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THERMOCHEMISTRY OF THE BINARY SYSTEM NITROCELLULOSE+ N-NITRODIETHANOLAMINE DINITRATE

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The melting and mixing enthalpy of the binary system nitrocellulose and N-nitrodiethanolamine dinitrate (DINA) was determined by DSC. The mixing enthalpy $H^{\mathrm{M}}_{\mathrm{max}}$=1.95 kJ mol^{-1} had maximum at mass fraction x_{wDINA}=0.46. The influence of samples storing on glass and endothermic transitions were studied. The temperature range of glass transition broadened with x_{wDINA} what proved the increase of samples heterogeneity. For $x_{\mathrm{wDINA}} \leq 0.750$ no influence of samples storing on the phase changes was observed. The heat capacity change decreased and temperature range of glass transition increased for $x_{\mathrm{wDINA}} \leq 0.500$ what indicated the reduction of glass phase fraction in studied samples.

Keywords: *DSC, glass transition, melting enthalpy, mixing enthalpy, nitrocellulose, N-nitrodiethanolamine dinitrate (DINA)*

Introduction

Nitrocellulose (NC) is a raw material not suitable for direct applications. To improve properties of NC-based products and extend the range of their practical applications, the low molecular components acting as plasticizers are added. There were carried out intensive research under the properties of NC modified with low molecular additives as water, *s*-diethyldiphenylurea (C1) and dinitrotoluenes (2,4- and 2,6-DNT) [1–7]. The results given by these authors showed that differential scanning calorimetry (DSC) was especially useful for investigation of prepared binary samples. In this manner mixing and melting enthalpy were determined for the mixtures of NC with C1 [2], 2,6-DNT [6] and 2,4-DNT [7]. The pore sizes were calculated for mixtures with water [1] and C1 [4, 5], while the phase and glass transitions were studied for NC+C1 [3, 5], NC+2,6-DNT [6] and NC+2,4-DNT [7] samples. The Flory–Huggins parameter χ was also estimated for investigated NC mixtures [3, 7]. The long-term properties and influence of the thermal history of NC based samples were studied in details [4–7].

It is commonly known that the chain-like structure of NC is similar in properties to polymers what leads to the assumption that the effects resembling relaxation should be observed during their thermal treatment. From published data [8–12] one can conclude that for the NC binary mixtures several separate relaxation steps were observed instead of one general phase change – glass transition. The authors proved using different methods (DSC, dynamic mechanical analysis, dielectric or volume dilatometry measurements) that the glass transition splits at least into two effects: a low temperature β-relaxation associated with the plasticizer and a high temperature α-relaxation attributed to the movement of NC structures. These relaxation steps were observed for NC based gunpowder [8], for the mixtures of NC with dibuthylphalate [9] or triethylene glycol dinitrate (TEGDN) [10, 11], and among other for binary mixtures of NC and nitroglycerine (NG) or diethylene glycol dinitrate (DEGDN) [10–12]. The samples of NC+dimethylacetamide were also studied from this viewpoint [12].

The structures and characteristics of nitrocellulose mixtures result both from the properties of pure components and their specific interactions. In the binary systems NC+low molecular component two kinds of aggregates are possible: molecular complexes [13–20] and liquid crystal structures [21–24].

N-nitrodiethanolamine dinitrate (DINA) is an example of low molecular additive which can be applied as a plasticizer and modifier of combustion of NC. The aim of this research was to determine enthalpies (melting, mixing) of the binary system NC+DINA and to examine phase transitions, occurring during the long time storage at ambient temperature.

