



Physical Aging of Cyclo Olefin Copolymer (COC)

Wu-Jang Huang^{1,*} and Feng-Chih Chang²

¹National Ping-Tun University of Science and Technology, Department of Environmental Science and Engineering, 91201 Ping-Tun, Taiwan, ROC

²Institute of Applied Chemistry, National Chiao-Tung University, 312 Hsin-Chu, Taiwan, ROC

(* Author for correspondence; E-mail: wjhuang@mail.npust.edu.tw)

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Abstract

The physical aging behaviour of the cyclo olefin copolymer (COC) has been investigated in this paper by using low temperature annealing in differential scanning calorimeter (DSC) measurements. The data of recovered enthalpies was fitted by means of Petrie–Marshall (PM), Cowie–Ferguson (CF) or Kohlrausch–Williams–Watts (KWW) form equation in describing the enthalpy relaxation. We have found that the COC sample has a stretched exponential factor near 1.0 ($\beta = 0.98 \pm 0.02$) at the annealing temperature range.

The apparent activation energy (E_H) of COC aging obtained by using the Petrie/Marshall (PM) analysis method is about 1521.7 ± 150 kJ/mole. That is substantially higher than 308 ± 50 kJ/mole for bisphenol-A polycarbonate, 407.4 kJ/mole for poly (vinyl methyl ether) and 1192 kJ/mole for polystyrene, but close to 1520 kJ/mole for polyterafluoroethylene (PTFE).

Introduction

The super-cooled liquids of amorphous polymers undergo physical aging by annealing above their glass transition temperatures (T_g), which has been well recognized in the past 20 years. The truly mechanism of physical aging is not yet clearly defined but commonly recognized as a structural relaxation process. The main characters of physical aging are enthalpy recovery, free volume recovery and creep relaxation retardation. Mathematical modeling in the kinetics of enthalpy recovery processes have been proposed by Tool and Narayanaswamy (TN), Petrie and Marshall (PM) and Cowie and Ferguson (CF), Adam and Gibbs (AG) et al. Tool and Narayanaswamy (TN) [1] proposed a formalism to describe the structural relaxation of polymer chains that associated with glass transition and extended the Berens–Hodge approach of enthalpy relaxation in his equations. Petrie and Marshall (PM) and Cowie and Ferguson (CF) [2] described the enthalpy relaxation by modifying the Kohlrausch–Williams–Watts (KWW) equation. Adam and Gibbs [3] proposed an entropical interpretation on the relaxation of a supercooled liquid and rubber above its T_g . Scherer and Hodge extended the explanation to link the change of chains' configurations and the conformations during glassy-rubber transitions.

Cyclo olefin copolymer (COC) with norbornene (NB) and ethylene comonomers possessed excellent physical properties, such as high transparency, low moisture content, high T_g and high T_d (decomposition temperature). This novel polymer has a potential application in optical fiber and transparent engineering thermoplastic as well as the polycar-

bonate does. To increase the content of ethylene in COC to increase the higher flow rate of polymer melt, which makes COC have a thermoplastic property that can be processed by extrusion and injection molding [4–7].

In our earlier report, [8] we have demonstrated that the polynorbornene (PNB) and its copolymers can undergo conformational conversion into more stable conformers by thermal annealing above its T_g . The conformational conversion constitutes the nascent stage for the re-ordering process of the COC [5]. Chain reordering by the above T_g annealing was able to induce the conformational conversion leading to the densification of the precipitated COC powder and raises its T_g substantially [8]. This behaviour might be confused with the conventional physical aging behaviour of amorphous polymers because of the practice of physical aging was normally carried out below the T_g of polymer. In this paper, we will explore the physical aging behaviour of a commercial COC product to clarify this issue.

Experimental

Material and Instruments. The COC copolymer was an extruded disc (Topas® # 6015 COC) manufactured by Hoechst Ticona. The enthalpy relaxation measurements were carried out using a Perkin-Elmer DSC, model DSC-7, with a thermal analysis data analyzer and an isopropyl alcohol liquid controlled cooling system.

Microstructure Characterization of the COC Sample. Microstructure of the COC polymer was characterized by

solution ^{13}C NMR ($\nu_{\text{C}} = 50$ MHz) at 70°C using the trichlorobenzene (TCB) as solvent and the $\text{C}_2\text{D}_2\text{Cl}_4$ as the lock solvent.

