

DYNAMIC MECHANICAL AND THERMAL ANALYSIS OF CRYSTALLINITY DEVELOPMENT IN Kel-F 800 AND TATB/Kel-F 800 PLASTIC BONDED EXPLOSIVES. PART I. Kel-F 800 *

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ABSTRACT

Dynamic mechanical and differential scanning calorimeter measurements were made on Kel-F 800, a copolymer of chlorotrifluoroethylene and vinylidene fluoride, as a function of time. Samples annealed over a 30 day period at 50 °C showed reduced relaxation strength in the glass transition which directly correlated with the development of between 10 and 15% crystallinity in this polymer. Kel-F 800 samples thermally cycled from –54 to 74 °C without annealing for 12, 24, and 36 cycles developed only about half the crystallinity of the annealed samples. Kel-F 800 which was annealed 30 days and subsequently subjected to the above thermal cycling retained almost all of the crystallinity which developed during the annealing process. These results indicate that Kel-F 800 copolymer crystallizes at an extremely slow rate, but as long as the thermal excursion remains below the major melting peak most of the crystallinity remains.

INTRODUCTION

Kel-F 800 is a copolymer of chlorotrifluoroethylene (CTFE) and vinylidene fluoride (VF₂) manufactured by 3M Corporation and used by Lawrence Livermore (LLNL) and Los Alamos (LANL) National Laboratories as a polymeric binder for the insensitive explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [1]. Kel-F 800 is used because of its good energy-transfer characteristics [2]. TATB and its Kel-F 800 plastic bonded explosive (PBX) expand irreversibly by about 1.6 vol.% when cycled over the stockpile-to-target sequence (STS) temperature range (–54–74 °C). When glassy polymers are used as binders, the irreversible growth of the PBX is substantially suppressed. Kel-F 800 is partially crystalline [3] and the extent of crystallin-

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ity depends on thermal history. In the molding processes for making PBX parts, 120°C temperatures are used which melt the crystals in the polymer. Therefore the effect of Kel-F 800 crystallinity on PBX irreversible growth is of considerable interest. Before studying the effect of binder crystallinity on the PBX, the crystallinity of Kel-F 800 alone will be considered.

Crystallization in semicrystalline polymers over moderate supercoolings occurs by a kinetic process of heterogeneous nucleation and growth [4]. Crystallites form on heterogeneities randomly distributed in the polymer melt. At constant supercooling ($T - T_m^0$ where T_m^0 is the equilibrium melting temperature) the crystal growth rate, $G(t)$, follows the Fischer–Turnbull relationship

$$G(t) = G_0 \exp\left[-K_g/T(T - T_m^0)\right] \exp\left[-E/R(T - T_\infty)\right] \quad (1)$$

where G_0 is a constant, K_g is a constant derived from the free energy difference between the melt and the crystal, E is the activation energy for diffusion of chains at the crystal interface, and T_∞ is a temperature approximately 30°C below the glass transition. From this equation it is clear that above the melting point and below T_∞ no crystal growth occurs. Somewhere between these two temperatures crystal growth passes through a maximum. In order to minimize the time to achieve maximum crystallinity, the crystallization temperature should be near $(T_m + T_g)/2$. From DSC traces of crystalline Kel-F 800 [5], $T_g = 30^\circ\text{C}$ and $T_m = 100^\circ\text{C}$ so crystallites should grow most rapidly near 65°C.

Unfortunately, crystals grown at the highest rate are not the most perfect crystals. Increases in crystal perfection occur when crystals are annealed above their crystallization temperature [6]. Copolymers which can crystallize generally do so more slowly than their homopolymer and can also contain a distribution of crystallite sizes depending on the crystallizable monomer sequence distribution and the temperature [7].

EXPERIMENTAL

Three lots of Kel-F 800 (618, 629, and 643) were obtained from 3M. The resins were compression molded into bars $6.35 \times 1.27 \times 0.318$ cm at 120°C at moderate pressure for 5 min, then removed from the press and cooled in air. Eleven specimens of each lot were prepared. Five were annealed for 0, 1, 3, 10, and 30 days at 50°C. Three were thermally cycled from -54 to 74°C for 12, 24, or 36 times. Finally, three were annealed at 50°C for 30 days and then thermally cycled as above. Each of the 33 samples was tested using the Rheometrics Model 7200 mechanical spectrometer from -100 to 150°C over five frequencies in 3–4°C temperature steps. Polymer crystallinity measurements were made using a DuPont DSC.