Experimental

The nitrocellulose utilised in this investigation was produced from sulphite pulp in ZTS PRONIT (Pionki, Poland). According to the producer's specifications it con-

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tained 13.2 mass% of nitrogen and had average molecular mass M_n=41.3·10^3 g mol^{-1}. Before experiments initial material was dried to constant mass under the vacuum. The structural parameters of the NC were investigated with the BJH adsorption–desorption method. The mean surface of fibres was 8.8 m^2 g^{-1}, mean pore volume 0.023 cm^3 g^{-1} and mean pore diameter 14.9 nm. The nitrogen adsorption-desorption measurements were carried out on Micrometrics ASAP 2405 analyser. The endothermic peak (D) of studied nitrocellulose occurred approximately at 322 K and with thermal effect ΔH_D=0.9 J g^{-1}. This peak was absent if the sample was rerun immediately, but could be registered after several hours of storing at room temperature. According to Warren [12] such transition has the characteristics of a form of melting.

DINA applied in these experiments was synthesized in Department of Chemistry, Warsaw University of Technology. It was crystallised three times from acetone and its purity determined by cryometric method was 99.6 mol%. The mixtures of NC with DINA were prepared by exact mixing and grinding of components and pressing under pressure 0.5 GPa during 1 min to form the pellets with dimension of calorimetric pan. The samples were hermetically closed in aluminium pans under reduced pressure about 1.3 kPa.

Methods

Measurements were performed on Perkin-Elmer Pyris DSC-1 microcalorimetry. The melting process of DINA investigated with heating rate β=2 K min^{-1} in temperature range 293–380 K (method I) was applied for the estimation of mixing enthalpy. The influence of the storage time at room temperature on the phase transitions was examined in the range 173–380 K with heating rate β=20 K min^{-1} (method II). The measurements carried out according method III consisted of three consecutive steps performed with β=20 K min^{-1}: heating from 173 to 380 K, cooling from 380 to 173 K and heating from 173 to 380 K. Only DSC measurements with heating were analyzed in this paper.

It is assumed that the penetration of DINA into amorphous structure of NC starts in samples at the beginning of melting during the first DSC measurements. Endothermic peaks observed on the DSC curves results both from the melting and the molecular interaction between DINA molecules with NC chains. The contribution of DINA melting enthalpy per 1 g of the mixture can be calculated according to the following relation:

$$\Delta H_{\mathrm{mDINA}} = \Delta H^0_{\mathrm{mDINA}} x_{\mathrm{wDINA}} \tag{1}$$

where $\Delta H^0_{\mathrm{mDINA}}$ is the melting enthalpy per 1 g of pure DINA, and x_{wDINA} the mass fraction of DINA in samples. The mixing enthalpy H^M corresponding to the interaction of DINA molecules with NC chains is given by the equation:

$$H^M = \Delta H - \Delta H_{\mathrm{mDINA}} \tag{2}$$

where ΔH represents measured enthalpy of melting and mixing processes of DINA per 1 g of the mixture. It is more convenient to express H^M per 1 mole of the mixture:

$$\overline{H}^M = H^M M_{\mathrm{am}} = H^M [x_{\mathrm{DINA}} M_{\mathrm{DINA}} + (1 - x_{\mathrm{DINA}}) M_{\mathrm{NC}}] \tag{3}$$

where M_{am} is average molar mass of samples, x_{DINA} – DINA mole fraction, M_{DINA} – DINA molecular mass, M_{NC} – molecular mass of unit (submole nitrocellulose) which is a function of the average number (Y) of the groups attached to one anhydroglucose ring according to the formula: $(C_6H_7O_2)(OH)_{3-Y}(ONO_2)_Y$.

Results and discussion

It follows from DSC measurements carried out with heating rate β=2 K min^{-1} that the beginning of melting process of applied DINA was at T^0_m=324.3 K (the reported melting temperature of DINA was 324.4 K [25]) and melting enthalpy was ΔH^0_m=121.6 J g^{-1}. On the DSC curve shown in Fig. 1 phase changes of the DINA sample, which was obtained after fast cooling of preheated pure substance, are presented. As a result of instantaneous cooling it was possible to completely over-cool liquid phase to glass phase. In this measurement the thermal effect of glass transition occurred at T_{g1}=216.3 K, and the heat capacity change was ΔC_{p1}=0.631 J g^{-1} K^{-1}. On this curve at temperature 255.1 K falls sharp maximum of the crystallization

