

THERMOCHEMISTRY OF THE BINARY SYSTEM NITROCELLULOSE+2,4-DINITROTOLUENE

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Abstract

Melting enthalpy and mixing enthalpy of binary system 2,4-dinitrotoluene and nitrocellulose were determined by DSC method. The maximum value of mixing enthalpy was $H_{\max}^M = 1.38 \text{ kJ mol}^{-1}$ for molar fraction $x_{w24DNT} = 0.501$. The Flory–Huggins parameter (χ) was estimated. The solubility curves and glass transition temperatures were predicted and compared with the experimental results.

The measurements were performed for the samples with different times of storage at room temperature. The analysis of melting peaks for the mixture leads to the conclusion that for the long periods of storage the melting of 2,4-dinitrotoluene takes place in the confined spaces (pores) and unconfined space (bulk). The crystallization and melting is observed during the short time of storage in mixtures with low nitrocellulose content and in the case of mixtures with a large amount of NC the glass transition is additionally observed.

Keywords: 2,4-dinitrotoluene, DSC, glass transition, mixing enthalpy, nitrocellulose

Introduction

Nitrocellulose (NC) is rigid material and it is not suitable for direct application. To improve NC utility value and improving the processing properties, the low molecular components acting as plasticisers are added. There have been done some research under the addition of low molecular compounds and its influence for the property of mixtures with NC. The properties of NC+diphenylodietylurea system were presented in article [1, 2] and NC+2,6-dinitrotoluene system in article [3].

The 2,4-dinitrotoluene (24DNT) is an example of low molecular additive to NC, which acts as plasticizer and modifier of combustion of nitrocellulose. Brodman [4] was examined the different isomers of dinitrotoluenes and concluded that 24DNT has weaker hydrogen bonds than others member of this group. Winkler [5] has performed the molecular modeling of energy of hydrogen bonds. It was shown that one DNT particle can interact with only one glycoside ring of NC, and bonding energy was 4.8 kJ mol^{-1} .

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The aim of this work was the estimation of Flory–Huggins interaction parameter (χ) based on the mixing enthalpy in 24DNT+NC system and examination of phase transitions, occurring during the long time storage in ambient temperature.

Experimental

The NC used in this work was obtained from wood produced by ZTS ‘Pronit’ in Pionki. It contained approximately 13.2% of nitrogen and has average molecular mass $M_n = 54 \cdot 10^3 \text{ g mol}^{-1}$. NC was washed by distilled water during 24 h due to removing the impurities before application. NC was dried and stored in desiccator under P_2O_5 .

24DNT was obtained in Chemical Factory ‘Nitrochem’ in Bydgoszcz. 24DNT was crystallized from acetone several times. The cryometric purity measured after crystallization was 99.6%, and melting enthalpy was $\Delta H_m = 112.4 \text{ J g}^{-1}$. According to literature data [6] the melting enthalpy was $\Delta H_m = 121.8 \text{ J g}^{-1}$.

The mixtures of NC with 24DNT was performed 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 alumina pans under reduced pressure about 1.3 kPa. The measurements were carried out using the differential scanning calorimeter by Perkin Elmer model Pyris 1. The melting process of 24DNT in the mixture was measured with heating rate $\beta = 2 \text{ K min}^{-1}$ in temperature range from 293 to 380 K for the estimation of the mixing enthalpy. The influence of storage time at room temperature on phase transitions was examined at temperature range from 173 to 380 K with heating rate $\beta = 20 \text{ K min}^{-1}$.

Method background

It was assumed that the penetration of 24DNT into amorphous NC starts at the beginning of 24DNT melting processes during the first DSC measurements. Endothermic peaks observed in the DSC curves are due to the melting of 24DNT and the molecular interaction between 24DNT molecules with NC chains. The contribution of 24DNT melting enthalpy per 1 g of the mixture can be predicted according to the relation:

$$\Delta H_{m\ 24DNT} = \Delta H_{m\ 24DNT}^0 x_{w\ 24DNT} \quad (1)$$

where $\Delta H_{m\ 24DNT}^0$ is the melting enthalpy per 1 g of pure 24DNT, and $x_{w\ 24DNT}$ is the mass fraction of 24DNT in the investigated mixture. The mixing enthalpy corresponding to the interaction of 24DNT molecules with NC chains is given by:

$$H^M = \Delta H_{m\ 24DNT}^{M1} - \Delta H_{m\ 24DNT} \quad (2)$$

where $\Delta H_{m\ 24DNT}^{M1}$ is the measured enthalpy for 24DNT melting and mixing processes per 1 g of mixture. For better discussion it is more convenient to express H^M per 1 mole of mixture of

$$\bar{H}^M = H^M M_{ST} = H^M [x_{24DNT} M_{24DNT} + (1 - x_{24DNT}) M_{NC}] \quad (3)$$

where $x_{24\text{DNT}}$ – mole fraction 24DNT, $M_{24\text{DNT}}$ – molecular mass of 24DNT, 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:



Results and discussion

There was considered that during the preparation of sample by mechanical mixing and preparation of tablets using the amorphous NC and powdered 24DNT at the room temperature there were no mixing of components in the molecular level. The first DSC measurements were performed on the freshly prepared samples for the purpose of determination of the mixing heat. The whole thermal effect measured is a sum of effects of 24DNT melting process and heat of mixing. Figure 1 presents the typical DSC curve of first measurements for mixture with $x_{w24\text{DNT}} = 0.501$. It is visible on the DSC curve that the endothermic (melting) process and the exothermic (mixing) are overlaid. The mixing enthalpy was estimated using Eqs (2) and (3). The values of mixing enthalpy (H^M) were placed in the Table 1. The estimation error of H^M was about 10%. The values of (H^M) were used for calculation the Flory–Huggins (χ) interaction parameters [7, 8]. The interaction parameter was calculated according to the equation:

$$\chi = \frac{H^M}{RT\phi_1\phi_2\left(x_1 + x_2\frac{V_2}{V_1}\right)} + \chi_s \quad (4)$$

where ϕ_1 ϕ_2 are the volume fractions for components 1 and 2, V_1 and V_2 are molar volumes of component 1 and 2, respectively, R is the gas constant, T is 24DNT melting temperature, x_1 and x_2 are molar fractions expressed for the monomer unit, χ_s is entropy share as the constant value 0.34 [9–11].

It was considered for prediction the liquid-solid equilibrium that parameter of interaction (χ) is not dependent on temperature and components are completely soluble

Table 1 Mixing enthalpy (H^M) and Flory–Huggins parameter (χ) for 24DNT+NC system

$x_{w24\text{DNT}}$	$H^M/\text{J mol}^{-1}$	χ
0.878	–264	–0.7
0.750	–376	–0.4
0.601	–628	–0.6
0.501	–1379	–1.5
0.401	–1332	–1.4
0.320	–968	–0.9
0.248	–957	–1.1
0.125	–785	–1.5

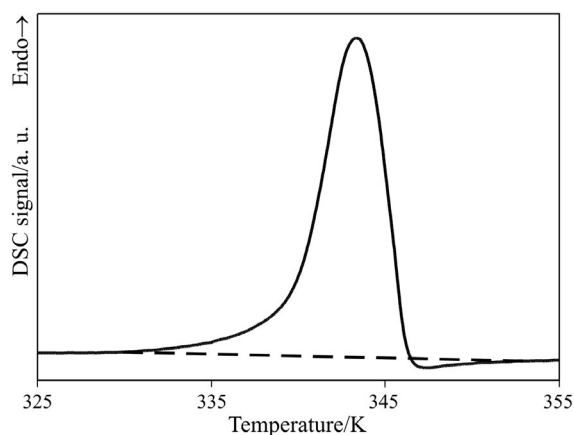


Fig. 1 Typical DSC curve for the first measurement for freshly prepared sample of mixture NC+24DNT with mass fraction $x_{w24DNT}=0.501$

in liquid phase and are completely immiscible in solid phase (eutectic system). The dependency between χ and $x_{w2,4DNT}$ was approximated by linear equation for the predicting the phase equilibrium. The solubility curves of nitrocellulose and 24DNT were calculated according to equations from [12]. The glass transition temperature for mixture was calculated by Lu–Weiss model [13], using the interaction parameter (χ).

Results of calculations were presented in Fig. 2. The eutectic temperature is $T_e=335.5$ K for mass fraction $x_{w24DNT} = 0.576$. The eutectic temperature is higher than the storage temperature. It leads to the conclusion that during the storage system is going to forming the solid phases NC and 24DNT as a result of migration of low molecular component from polymeric matrix into confined space forming the pores. The solubility curve of NC is crossing the glass transition curve at $T_{gc} = 226.2$ K for mass fraction $x_{w24DNT} = 0.817$. The temperatures of glass transition determined experimentally were placed in Table 2. In this table there were given only the values of T_g , when the jump of heat capacity was enough great duo to a glass transition process. The maximum experimental glass transition temperature is $T_{gm} = 238.95$ K and is about 12 K higher than predicted basing on parameter χ ($T_{gc} = 226.2$ K). This difference can be caused by the experimental errors of determination of mixing enthalpy.