RESULTS AND DISCUSSION

Preliminary thermal analysis

A typical DSC curve from as-received Kel-F 800 in Fig. 1a showed two melting endotherms at 67 and 96°C and a glass transition at 28°C. When the sample was rerun, only the glass transition was observed (see Fig. 1b). Annealing as-received Kel-F at 60°C for 4 or 11 days (curve c) shifted the 75°C endotherm to a shoulder at 82 or 90°C, respectively, but the percent crystallinity increased only slightly. When annealed at 80°C for 3 or 11 days (curves d and e), no 70°C peak or shoulder were observed, the main peak shifted to 102–104°C, and the degree of crystallinity was reduced slightly. Clearly, annealing as-received Kel-F 800 at 60°C increased the crystallite perfection of the lower melting crystals. Annealing at 80°C, however, increased the crystallite perfection of the higher melting crystals at the expense of less crystallizable copolymer.

After melting all crystallites in the as-received Kel-F at 110°C for 24 h, crystals could be grown under isothermal conditions within or slightly above the STS temperature range. Isothermal crystallization at 60 and 80°C for up to 12 days showed crystal growth even after 12 days (see Fig. 2). The degree of crystallinity was estimated from

$$X_c = H_m/H_f^0 \quad (2)$$

where H_f^0 is the heat of fusion of perfectly crystalline material. For Kel-F 800, only the major component, CTFE, is assumed to crystallize. H_f^0 of CTFE is 43.5 J g⁻¹ [8]. Overall crystallization kinetics are expected to follow the Avrami relationship [9]

$$X_c(t) = H(t)/H_\infty = 1 - \exp - (kt^n) \quad (3)$$

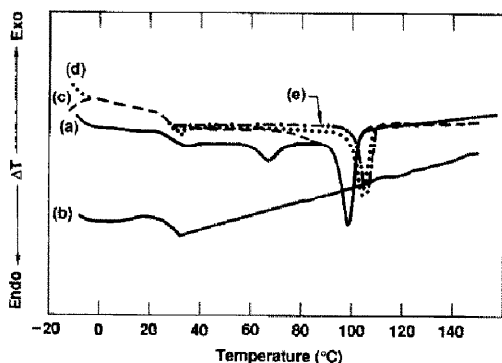


Fig. 1. DSC thermograms of (a) as-received Kel-F 800, (b) 2nd run after rapid cooling, (c) annealed at 60°C for 4 or 11 days, and (d and e) annealed at 80°C for 3 or 12 days showed removal of all crystals on rapid cooling from above T_m or shifting of the endotherms to higher temperatures on annealing slightly below the respective melting points.

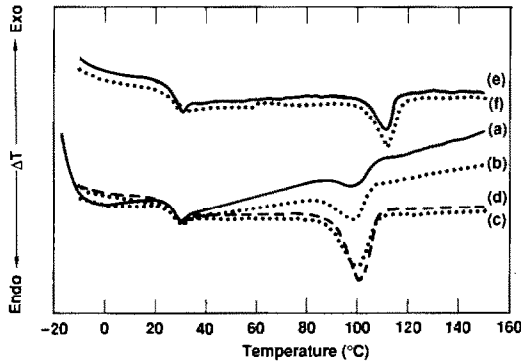


Fig. 2. DSC thermograms of Kel-F 800 isothermally crystallized from the amorphous state at 60°C for (a) 1, (b) 2, (c) 5, and (d) 10 days showed more rapid growth and higher degree of crystallinity than Kel-F crystallized at 80°C for (e) 3 or (f) 12 days.

or

$$\ln\{-\ln[1 - X_c(t)]\} = \ln k + n \ln t \quad (4)$$

where H_∞ is the endotherm of completely crystallized polymer. If we assume $H(t) = H_m$ from Table 1 and $H_\infty = H_f^0$, fractional values of the Avrami coefficient n are obtained. This implies that unconventional nucleation and growth morphologies are occurring in this polymer. However, it is clear that even after 12 days at 60°C the degree of crystallinity in Kel-F 800 is slowly increasing.

