

INTERMOLECULAR INTERACTIONS AND PHASE EQUILIBRIA IN NITROCELLULOSE – s-DIETHYLDIPHENYLUREA SYSTEM

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Abstract

Values of the Flory–Huggins interaction parameters χ were predicted on the base of mixing enthalpy H^M for nitrocellulose–s-diethyldiphenylurea system. The phase diagram of the system and the glass transition temperature of mixtures T_{g12} were estimated using calculated χ parameters. The predicted glass transition temperatures were in accordance with values determined experimentally.

Keywords: cellulose nitrate, DSC, glass transition temperature, interaction parameter, phase diagram, s-diethyldiphenylurea

Introduction

Nitrocellulose (NC, cellulose nitrate) processing requires a low molecular compounds addition. These compounds can act as plasticizers and solvents enabling low temperature treatment of nitrocellulose masses, stabilisers protecting the polymer durability, or in other way modifying its properties.

Symmetric diethyldiphenylurea (C1, centralite I) is applied in the nitrocellulose processing technology as a plasticizer and stabiliser. There is very little information in the literature on the way, which it interacts with NC [1–3]. It is known that C1 forms strong hydrogen bonds with hydroxy groups of NC [2, 3]. Mikhailov *et al.* [2] proves on the basis of IR spectra analysis of NC–C1 films, that the molecular complexes can appear in this system.

The mixing enthalpy H^M dependence on concentration in the system NC–C1 was determined in our previous work [1]. The aim of this work is to evaluate the usability of this calorimetric data in estimating the Flory–Huggins interaction parameter χ . We can predict the phase diagram for the NC–C1 system and the dependence of glass transition temperature on the mixture composition using this parameter.

Experimental

Nitrocellulose used in our investigations was produced in ‘Pronit’ polymer plant in Pionki and contained 13.2% of nitrogen. Before the preparation of the mixtures it was

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repeatedly rinsed and mixed with large amounts of water to eliminate traces of acids and to homogenise its composition. Centralite I was crystallised many times and its purity determined by cryometric method was 99.9 mol%. Glass transition temperature T_{g12} measurements were performed on Pyris DSC 1 calorimeter using the heating rate $\beta=20 \text{ K min}^{-1}$ in the temperature range 173–390 K similarly to the method used in the investigations of NC-2,6-dinitrotoluene system [4]. The samples utilised in measurements were the same as ones used previously in works devoted to estimating the mixing enthalpy of the NC–C1 system [1]. All discussed effects were recorded during heating of the sample.

Results and discussion

The centralite I investigated in different conditions of heating and cooling crystallised in one crystalline form. Its melting temperature was $T_m^0=343.3 \text{ K}$ and melting enthalpy was $\Delta H_m^0=110 \text{ J g}^{-1}$. C1 has a tendency to overcool, and we determined the glass transition temperature $T_{gC1}=225.8 \text{ K}$. The heat capacity change during the glass transition was $\Delta C_p=0.629 \text{ J g}^{-1} \text{ K}^{-1}$. The sample of pure C1 was heated to 373 K before the measurement and cooled to 173 K. The cooling rate was the same as the heating rate, i.e. $\beta=20 \text{ K min}^{-1}$. The DSC curve registered during subsequent heating of sample is presented in Fig. 1. Two crystallisation processes were observed: the first one, at the temperature $T_{p1}=266.9 \text{ K}$ (sharp peak), and the second one, much broader, with maximum at $T_{p2}=295.5 \text{ K}$ (symmetric peak). Different patterns of these peaks indicate that they originate from different processes. The last endothermic effect is connected with the melting process.