DSC Enthalpy Relaxation Experiments

Annealing at higher T_a temperature causes a more significant recovery value of excess enthalpy in most amorphous polymers, but for COC, the more rigid amorphous polymer, we tried to clarify the difference between processes of densification and physical aging. The procedure for determination of enthalpy recovery values of COC (as shown in Figure 2) was modified from traditional method. In order to avoid the effect of densification process of COC [8], so that we have to anneal the COC sample in a rather lower temperature, T_g 30°C . All the aging temperatures are investigated which are far below the original T_g of 158.8°C (measured with a heating rate of $10^\circ\text{C}/\text{min}$, not shown here). We think that the used lower T_a temperature (T_g 30°C) is lower than that of (T_g 15°C) for large numbers of glassy polymers such as PMMA, PC and PS.

The extruded disc was cut into small pieces (<1 mm length) and sealed in an aluminum pan for DSC analysis. Each fresh sample initially was heated to 300°C with a heating rate of $60^\circ\text{C}/\text{min}$, and maintained at 300°C for 5 min. Then it was cooled to the preset aging temperature (T_a) at 121, 125, 129 or 132°C at a cooling rate $40^\circ\text{C}/\text{min}$ for annealing. Each fresh sample was annealed isothermally for a set annealing time (maximum to $3 \cdot 10^4$ seconds). Then the sample was cooled to 50°C with a cooling rate of $60^\circ\text{C}/\text{min}$ and immediately re-heated to 300°C with a heating rate of $20^\circ\text{C}/\text{min}$. The T_g and excess enthalpy during glass transition region of DSC traces of each annealed sample was analyzed and calculated by using traditional three-point method.

Table 1. Characterization results of the COC sample

| NB content (wt%) | $T_g^{\#}$ ($^\circ\text{C}$) before aging | T_g ($^\circ\text{C}$) after quenching |
|------------------|--|--|
| ~ 75 | 159.8 | 154.5 |

$\#$ Glass transition temperature.

Results and Discussion

The characteristics of the COC sample (Topas 6015) has been summarized in Table 1. Figure 1 showed the high resolution C-13 NMR of the sample and peak assignments are following our previous definitions [9]. DSC traces of the COC sample annealed at 121°C for different periods have been shown in Figure 2. It clearly showed a release process of excess enthalpy as increasing the aging time.

Enthalpy Recovery Behavior of COC

Petrie and Marshall (PM model) [2] and Cowie and Ferguson (CF model) [10] have formulated similar equations based on Kohlrausch–Williams–Watts (KWW) equation to describe the change of excess enthalpy (ΔH) with increasing aging time (t_a) at a given annealing temperature (T_a).

$$\Delta H(t_a, T_a) = \Delta H_{\infty}(T_a)[1 - \varphi(t_a)], \quad (1)$$

$$\varphi(t_a) = \exp[-t_a/\tau]^{\beta}. \quad (2)$$

In above equations, ΔH_{∞} is the excess enthalpy value when $t = \infty$, τ is the retardation time and β is the stretched exponent. We have to keep in mind that the retardation time (τ) in Equation (2) should be depended on the fictive temperature due to non-linearity in the Petrie–Marshall approach.

Four curves of enthalpy recovery at various aging temperatures that ranging from (T_g 20°C) to (T_g 30°C) have been shown in Figure 3. The values of β , ΔH_{∞} and τ have

