Research on the Mechanism and Kinetics of Polymorphic Transitions of ε-CL-20 in Composite Systems

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Abstract: In order to explore the polymorphic transition law for ε-CL-20 in composite systems, the polymorphic transition process of pure ε-CL-20 crystals stimulated by heat was investigated by the X-ray Diffraction (XRD) method, and the kinetic parameters of the polymorphic transition process were calculated (including the apparent activation energy E_a and the pre-exponential factor ln$A$). Meanwhile the effects of different additives on the polymorphic transition process and kinetics of ε-CL-20 were explored in detail. The experimental results showed that the ε-form tends to transform into the γ- form on heating and that the E_a and ln$A$ for the transition process were 209.97 kJ/mol and 57.47, respectively. The first group of additives clearly promoted the polymorphic transition of ε-CL-20 and lowered the initial transition temperature and the activation energy. The second and third groups of additives inhibited the polymorphic transition of ε-CL-20 and raised the initial transition temperature and the activation energy.

Keywords: polymorphic transition, kinetics, activation energy, transition temperature

1   Introduction

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, also known as CL-20) was first synthesized in 1987 by Nielsen at the US Naval Weapons Center, China Lake [1, 2]. The highly strained molecular cage structure of CL-20 causes it to be a very high-energy density material, with potential for widespread application in many munitions [3, 4]. Four stable polymorphs (α, β, γ, ε) of CL-20 have been obtained at ambient temperature and atmospheric pressure [5-8], and the ε-form has been used in practice because of its largest density (2.044 g/cm^3) and best thermal stability [9, 10].

Former researchers have found that ε-CL-20 would transform to other polymorphs under specific conditions (*e.g.* high temperature, high pressure, and ambient medium) [11, 12]. After the polymorphic transformation has occurred in the CL-20 crystal, the particle volume will have expanded to a certain extent and resulted in cracks and cleavage in the crystal. These defects could generally increase the sensitivity and decrease the thermal stability and detonation power, and thus reduce the safety and performance of CL-20 based composite explosives [13-15].

In the production, processing, storing and usage of CL-20 based composite explosives and propellants, it is inevitable that the CL-20 crystals encounter various additives, including both solid-state and liquid-state, and the complex compositions tend to initiate the polymorphic transition of ε-CL-20 [16-20].

In order to avoid the polymorphic transition of ε-CL-20 in practical applications, the present work attempted to analysis the transition mechanism of ε-CL-20 in composite systems. On the basis of the self-transition law of pure ε-CL-20, the transition law in composite systems and the kinetic parameters of the transition process were obtained. The effect of additives on the polymorphic transition law of ε-CL-20 is explained from the point of view of kinetics. This study will provide guidance for the effective control of CL-20 polymorphs in its application in composite explosives and propellants.

2   Materials and Methods

2.1 Materials

Raw CL-20 was provided by Qingyang Chemical Industry Corporation. Dioctyl adipate (DOA), dioctyl sebacate (DOS), N-butyl-2-nitratoethylnitramine (BuNENA), toluene di-isocyanate (TDI), hydroxy-terminated polybutadiene (HTPB), paraffin wax, ethylene-vinyl acetate copolymer (EVA), ethylene-

propylene-diene monomer (EPDM), and Fluororubber (F_{2602}) were all provided by Shenyang Chemical Works.

2.2 Preparation of the XRD test samples

Samples of CL-20 crystals, mixed thoroughly with different additives (mass ratio 10/1), were prepared for the XRD experiments. To ensure that the CL-20 crystals were thoroughly mixed and homogeneously coated with the additives, the procedure was as follows:

Because wax, EVA, EPDM, and F_{2602} are all macromolecular elastomers, these additives were first dissolved in a solvent (*e.g.* petroleum ether), and the CL-20 crystals were then added to the binder solution. With uniform mixing, the CL-20 crystals were wetted and coated with the binder solutions and then sufficient solvent was evaporated by heating and by vacuum. After drying, granules of the CL-20 crystals coated with the additives were obtained. The other additives, DOA, DOS, NENA, TDI, and HTPB, are all liquids which can be integrated uniformly with the CL-20 crystals without introducing solvents.

2.3 Characterization of the CL-20 crystals

The images of CL-20 crystals were characterized by an S-4700 scanning electron microscope (SEM), made in Japan.