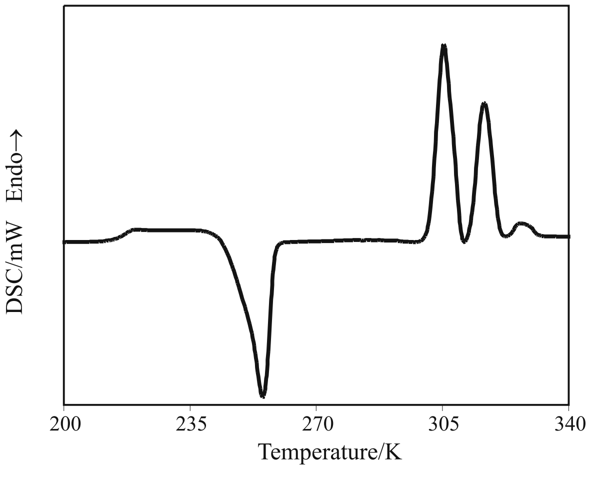

Fig. 1 DSC curve of DINA phase transition after fast cooling of the sample

Table 1 Mixing enthalpy H^M for NC+DINA mixtures

x_{wDINA}	H^M/kJ mol^{-1}
0.750	–0.94
0.750	–0.94
0.500	–1.20
0.500	–1.48
0.460	–1.94
0.400	–0.66
0.200	–0.52
0.200	–0.18

peak. As a consequence of this process three different crystalline forms were created. Their melting processes can be seen on presented DSC curve as endothermic peaks with the beginnings at 301.2, 312.8 and 323.8 K. The position of high temperature melting peak on the discussed curve is consistent with the melting peak of pure DINA crystallized from acetone. In Table 1 the values of mixing enthalpies H^M calculated for average molar mass of the samples are listed. The extrapolated maximum of the mixing enthalpy reaches approximately H^M_{max}=1.95 kJ mol^{-1} for mass fractions of DINA x_{wDINA}=0.46. It is assumed that during the first DSC measurements samples are mixed e.g. DINA melts and its molecules start to penetrate into NC structures.

The DSC measurements were repeated after different periods of time (t_p) on previously used samples which were stored at room temperature in hermetic pans. The melting process of sample containing mass fractions x_{wDINA}=0.93 was carried out after t_p=41 days using method III. The registered plots are presented in Fig. 2. On the DSC curve obtained during the first heating (thick line) only one sharp melting peak of stable DINA form is observed at temperature T=315.2 K. The determined enthalpy of this process is ΔH_m= 103.7 J g^{-1}. A sharp change of heat capacity appears at low temperatures during the next melting process (thin line) which is connected with the glass transition. An intensive effect of DINA crystallization (ΔH_m= –54.1 J g^{-1}) begins approximately with temperature 240 K, then the curve reaches its maximum at T_p=279 K. The melting temperature of obtained metastable form is T=302.1 K which is close to the melting temperature of metastable (low temperature) form of pure substance. The corresponding melting enthalpy ΔH_m=54.5 J g^{-1} is in a good agreement with thermal effect of crystallization. At T=320.4 K a small peak with enthalpy of the process ΔH_m=1.04 J g^{-1} can be observed. This peak refers to the melting of the stable form of DINA. The next measurement of the same sample was performed after t_p=621 days and the value of the melting enthalpy ΔH_m=103.2 J g^{-1} was obtained. This result is consistent with the value of melting enthalpy evaluated from the first heating process during the previous experiment. A small change of heat capacity DC_p= 0.038 J g^{-1} K^{-1} which appears at T_{g12}=234.2 K corresponds to the glass transition. For this sample melting process in confined spaces (pores) was not observed, contrary to the results registered for the other plasticizers of nitrocellulose [4–7]. It follows from this observation that the molecules of DINA were not able to crystallize in pores of NC although the sample were stored for a long time at room temperature.