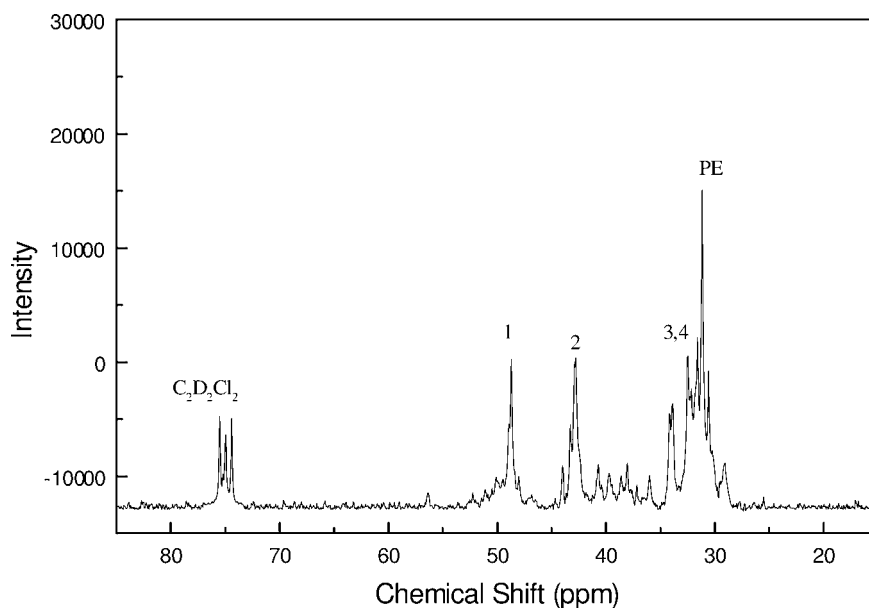


Figure 1. High resolution C-13 NMR spectrum of COC sample.

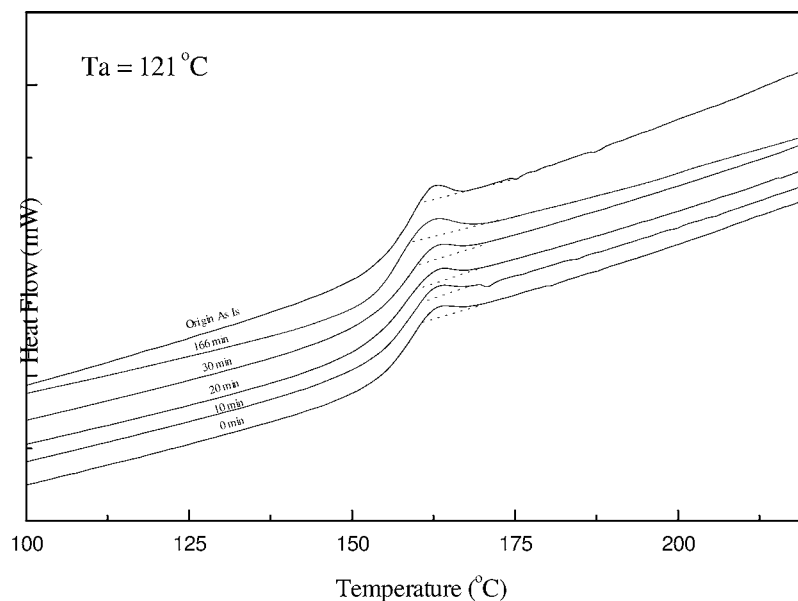


Figure 2. Representative DSC traces of the COC with various aging times at 121 °C.

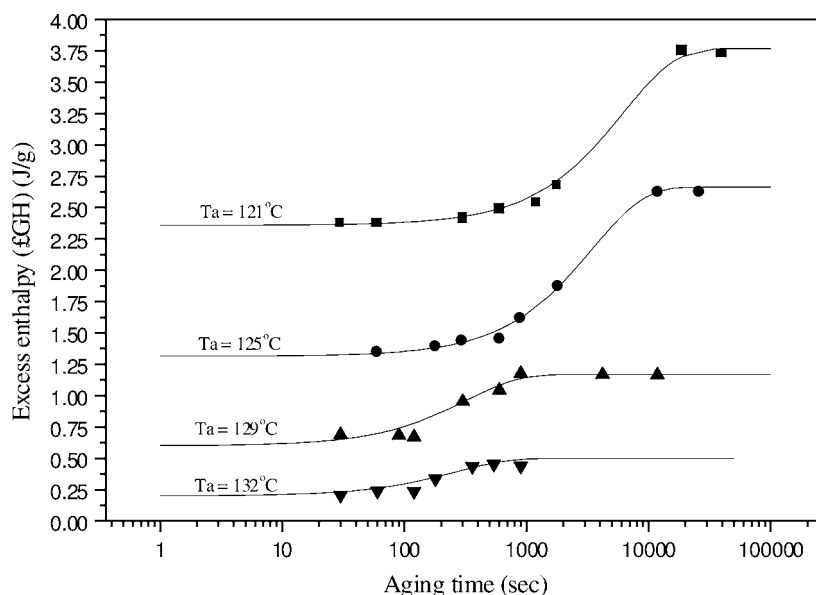


Figure 3. Plots of $\Delta H(T_a, t_a)$ versus $\text{Log}(t_a)$ for four aging temperature.