The particle size and size distribution of the CL-20 crystals were measured with a Malvern MASTERSIZER 2000, made in UK.

The purity of the ε-CL-20 was analyzed by an Agilent Series 220 high performance liquid chromatograph (HPLC), made in US, with C-18 column and using acetonitrile-water as the mobile phase.

The density of the CL-20 crystals was measured by a density gradient apparatus, made by the Institute of Chemical Materials, Chinese Academy of Engineering Physics (CAEP).

The shock sensitivity of the CL-20 crystals was determined by the small scale gap test (SSGT).

2.4 X-ray diffraction (XRD) test

All polymorphic transformations were performed on a Bruker D8 Advance using Cu Kα radiation ($\lambda = 1.54180$ Å) without a monochromater, equipped with a Vantec-1 detector and operating under the conditions of 40 kV/40 mA. The 2θ range measured was 5-50°, in intervals of 0.02°/0.1 s.

A series of XRD measurements were made through the complete temperature increase by using the following programme to control the temperature. Firstly the temperature was raised from ambient temperature to 30 °C, and the first

scanning data was collected. Then the temperature was slowly raised to 135 °C and the second scanning data was collected. During the period of increasing temperature, scanning date was collected every 5 °C. Subsequently scanning date was collected at 180 °C, and then the temperature was reduced to 30 °C. The complete procedure was performed at the rate of 0.1 °C/min.

3   Results and Discussion

3.1 Characterization of raw CL-20

The polymorphic transition of ε-CL-20 is closely related to factors such as crystal purity, particle size and crystal defects [21]. Defects are the weaknesses in the CL-20 crystals which could easily induce a phase transition. A higher purity, with less defects and approximating more closely to the theoretical maximum density, reduces the tendency that phase transitions would occur. The CL-20 samples were optimized by solvent-antisolvent recrystallization; the profile of the CL-20 crystals, observed by SEM, is shown in Figure 1.
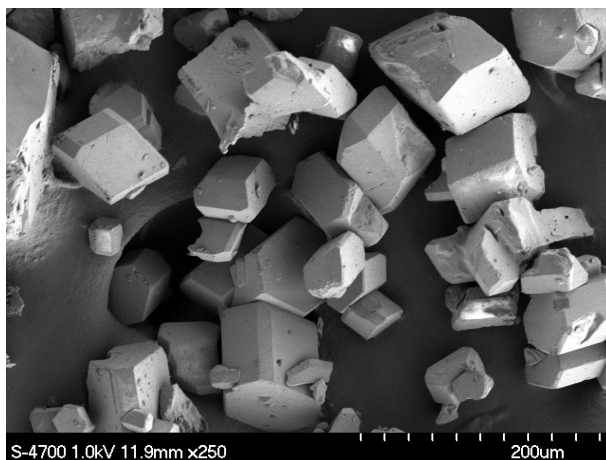

Figure 1.   SEM image of a sample of a CL-20 crystal.

From Figure 1, it can be seen that the crystal quality of the raw CL-20 was high, with few crystal defects and the morphological shape was mostly in the form of short rods with pliable edges.

The characterization results of the CL-20 crystal sample revealed that the average density was 2.035 g/cm^3 with an ε-form purity of 99.7%, and a particle size distribution of $50 \sim 200$ μm.

In the small scale gap test (SSGT), the critical thickness of the gap (when the initiation probability was 50%) for crude CL-20 was 18.7 mm, and 14.3 mm for the ε-CL-20 after recrystallization. The SSGT tests showed that the ε-CL-20 crystals used were less sensitive to the shock wave.

The XRD patterns of standard α-, β-, ε- and γ-CL-20 are shown in Figure 2, covering 2θ from 5° to 50°, and the crystallographic parameters were referred from the records PUBMII(α-), PUBMUU01(β-), PUBMUU02(ε-) and PUBMUU(γ-) of the Cambridge Structural Database (CSD). The standard XRD patterns and Total Pattern Solution (TOPAS) were used to quantitatively calculate the content of each polymorphic form.
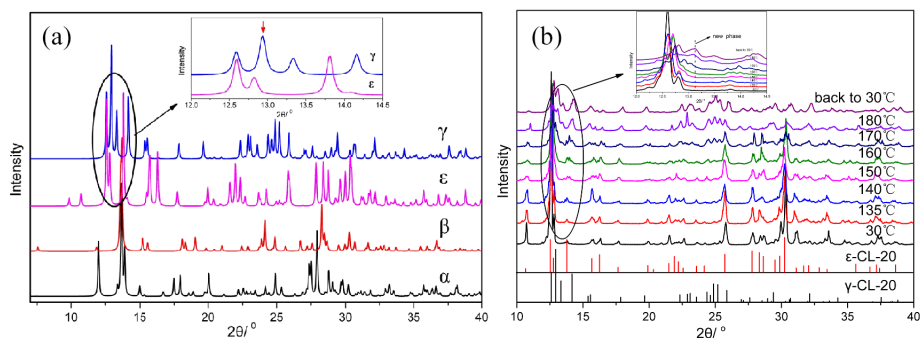