The melting process of samples containing mass fractions x_{wDINA}=0.850 was studied within a period of 730 days. Two typical DSC curves registered for these samples are presented in Fig. 3. For all taken experiments the shape of registered curves remained in good agreement with one another. There were obtained reproducible values of two parameters e.g. glass transition temperatures close to T_{g12}=

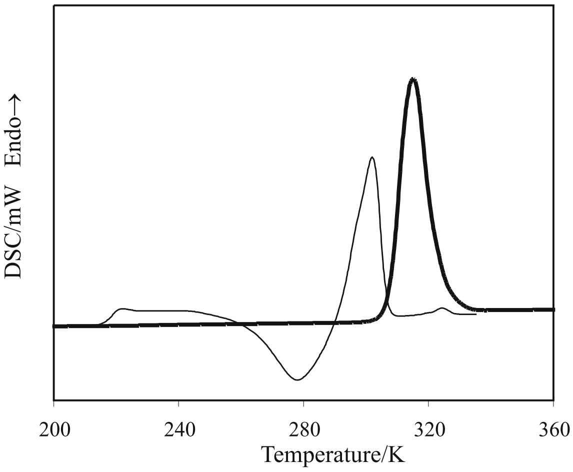

Fig. 2 DSC curves of NC+DINA mixture (x_{wDINA}=0.930) obtained by method III. The thick line – the first heating and the thin line – the second heating

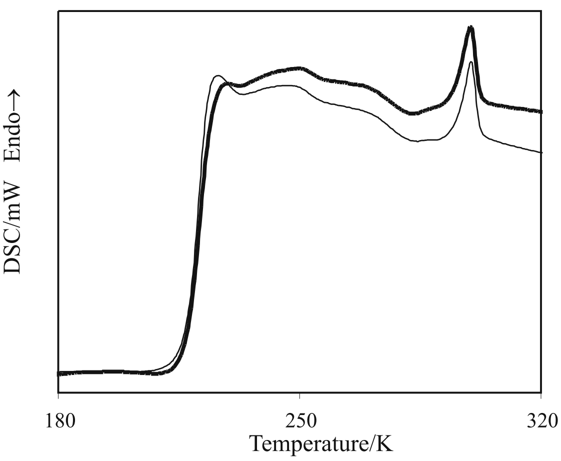

Fig. 3 DSC curves of NC+DINA mixture (x_{wDINA}=0.850) obtained by method III. The thick line – the first heating and the thin line – the second heating

Table 2 The temperature of peak maximum T_p and enthalpy ΔH_D of endothermic process (D) for successive measurements; Lp – the number of melting process, t_p – time between measurements

x_{wDINA}	Lp	t_p/day	T_p/K	ΔH_D/J g^{-1}
0.400	3	161	337.5	0.81
	4	200	337.4	0.32
	5	341	339.4	0.44
0.309	2	40	326.6	1.39
	4	0.83	318.0	0.73
	5	78	333.2	0.32
0.200	2	0.03	301.1	0.18
	3	228	335.1	1.45
	4	343	335.1	1.34
0.102	2	0.16	321.2	0.14
	3	228	336.7	0.15
	4	342	341.3	0.16
	5	34	339.4	0.31

221.0 K and heat capacity change ΔC_p=0.59 J g^{-1} K^{-1} for repeated immediately melting processes and for the experiments conducted successively after the longer periods of samples storing. At temperature T=299.5 K a small endothermic peak characterized by insignificant thermal effect ΔH_m=0.35 J g^{-1} is observed for samples stored for different time and analysed according method III. The results obtained using the same method for mixtures x_{wDINA}=0.750 show that only glass transition occurred. The value of ΔC_p is constant and independent on the time between consecutive experiments.