TABLE 1

Heats of melting (H_m) and approximate degree of crystallinity (X_c) of Kel-F 800

Annealing		H_m (cal g ⁻¹)	T_m (°C)	X_c (%)	T_g (°C)
Temp.	Time				
A Effect of annealing as-received (crystalline) Kel-F 800 (see Fig. 1)					
RT	0	0.796	92 (59) ^a	7.7	26
60	4d	0.88	92		24
60	11d	0.88	91		24
80	3d	0.577	96	5.5	24
80	10d	0.531	98	5.1	24
B Isothermal crystallization of Kel-F 800 melted at 110°C for 24 h (see Fig. 2)					
60	1d	0.252	84	2.4	24
60	2d	0.597	84	5.7	22
60	5d	0.872	86	8.4	24
60	12d	0.885	90	8.5	22
80	3d	0.389	102	3.7	23
80	10d	0.602	102	5.8	23

^a Bimodal melting (low temperature transition in parentheses).

Anelastic behavior of Kel-F 800

Amorphous Kel-F 800 contains two relaxations. A broad low temperature secondary relaxation occurs at about -40°C in the loss tangent at 1 Hz. The glass transition occurs at 34°C in G'' and 46°C in $\tan \delta$ at 3.15 Hz. In the three lots of Kel-F 800 tested in these experiments, the glass transition temperature shifted slightly upward (to about $37 \pm 1^{\circ}\text{C}$) when measured by the G'' maximum but remained constant from $\tan \delta$ measurements. When Kel-F 800 is allowed to crystallize, a third relaxation (the α -relaxation) develops at about 10°C below the melting point of the highest melting crystals when measured from the G'' peak ($86 \pm 3^{\circ}\text{C}$) and well above 100°C in $\tan \delta$.

The effect of isothermal crystallization at 50°C on the shear storage modulus (G') is shown in Fig. 3 for 3.15 Hz data from lot #629. The "a" curve specimen was removed immediately from the press and quenched in water. Curve "b" was slowly cooled in air to ambient and kept at ambient several days prior to annealing. This was expected to be more representative of the PBX molding procedure. Considerable crystallization has occurred during the cool down and ambient aging period. Annealing at 50°C caused the modulus (and crystallinity) to increase continuously for up to 30 days. A considerable change in mechanical properties occurred within the first day of annealing. It is quite remarkable that about 10% crystallinity should increase the modulus by one and a half orders of magnitude.

The loss tangent maximum (Fig. 4) associated with the glass transition is substantially reduced. There will be less damping due to lower amorphous content and amorphous material constrained by crystals. The breadth of the

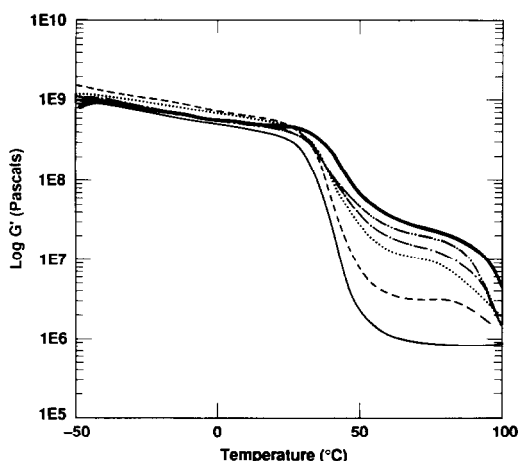


Fig. 3. Shear storage modulus (G') of Kel-F 800: —, quenched in water; ---, slowly cooled in air; or annealed at 50°C for (\cdots) 1, ($- \cdot -$) 3, ($- - -$) 10, and ($- - - -$) 30 days showed increased modulus between T_g and T_m due to crystal development during the annealing process.