been obtained by fitting to those equations and summarized in Table 2. From Figure 4, we have found that the enthalpy recovery data of COC can be fitted well with a stretched exponential $\beta = 1$ in all aging temperatures. This result has a large difference on a comparison with most amorphous polymers (PS, PMMA, etc.) which have a β value less than 1.0. We think that the fact of $\beta = 1$ in COC is due to the used lower T_a temperature (T_g 30 °C) in comparing to that of (T_g 15 °C) for large numbers of glassy polymers such as PMMA, PC and PS.

The β value is originally considered as an indicator of the non-linearity of KWW equation, and means the distribution of the retardation time of chains toward to an equilibrium state. We suggested that the chain motions of COC annealed at lower T_a temperature is simpler than PMMA or PS annealed at higher T_a temperature. The COC polymer has a

Table 2. Values of the parameters obtained from different aging temperatures of the cyclo olefin copolymer

| T_a (°C) | $\Delta H_\infty(T_a)$ (J/g) | τ (sec) | β (± 0.02) |
|------------|------------------------------|--------------|------------------------|
| 121 | 1.395 | 2450 | 0.98 |
| 125 | 1.35 | 1650 | 0.99 |
| 129 | 0.57 | 320 | 0.98 |
| 132 | 0.30 | 260 | 0.98 |

high viscosity at molten state, so that a β value of 1.0 could be obtained.

The relation of $\Delta H_\infty(T_a) = \Delta C_p(T_g - T_a)$ can be confirmed under a condition of $T_g = 137.5$ °C (defined as T_g^*), where T_g^* is 20 °C lower than the normally detected T_g of the polymer (159.8 °C). And ΔH_∞ was the value of the aging

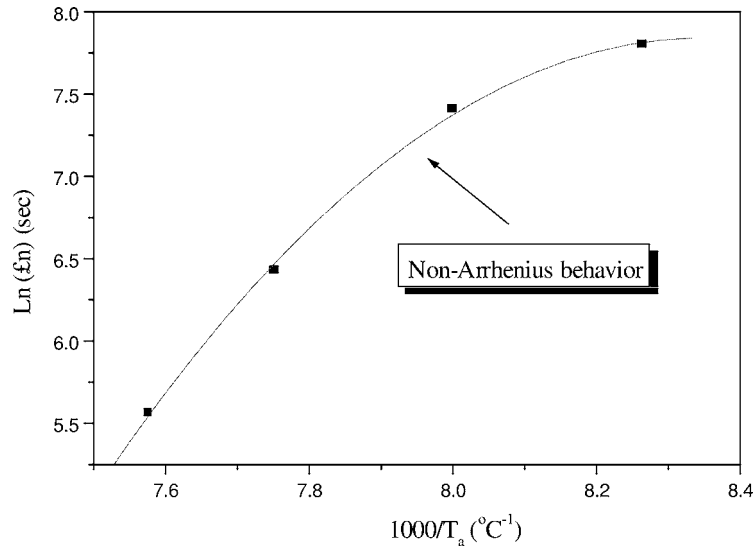


Figure 4. Arrhenius plot of $\text{Ln}(\tau)$ against T_a^{-1} .

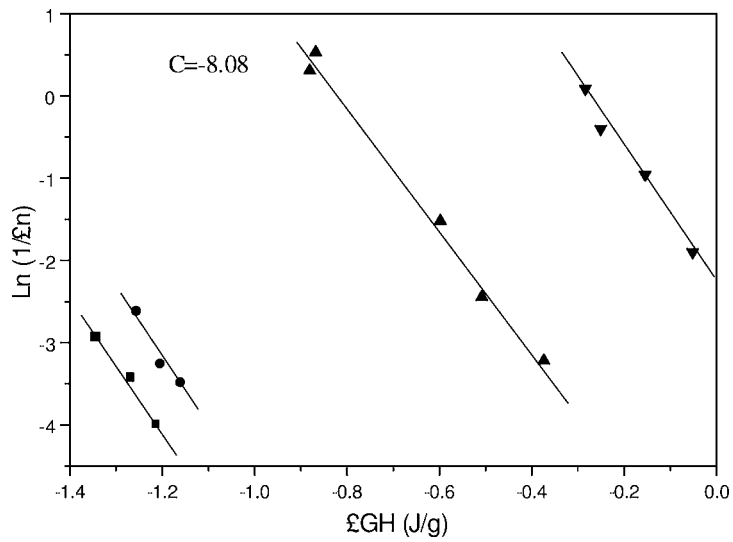


Figure 5. Petrie/Marshall plot of $\text{Ln}(1/\tau)$ versus ΔH for four aging temperature as given in Figure 3.