Figure 2. XRD patterns of CL-20 crystals.

From Figure 2a, it can be seen that the characteristic peak of the ε-form is at 10.70°, while the characteristic peak of the γ-form is at 13.36°; these peaks were the basis for estimating the polymorphic forms of the CL-20 samples.

3.2 Self polymorphic transition law of pure ε-CL-20

In order to investigate the self polymorphic transition of pure ε-CL-20 on heating, an XRD experiment was used to characterize the self-transition process with the experimental process being controlled by the temperature programme described in Section 2.4. The results of the XRD patterns indicating the ε- to γ-phase transition of pure CL-20 at elevated temperature are also shown in Figure 2.

From Figure 2b, the diffraction pattern of the pure ε-phase peaks were visible when the temperature was below 130 °C. When the temperature reached 135 °C, a new weak peak was observed at 13.36°, which was attributed to the γ-form. As the temperature increased, the intensity of the peak at 13.36° increased, while the characteristic peak at 10.70° of ε-CL-20 became increasingly weak. When the temperature had risen to 180 °C, the main component of the mixture was

the γ-form. We also found that the phase transition was irreversible on cooling.

The essence of the phase transition of the polymorphs is that one crystal form is transformed to another more stable form. From a thermodynamic point of view, the stability of the CL-20 polymorphs is strongly related to temperature. As the temperature rises, heat is continuously absorbed and sufficient energy is available to overcome the phase transition activation barrier. There is a critical temperature related to the ε- and γ-transition, the ε-form being more stable below the critical temperature while the γ-form is more stable above the critical temperature. Consequently, when heated above the critical temperature, the ε-CL-20 strongly tends to transform into the γ-form.

3.3 Polymorphic transition law of ε-CL-20 in composite systems

Samples of CL-20 mixed with 9 different kinds of additives were prepared according to the method described in Section 2.2, and the CL-20 crystal phase transition behaviour in the composite systems was characterized by XRD experiments. The experimental plots of the extent of the ε→γ phase transition in the temperature range 120-180 °C are shown in Figure 3. The initial phase transition temperature (T_0), 50% phase transition temperature (T_{50}) and complete phase transition temperature (T_{100}) were obtained from these plots and were used to investigate the effects of different additives on the polymorphic transition of ε-CL-20.
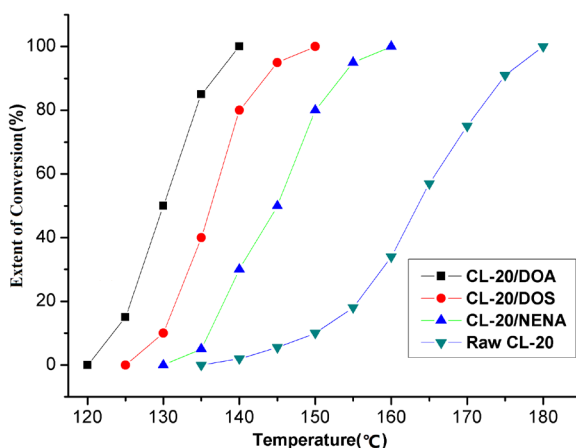
a. First group, T_0 shifted lower with T_{50} shifted lower.
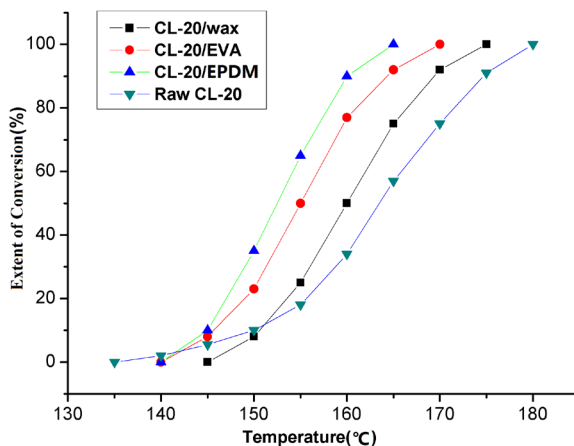
b. Second group, T_0 shifted higher with T_{50} shifted lower.
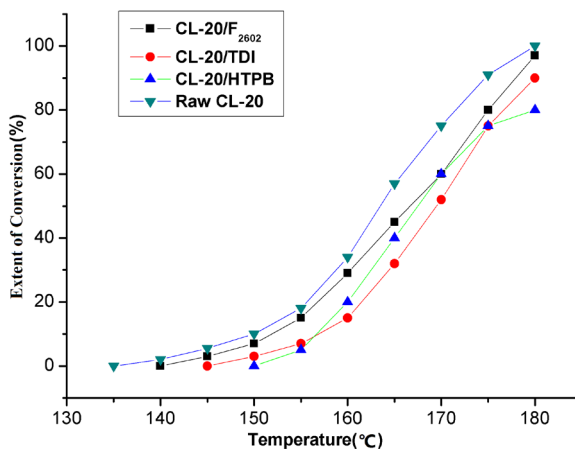
c. Third group, T_0 shifted higher with T_{50} shifted higher.