Table 2 The glass transition temperature for binary system 24DNT+NC

x_{w24DNT}	T_{gm}/K
0.745	238
0.601	237
0.512	231
0.401	235
0.320	236
0.320	227

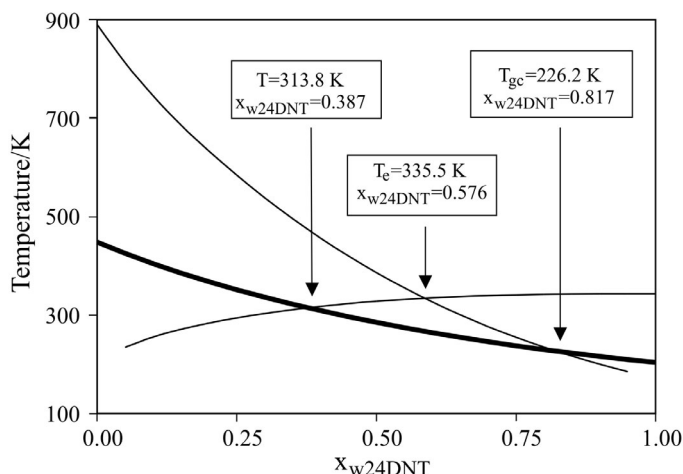


Fig. 2 The liquid–solid equilibrium for system NC+24DNT (thin line) and temperatures of glass transition (thick line) predicted from the interaction parameters λ .

The glass transition process was observed in consecutive measurements performed on the same sample for the different storage time between measurements. During long-term storage the glassy phase disappears. It is caused that 24DNT molecules migrate from NC matrix forming the great pores enabling the arising 24DNT nuclei formation of the crystallization. The low values of glass transition temperatures suggests that the changes of solution content are in agreement with the solubility NC curve till to the crossing point with the glass transition curve during the cooling of samples with $x_{w24DNT} < 0.817$. The mixtures from $x_{w24DNT} > 0.576$ has great tendency to overcooling.

The glass transition was not observed for pure 24DNT in spite of applying the different overcooling techniques. The sample obtained by the mixing of equal amount of 24DNT and ceramic porous material (pore diameter about 12 nm) enabled the observation of glass transition. It was presented in the Fig. 3. These results confirm the proposed mechanism of the glass transitions formation in small space. In small spaces the tendency of forming glassy phase is duo to lack of condition for the formation of crystallization nuclei.

The DSC curves of the sample with $x_{wDNT} = 0.501$ for measurements after 181 days of storage (thin line) and after another day (thick line) performed on the same sample are presented in the Fig. 4. The complex peak of 24DNT melting is visible in the first DSC curve, showing that melting occurs in confined and unconfined space. The description of pore structures will be published in the next our work (in preparation). After the long time storage the migration of 24DNT molecules form matrix into the pores with dimensions enabling the forming of crystallization nuclei. The lack of glass transition means that the rest of 24DNT molecules in polymer matrix are strongly bonded with NC chains. In next DSC curve is visible the glass transi-

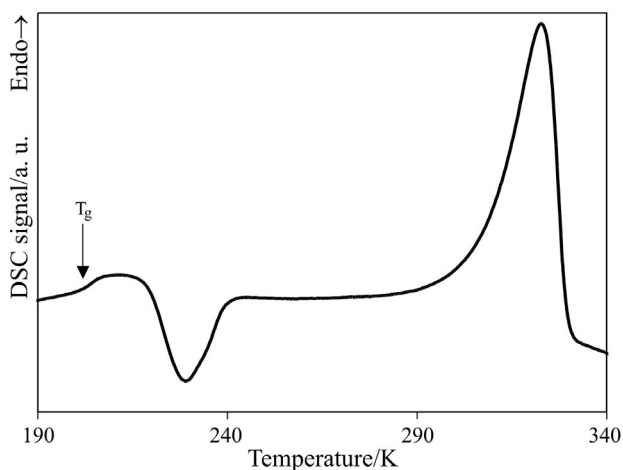


Fig. 3 DSC curve of phase transition for the mixtures of ceramic porous material and 24DNT with mass fraction $x_{w24DNT}=0.5$