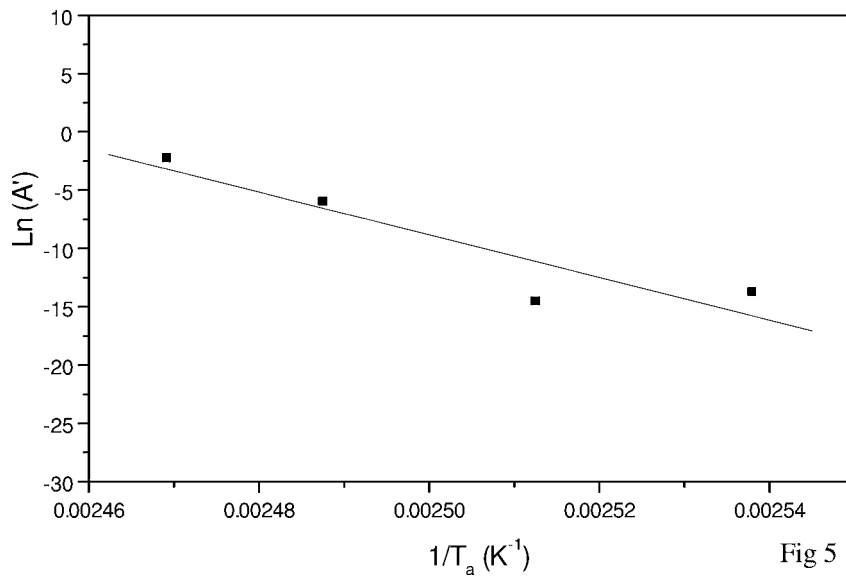
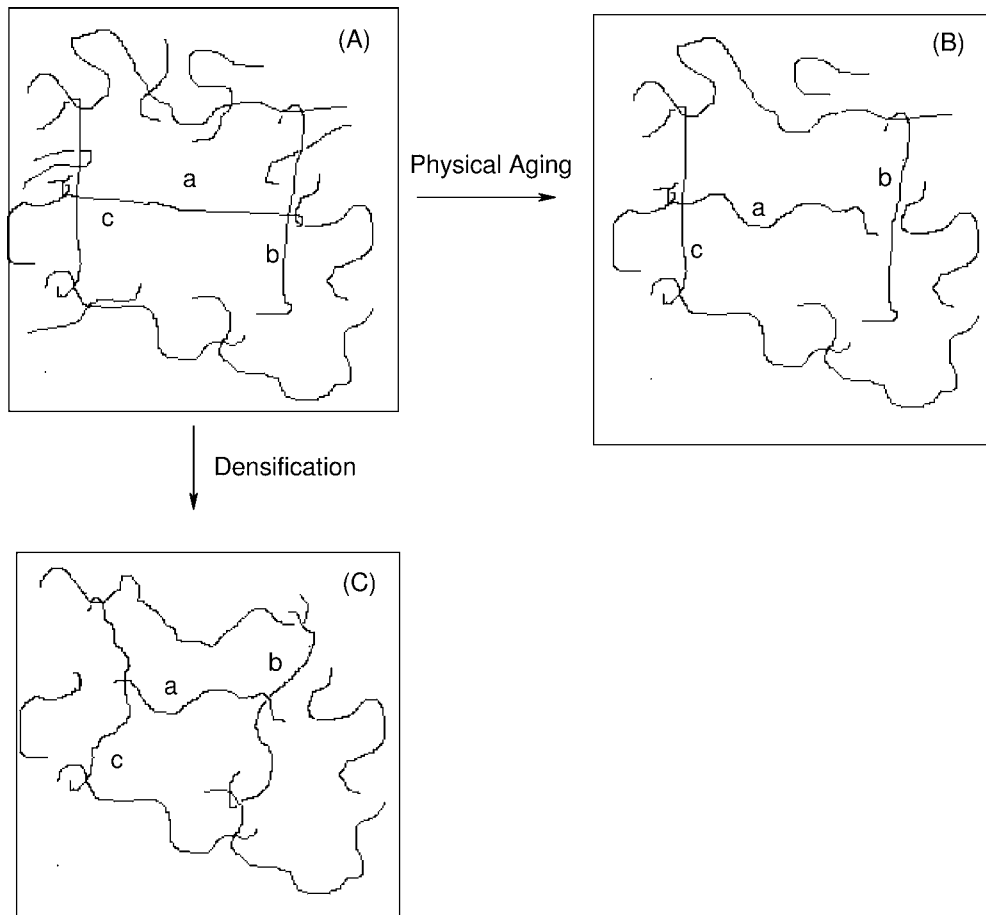