Figure 3.   Extent of conversion of ε-CL-20 crystals in composite systems at elevated temperature.

It can be seen from Figure 3 that the additives can be classified into three groups according to variations in the phase transition temperature.

The first group contains DOA, DOS and NENA. Compared with pure ε-CL-20 crystals, the initial phase transition temperature (T_0) and the 50% phase transition temperature (T_{50}) both shifted to a lower temperature when mixed with additives of this first group. Furthermore, the ε-form transformed to the γ-form

completely before the temperature reached 180 °C. These results demonstrated that additives of the first group promote the ε- to γ-phase transition of CL-20.

When the ε-CL-20 crystals are mixed and coated thoroughly with polar additives, the kinetic barrier and the critical temperature of the ε- to γ-phase transition can be decreased. DOA is a long-chain ester, containing a carbonyl group in the molecule which exhibits much polarity and can dissolve CL-20 crystals. Surrounded by the carbonyl group, the surface free energy of the CL-20 crystals is reduced and the CL-20 is partially dissolved. The polymorphic transition is more likely to occur in a fluid medium and the activation energy barrier of the transition process is much lower than that in a solid matrix. The formation of a small amount of γ-CL-20 acts as crystal seeds and induces further polymorphic transitions. In the surroundings of additives of good solubilizing character and a high dipole moment, the ε-form can be easily polarized and tends to transform into the γ-form. The macroscopic result was that DOA decreased the energy barrier of phase transition, and lowered the initial crystal transition temperature.

The second group contains wax, EVA, and EPDM, and the third group contains F_{2602}, TDI, and HTPB. Compared with pure ε-CL-20 crystals, the initial phase transition temperature (T_0) is shifted to a higher temperature when mixed with additives of the second and third groups. The results demonstrated that additives of the second and third groups inhibited the ε- to γ-phase transition of CL-20. But there was a difference between the additives of the second and third groups. The second group caused the T_{50} to shift to a lower temperature and the ε-form transformed to the γ-form completely below 180 °C, while the third group caused the T_{50} to shift to a higher temperature and the ε-form did not completely transform to the γ-form until 180 °C.

Unlike crystallization from solution, there is no solvent as a medium in a solid matrix polymorphic transition. New crystal seeds have to overcome a much higher activation energy barrier to nucleate and grow in a solid matrix, and therefore the process of polymorphic transition in a solid matrix is much more difficult. The molecules of the second and third groups were symmetrical with low polarity, liquid paraffin did not possess CL-20 dissolving groups, and cannot dissolve CL-20 crystals. Polymorphic transitions in a solid matrix can only occur under higher temperature conditions. During the heating process, the polymorphic transition was also affected by heat transmission. As a result, coating with additives with poor thermal conductivity can enhance the coating efficiency, block heat transfer and inhibit the polymorphic transition of the inner ε-CL-20.