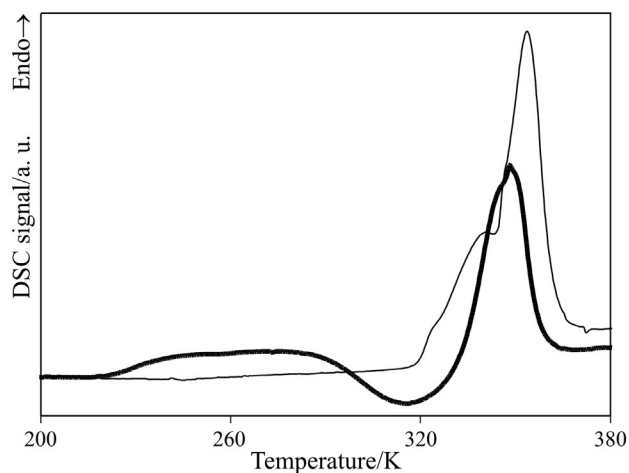


Fig. 4 DSC curves for $x_{w24DNT}=0.5001$ for measurement after 181 days (thin line) and consecutive after 1 day (thick line)

tion and crystallization and melting process of 24DNT. The shift of melting peak towards the low temperatures shows that it occurs in confined space, with lower dimensions than melting in previous measurement. The exothermal effect is connected with the some desolvation process and next crystallization. Due to increase temperature the movement of molecules increases to promote tearing off from NC chains and their crystallization. The confirmation of this mechanism is the comparison of obtained DSC curve (thick line) with curve presented in the Fig. 3. There is no penetration into walls of pores in the case of porous ceramic material. The crystallization occurs after termination of the glass process. There is no solvation in this case. The

shifts of crystallization toward higher temperatures should be attributed to intermolecular interactions between 24DNT and NC. For mass ratio $x_{w24DNT} < 0.32$ thermal effects of phase transitions are low and burdened by great error. For this reason it was omitted in further considerations.

There is no glass transition occurs in mixtures with low content of NC. The enlarged fragments of DSC curves before main melting peak in two consecutive measurements for the sample with $x_{w24DNT} = 0.987$ were presented in the Fig. 5. Thin line represents DSC curve obtained after 247 days of storage at ambient temperature. Thick line presents DSC curve for next measurement performed after 11 min. The glass transition is not observed in both discussed DSC curves. The crystallization begin at 230 K for the sample stored for a long time with thermal effect $\Delta H_c = -10.4 \text{ J g}^{-1}$ for the first measurement (calculated using the extrapolation of baseline from the low temperature range). It can be seen that the oscillations in the enlarged fragment of DSC curve proves that the melting process in small spaces is complicated. The crystallization process in following measurement (after 11 min) gives the effect $\Delta H_c = -2.7 \text{ J g}^{-1}$, and crystallization begins at temperature about 270 K. The maximum of crystallization peak in both processes was almost similar and was 341 K. After 606 days of this sample storage the crystallization was not observed and it suggested that after such a long time all weakly bonded particles 24DNT with NC chains underwent crystallization. The enlarged fragments of DSC curve for mixtures with mass fraction $x_{w24DNT} = 0.969$ after 217 days of storage (thin line) was presented at the Fig. 6. The crystallization is not observed for this measurement. In the next measurement performed after 11 min on the same sample, thermal effect of crystallization is $\Delta H_c = -5.2 \text{ J g}^{-1}$. The beginning temperature of crystallization is similar. For the sample with $x_{w24DNT} = 0.937$ analyzed after 11 min the enthalpy of crystallization is

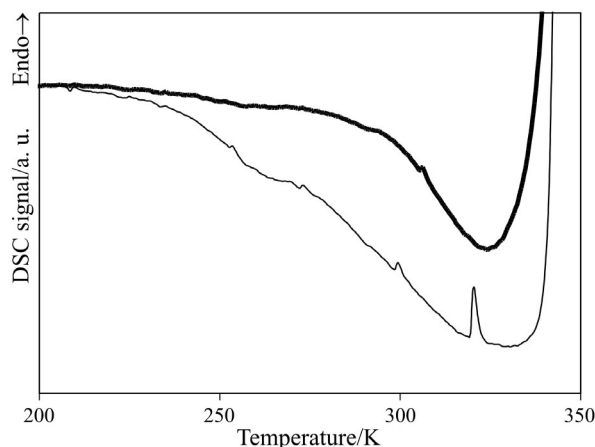


Fig. 5 The enlarged fragments of the DSC curves before the main melting peak in two consecutive measurements for mass fraction $x_{w24DNT}=0.987$. The thin line presents DSC curve for measurement after 247 days, thick line for consecutive measurement after 11 min