The investigation of sample x_{wDINA}=0.500 was performed after 354 days using method III. During the first heating glass transition appeared at T_{g12}=238.8 K and had the value of ΔC_p=0.320 J g^{-1} K^{-1}. In the second measurement of this experimental cycle the observed at T_{g12}=237.1 K heat capacity change was lower e.g. ΔC_p=0.288 J g^{-1} K^{-1}. The difference in T_{g12} and ΔC_p values of the ‘deglassing’ process can be connected with the interactions of DINA molecules with NC chains. Recently it was shown for binary biocomposites that strong interactions between cellulose chains and modified starch matrix had the substantial influence on glass transition temperatures [26].

For mixtures containing mass fraction of DINA x_{wDINA}=0.400 and lower a small endothermic effect ΔH_D (0.14–1.45 J g^{-1}) was observed. The temperature of this peak and the value of measured effect was dependent on the intervals between successive experiments, with the exception of short intervals when this effect was not observable. These properties are typical for endothermic effect (D) of NC based materials [12]. The temperatures T_p of peak maximum and the values of thermal effects are summarized in two last columns of Table 2.

The glass transition temperature T_{g12} increases with the lowering of the DINA content in analysed samples. The dependence of T_{g12} on the mass fraction x_{wDINA} is described by the following equation, determined with the correlation coefficient R^2=0.97:

$$T_{g12} = -41.1 \pm 2.6 x_{wDINA} + 255.7 \pm 1.7 \qquad (4)$$

The value of T_{g12} calculated for x_{wDINA}=0 from the Eq. (4) is 255.7 K. This value is considerably lower than the glass transition temperature of pure NC [3].

The relation between ΔC_p and mass fraction x_{wDINA} for short t_p is described by the following equation, determined with the correlation coefficient R^2=0.96:

$$\Delta C_p = 0.599 \pm 0.045 x_{wDINA} + 0.034 \pm 0.030 \qquad (5)$$

The temperature range of glass transition ΔT_{g12} can be defined as a difference between extrapolated onset temperature of the beginning and extrapolated temperature of the ending of a process. The value of ΔT_{g12} depends on mass fraction of DINA in studied mixtures. This linear dependence can be described by the Eq, (6), determined with the correlation coefficient R^2=0.97:

$$\Delta T_{g12} = -30.3 \pm 2.7 x_{wDINA} + 33.1 \pm 1.7 \qquad (6)$$

The influence of the storing time of the sample x_{wDINA}=0.310 on the temperature range of glass transition ΔT_{g12} are given in Table 3. It follows from the summarized data that ΔT_{g12} increases with the intervals between measurements and therefore can be considered as a measure of heterogeneity of the investigated samples. Both the changes of ΔT_{g12} and ΔC_p proves that for the studied binary system a slow migration of DINA molecules occurred.

Table 3 The changes of temperature range ΔT_{g12} and heat capacity ΔC_p of the glass transition for NC+DINA mixture (x_{wDINA}=0.310) for different t_p – time between measurements

t_p/days	ΔT_{g12}/K	ΔC_p/J g^{-1} K^{-1}
42	20.5	0.292
342	24.0	0.175
621	26.5	0.151

Conclusions

A substantial thermal effect observed for studied mixtures provided evidence for the presence of strong interactions between DINA molecules and NC chains. The subsequent DSC measurements carried out on the same samples proved that the time between them had influence on phase changes. At low temperatures a glass transition process occurred while at temperatures close to 320 K a small endothermic effect (D) was also detected (0.14–1.45 J g^{-1}).

The intervals between measurements (t_p) for the samples with high DINA content (x_{wDINA}≥0.750) had no effect on phase transitions. But for the mixtures with lower DINA content (x_{wDINA}≤0.500) the influence of t_p on the values of heat capacity change (ΔC_p) and temperature range of glass transition (ΔT_{g12}) was observed. Appling method III for samples characterized by short t_p we could not observe endothermic effect (D) on the registered DSC curves. When the values of t_p increased the parameter ΔC_p became smaller what indicated the lowering of the content of glass phase in samples. At the same time the parameter ΔT_{g12} increased what led one to the conclusion that heterogeneity of the studied systems was substantially enlarged.

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