3.4 Kinetics of the polymorphic transition of pure ε-CL-20 crystals

The kinetics of the polymorphic transition of pure ε-CL-20 crystals was determined under isothermal conditions in the temperature range 158-165 °C. The extent of conversion at different times was obtained and the experimental kinetic plots of the CL-20 ε→γ phase transformation are shown in Figure 4.
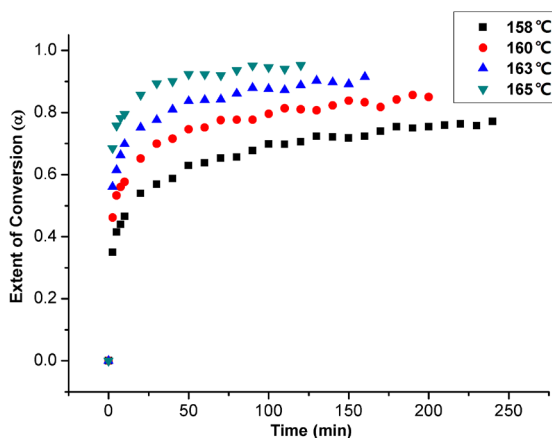

Figure 4.   Plots of the extent of conversion *vs*. time at different temperatures (158, 160, 163 and 165 °C).

From Figure 4, it can be seen that the extent of conversion is related to time and environmental conditions, and is directly modulated by temperature.

For the isothermal isoconversional phase transition, the Avrami equation was used to calculate the kinetic parameters (including the apparent activation energy E_a and the pre-exponential factor $\ln A$) of the transition process [22]:

$$\alpha = 1 - e^{-k(T)t^n}$$

where α is the extent of conversion, %; T is the experimental temperature, K; t is the time required to reach α conversion at temperature T, s; $k(T)$ is the temperature dependent rate constant; n is little affected by temperature.

When $\ln\{\ln[1/(1-\alpha)]\}$ is plotted against $\ln t$, a straight line is obtained and $\ln k(T)$ is calculated from the intercept and n is calculated from the slope. The plots of $\ln\{\ln[1/(1-\alpha)]\}$ versus $\ln t$ are shown in Figure 5.
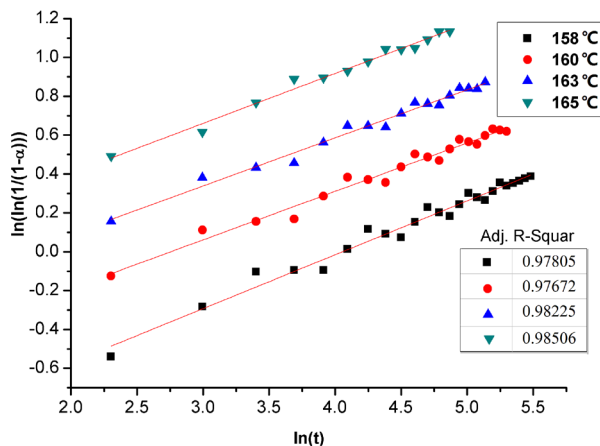
Figure 5. Log curve of the extent of conversion *vs*. time.

From Figure 5, it can be seen that the correlation coefficients were close to one at all of the temperatures tested, indicating that there was a good linear relationship between $\ln\{\ln[1/(1-\alpha)]\}$ and $\ln t$ in the conversion range 20-90%. Based on the intercept of the fitting lines, the rate constants $\ln k(T)$ at 158, 160, 163 and 165 °C were calculated to be 0.3358, 0.4908, 0.6523 and 0.9198, respectively.

With the supposition of single-step kinetics, the apparent activation energy and the pre-exponential factor could be calculated from the slope and intercept of the plot of the Arrhenius equation [23]:

$$k = Ae^{-E_a/RT}$$
$$\ln k = \ln A - E_a / RT$$

where E_a is the apparent activation energy of the phase transition, J/mol; T is the experimental temperature, K; $\ln A$ is the pre-exponential factor; R is the universal gas constant, 8.314 J/(mol·K).