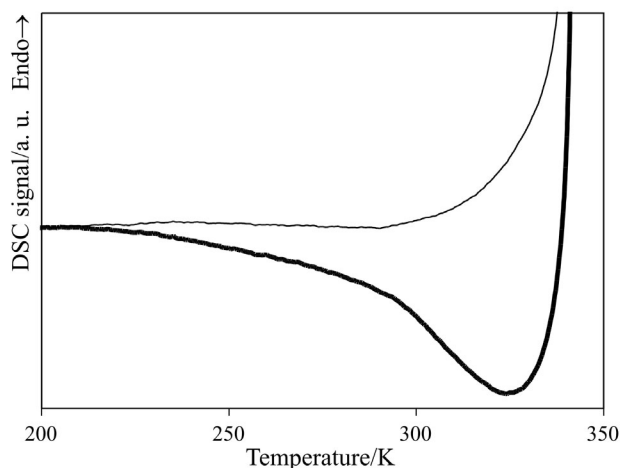


Fig. 6 The enlarged fragments of the DSC curves before the main melting peak in two consecutive measurements for mass fraction $x_{w24DNT}=0.969$. The thin line presents DSC curve for measurement after 217 days, thick line for after 11 min

$\Delta H_c = -1.4 \text{ J g}^{-1}$ for the mixture. The similar measurements are performed for the mixture with mass fraction $x_{w24DNT} = 0.878$ after 200 days. It can be observed on the DSC curve only the melting in confined and unconfined spaces. After performing measurement after 11 min it can be seen on the DSC curve the crystallization. This thermal effect is $\Delta H_c = -2.0 \text{ J g}^{-1}$ and melting occurs in unlimited spaces. There is no crystallization in the pores. The maximum temperature of melting peak after 11 min is approximately equal to the melting temperature of the main peak after 200 days.

The mixture with content $x_{w24DNT} = 0.82$ shows different behavior. After 419 days of conditioning, a complex melting peak, consisting of four overlaid peaks, is visible on the DSC curve. In the following measurement performed after 17 min, crystallization is not observed, but we can observe the melting in confined and unconfined spaces.

Conclusions

The phase diagram calculated on the basis of estimated enthalpy of mixing for the NC+24DNT system shows that long-time storage of the sample leads to displacement of 24DNT molecules from the polymeric matrix. This was observed on the DSC curve as only thermal effects of melting in confined (pores) and unconfined space (bulk).

We can conclude from the investigation of short storage periods that the mixture of NC+24DNT forms two structures. In mixtures with a great content of NC, the glassy phase is forming and in temperatures lower than the melting point, it crystallizes in limited spaces. The investigations for pure 24DNT and its mixtures with ceramic porous material lead to the conclusion that the samples undergo the process of glass transition in small limited spaces. The mixtures with small NC content do not form the glassy

state, but the pores with large dimensions are forming allowing for appearance of crystallization nuclei and the formation of overcooled liquid state is precluded. The crystallization process undergoes in considerably higher temperatures in comparison with system 24DNT+ceramic porous material. This shift of crystallization temperature can be explained by interaction between particles of NC and 24DNT.

References

- 1 A. Książczak and T. Książczak., *J. Therm. Anal. Cal.*, 54 (1998) 323.
- 2 A. Książczak, T. Książczak and M. Ostrowski, *J. Therm. Anal. Cal.*, 74 (2003) 575.
- 3 A. Książczak and T. Wolszakiewicz, *J. Therm. Anal. Cal.*, 67 (2002) 751.
- 4 B. W. Brodman and N. Lampner., *J. Eng., J. Appl. Polym. Sci.*, 27 (1982) 3621.
- 5 D. A. Winkler, *Polym. Commun.*, 30 (1989) 50.
- 6 W. E. Acree, Jr., *Thermochim. Acta*, 219 (1993) 97.
- 7 P. J. Flory, *Principles of Polymer Chemistry*, Ithaca, N.Y. Cornell University Press 1953.
- 8 P. J. Flory; *Principles of Polymer Chemistry*, Cornell University Press, New York 1966.
- 9 D. Patterson, *Macromolecules*, 2 (1969) 606.
- 10 O. R. Orwoll, *Rubber Chem. Technol.*, 50 (1977) 451.
- 11 A. F. M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion*, 1980.
- 12 A. Turi, *Thermal characterization of polymeric materials*, Second Edition, 1997, p. 420.
- 13 X. Lu and R. A. Weiss, *Macromolecules*, 25 (1992) 3242.