Figure 6. Petrie/Marshall Arrhenius plot of $\text{Ln}(A')$ against T_a^{-1} .



Scheme 1. Representative chain motions during physical aging versus densification of COC.

enthalpy for $t = \infty$, T_a was the aging temperature, and ΔC_p was the difference in the specific heat capacity above and below the T_g . T_g^* can be considered as the equilibrium T_g of the cyclo olefin copolymer.

The Petrie/Marshall (PM) Analysis

In the following section, we will discuss the application of Petrie/Marshall (PM) analysis on enthalpy recovery data in order to obtain a reliable apparent activation energy (E_H) for the COC sample.

$$\begin{aligned} 1/\tau &= -\text{Ln}(\varphi)/t \\ &= -\text{Ln}[1 - (\Delta H(t_a, T_a)/\Delta H_\infty(T_a))]/t. \end{aligned} \quad (3)$$

The dependence of on the aging temperature is

$$\text{Ln}(1/\tau) = \text{Ln}(A') + C^* \Delta H, \quad (4)$$

$$\text{Ln}(A') = \text{Ln}(A) - E_H/RT_a, \quad (5)$$

$$\Delta H = \Delta H_\infty(T_a) - \Delta H(t_a, T_a). \quad (6)$$

Which τ has a unit of minutes; A has a unit of min^{-1} ; the apparent activation energy (E_H) has a unit of kJ/mol and C^* is of mole/J-min. Figure 5 showed plots of $\text{Log}(1/\tau)$ versus ΔH for four aging temperatures as given in Figure 3. From Figure 5, C^* was calculated as -8.08 . Figure 6 was the Petrie/Marshall Arrhenius plot of $\text{Ln}(A')$ versus $1000/T_a$ which the E_H has been estimated to be 1521.7 ± 150 kJ/mole.

Which was substantially higher than 308 ± 50 kJ/mole for bisphenol A polycarbonate, 407.4 kJ/mole for poly(vinyl methyl ether) and 1192 kJ/mole for polystyrene, but nearly to 1520 kJ/mole for polyterafluoroethylene (PTFE) [1, 2, 10].

The Comparison of Densification versus Physical Aging in the COC System

Since COC annealed above T_g shows a densification process from our previous study [8]. In this study, we have tried to make a clear separation of the processes of structural relaxation (physical aging) and densification by annealing at relatively lower temperature, T_g 30 °C. Based on our observations on the behaviours of densification and physical aging of COC copolymer, we could define these two phenomena into two separated processes in Scheme 1.

The frozen and strained chains a, b, and c showed in Figure 12(A) are chains of the quenched amorphous COC. Principally, the structural relaxation (physical aging) tends to loose the strained chains maintained from the quenched state, and recovers glass transition enthalpy due to the softened structures (see Figure 12(B)). While the densification process, proceeds not only a fast chain relaxation but also denser chain-packing and substantial T_g increase (Figure 12(C)) [8]. Of course it must occur that a relaxation

of chain ends in cages sounding by strained chains in all processes to release all possible free space between chains.

Conclusions

The COC sample of Topas 6015 had been used to study its physical aging behaviour. The enthalpy recovery data shows that the apparent activation energy of COC aging is 1521.7 ± 150 KJ/mole. A detail of densification process and physical aging of COC has been compared to conclude that the densification process usually takes place in that COC is annealed above its original T_g and causes an increase in T_g . In contract to the densification process does, the physical aging of COC annealed far below its T_g causes in enthalpy recovery.

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