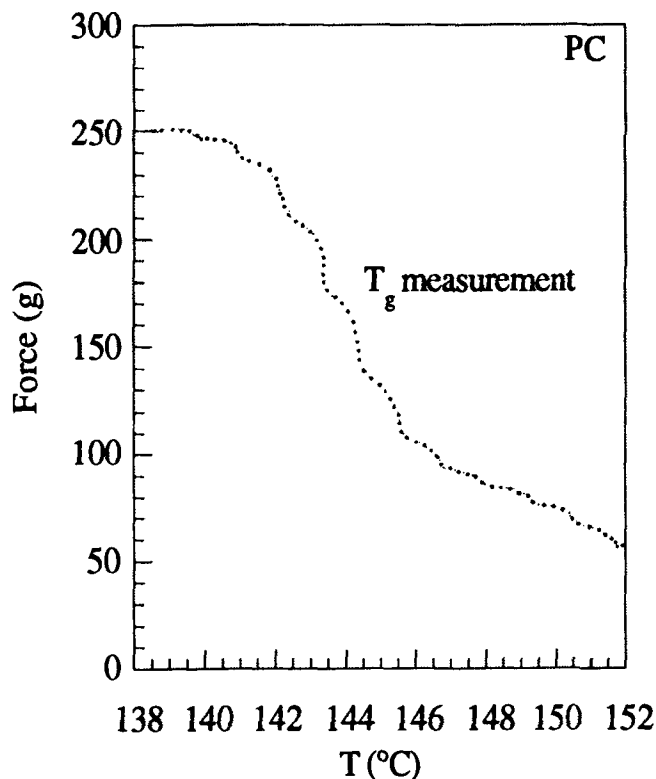


Fig. 5. Temperature sweep of impression test for PC at a heating rate of 20°C/h.

dashpot mechanical model with a Maxwell element connected in series to a Voigt element was set up to simulate the creep-recovery behavior of polymers. However, both linear springs and dashpots and non-linear springs and dashpots cannot explain the recovery phenomena. The use of the Boltzmann superposition principle has been proposed to study recovery processes²⁵⁻²⁸ by using linear spring-dashpot models with the constants being functions of time. However, the Boltzmann superposition principle was not found suitable to the indentation recovery of PS as pointed out by Chang and Li.¹⁰

It is known that plastic deformation underneath the punch is not homogeneous on a microscopic scale, defects of opposite signs may be produced in the plastic zone during loading. Upon unloading these defects may annihilate each other to allow the material to return to its original state. If a direct proportion between the recoverable depth and the defect concentration is assumed, second order kinetic laws are found applicable in both PMMA and PC impression recovery as just shown.

CONCLUSION

Impressions made on PMMA and PC surfaces by a cylindrical punch can recover and even disappear at the same temperature and the depth-time relations follow second order kinetics. The temperature dependence of the second order rate constants gives two activation energies corresponding to two simultaneous processes taking place consecutively. The transition between the two processes takes place at the glass transition temperature. This recovery phenomenon may be common to amorphous polymers since two common polymers already showed it.

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