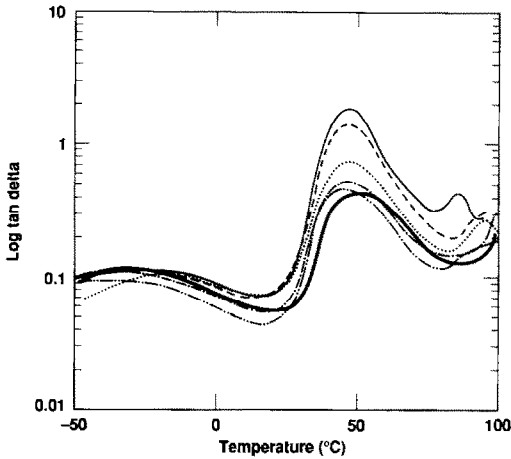


Fig. 4. Tan delta values of Kel-F 800 for the samples from Fig. 3 were reduced associated with decreased amorphous content and the development of the crystalline phase.

loss peak was also reduced. This is somewhat surprising as incorporation of filler into polymers typically reduces the maximum but broadens the transition [10]. Using simple models it has been shown [11] that crystallinity

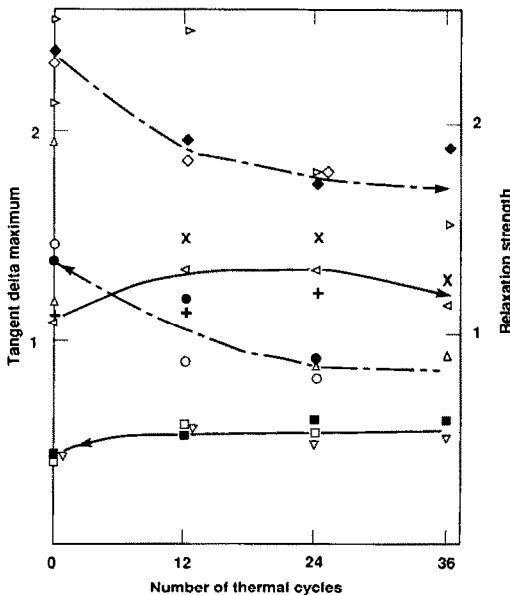


Fig. 5. Relaxation strengths and tan delta maxima for the Kel-F 800 glass transition as a function of the number of STS thermal cycles for lots 618 (open symbols), 629 (triangles) and 643 (solid symbols) showed decreasing values for unannealed polymer and increased slightly to a constant value for annealed Kel-F. Crystallinity should be inversely proportional to relaxation strength or tan delta.

should vary between limits for $\lg G'$ and $\tan \delta$. Our results agree with the model for moduli measured between T_m and T_g .

When air-cooled Kel-F 800 samples were thermally cycled over the STS temperature range, the shear storage modulus between T_g and T_m increased and the loss tangent decreased indicating continued crystal growth during thermal cycling. Figure 5 is a plot of relaxation strength and $\tan \delta$ versus number of thermal cycles. Although there was considerable scatter, both the relaxation strength and the loss tangent of the Kel-F glass transition were reduced with increasing number of thermal cycles. This would imply that PBX mechanical properties above T_g would increase during stockpile lifetimes because of diurnal thermal excursion above T_g .

When Kel-F 800 samples which had been annealed at 50°C for 30 days were subjected to the identical thermal treatment only a slight increase in relaxation strength and loss tangent were observed (see Fig. 5). This implies that sufficient crystallization has occurred during the annealing process to prevent further property changes during the thermal cycling. Since the maximum temperature in the STS cycle is 74°C, some of the less perfect crystals in the Kel-F 800 have melted, as evidenced by the slight increase in relaxation strength and loss tangent with number of cycles. As 74°C is somewhat high, thermal cycles to this temperature may occur less frequently in reality and produce less effect. Even with this upper temperature, only a small change in mechanical properties was observed.

CONCLUSIONS

Crystallization in Kel-F 800 is slow and continues at very slow rates even after 30 days. Crystallization of a remarkably small fraction of Kel-F 800 (approximately 10%) produces over an order of magnitude increase in modulus between T_g and T_m . Relaxation strength and loss tangent maxima of the glass transition were inversely proportional in a nonlinear way to the degree of crystallinity. Thermal cycling of samples over the STS temperature range showed that crystallinity would increase after parts had been molded due to diurnal thermal excursion. However annealing for 30 days at 50°C reduced the variation in mechanical properties of this polymer during thermal cycling. Work on the effect of binder crystallization on insensitive plastic bonded explosives is continuing.

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