According to the linear plot of $\ln k$ *vs*. $1/T$ the apparent activation energy was obtained from the slope and the pre-exponential factor from the intercept. The kinetic plot of the Arrhenius equation gave the apparent activation energy (E_a) and pre-exponential factor ($\ln A$) as shown in Figure 6.
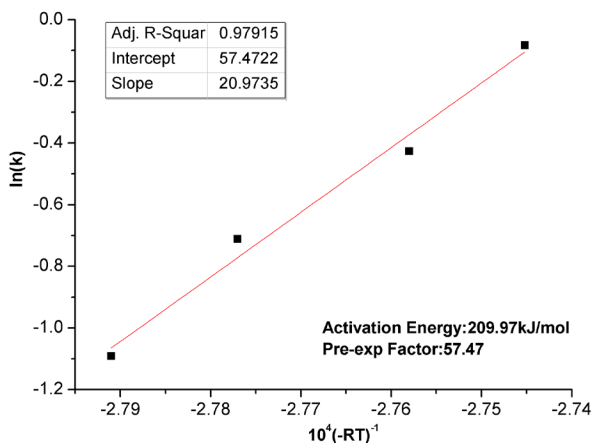
Figure 6.   Kinetic plot of the Arrhenius equation.

From Figure 6, it can be seen that the correlation coefficient of the fitted line was close to one, indicating that there was a good linear relationship between ln k and $1/T$ in the temperature range 158-165 °C. Based on the slope and intercept of the fitting line, the apparent activation energy (E_a) and pre-exponential factor (ln A) were calculated to be 209.97 kJ/mol and 57.47, respectively.

3.5 Kinetics of the polymorphic transition of ε-CL-20 in composite systems

In order to explore the effect of different additives on the polymorphic transition process and the kinetics of CL-20, samples of ε-CL-20 mixed with different additives (mass ratio 10/1) were prepared according to the method described in Section 2.2.

The kinetics of the polymorphic transition of ε-CL-20 crystals in the composite systems was also determined under isothermal conditions in the temperature range 158-165 °C. The extent of conversion at different times was obtained and the kinetic parameters of the ε- to γ-phase transformation in the different composite systems were calculated based on the Avrami and Arrhenius equations. The results are shown in Table 1.

Table 1.   Kinetic parameters of the ε- to γ-phase transformation in composite systems.

Component		E_a, [kJ/mol]	$\ln A$
Pure ε-CL-20 crystals		209.97	57.47
The first group	CL-20/DOA	170.54	59.32
	CL-20/DOS	183.43	58.58
	CL-20/NENA	189.94	60.83
The second group	CL-20/Wax	230.54	58.42
	CL-20/EVA	219.38	59.58
	CL-20/EPDM	220.64	58.92
The third group	CL-20/F$_{2602}$	213.18	54.73
	CL-20/TDI	218.72	54.14
	CL-20/HTPB	231.63	53.21

From Table 1, it can be seen that the apparent activation energy decreased in the first group, which illustrated that the first group decreased the transformation barrier of the ε- to γ-phase transition process and the process was easier. The apparent activation energy increased in the second and third groups, which illustrated that the ε- to γ-phase transition was more difficult.

The difference between the second and third groups was that $\ln A$ increased with the second group, while $\ln A$ decreased with the third group. This means that once the phase transition commenced, the transition rate in the second group was faster than that in the pure ε-CL-20 crystals, while the transition rate in the third group was slower than that in the pure crystals. The third group inhibited the transition throughout the whole process.

The results of the kinetic analysis were in consistent with the polymorphic transition phenomenon of ε-CL-20 crystals in the composite systems and explained the effect of the additives on the polymorphic transition law of ε-CL-20 from the point of view of kinetics.

4   Conclusions

The polymorphic transition process of ε-CL-20 crystals and the effects of different additives on the polymorphic transition of ε-CL-20 during heating were investigated by the XRD method. The kinetic parameters of the polymorphic transition process were calculated by the isothermal isoconversional method. The main conclusions were as follows:

The ε-form tends to transform into the γ-form on heating and the E_a and

ln$A$ during the transition process were found to be 209.97 kJ/mol and 57.47, respectively.

Molecular polarity and solubilizing ability have a significant effect on the kinetic parameters and the process of the ε- to γ-phase transition of ε-CL-20. Based on the variation of the transition temperature and kinetic parameters, the additives could be classified into three groups.

The first group, which included DOA, DOS and NENA, lowered the initial transition temperature and decreased the apparent activation energy and promoted the polymorphic transition of ε-CL-20.

The second group, which included wax, EVA and EPDM, and the third group, which included F_{2602}, TDI and HTPB, raised the initial transition temperature and increased the activation energy and inhibited the polymorphic transition of ε-CL-20.

Acknowledgment

5   References

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