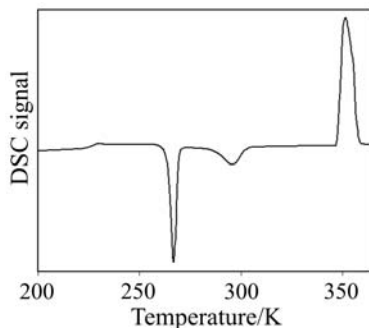


Fig. 1 DSC curve of phase transitions in pure *s*-diethyldiphenylurea at the heating rate of $\beta=20 \text{ K min}^{-1}$

The polymer – low molecular mass compound mixing process depends essentially on the character of interactions between molecules of both components. The interaction parameter χ introduced by Flory [5] is a very convenient method of describing such interactions. It is connected with mixing enthalpy by the dependence:

$$\chi = \frac{H^M}{RT\phi_1\phi_2\left(x_1 + x_2\frac{v_2}{v_1}\right)} + \chi_s \quad (1)$$

where T is temperature, R – gas constant, ϕ_1 , ϕ_2 – volume fractions of low and high molecular components correspondingly, v_1 , v_2 – mole volume of components, and x_1 , x_2 – their mole fractions. χ_s is the entropic contribution of the interaction parameter, for most systems equal 0.32 [6, 7]. Values of mixing enthalpy calculated basing on calorimetric measurements in NC–C1 system for whole compositions range were published in the previous work [1]. Predicted Flory–Huggins interaction parameter χ dependence on C1 concentration obtained using H^M and Eq. (1) are presented in Fig. 2.

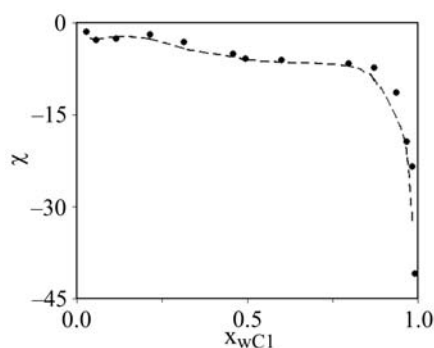


Fig. 2 Interaction parameter χ of binary system NC–C1; points – experimental data

A distinct change of the dependence character occurs around mass fraction $x_{wC1}^{sp} = 0.92$. Addition of small amounts of plasticizer for mass fractions of C1 below x_{wC1}^{sp} causes relatively low change of χ , while above this weight fraction the same small amount of plasticizer generates drastic drop of interaction parameter. The change of properties of the system follows in point x_{wC1}^{sp} – the character of interaction polymer and low molecular compound must be changed.

Interaction parameter χ enables predicting of liquid–solid equilibrium curves for the considering system. Flory’s solution theory gives equation, which describes liquid–crystal equilibrium temperatures for polymer in solution:

$$\Delta T_{mNC} = -\frac{RTT_{mNC}}{\Delta H_{fNC2}} [\ln\phi_2 + (1-\phi_2)(1-m) + \chi m(1-\phi_2)^2] \quad (2)$$

where T_{mNC} is the melting temperature of pure polymer, ΔH_{fNC} – melting enthalpy of pure polymer, m – degree of polymerisation and ϕ_2 – volume fraction of polymer in solution. A similar equation can be written for the low molecular component of solution:

$$\Delta T_{mCl} = -\frac{RTT_{mCl}}{\Delta H_{fCl}} \left[\ln\phi_1 + (1-\phi_1)\left(1 - \frac{1}{m}\right) + \chi(1-\phi_1)^2 \right] \quad (3)$$

It is very difficult to find proper values of melting temperature of nitrocellulose. It is well known, that this polymer decomposes before melting. Binke *et al.* [8] determined melting point of NC at 476.84 K using MDSC, microscopy and solid reaction cell in situ in conjunction with RSFT-IR method, but this value is much too low in our opinion, and corresponds to glass transition rather. The value 890 K given by Newman [9], basing on extrapolation of melting temperature of NC- γ -butyrolacton mixtures, seems to be more realizable. Substituting in Eqs (2) and (3) values for NC [9] and C1 [1], we get curves of solubility of NC (line B-e) and C1 (line A-e) presented in Fig. 3. These curves intersect at eutectic point (e) with co-ordinates $x_{wC1}^e=0.47$ and $T_e=313.8$ K. Mixtures were stored in temperature 298 K, that is below the eutectic temperature T_e . The system should then form two solid phases of pure components (NC and C1) in the thermodynamic equilibrium. However, the crystallisation is very slow in this system. It is overcooled and glass phase appears in temperatures below the glass transition temperature (line PQ in Fig. 3).

The typical DSC curve with glass transition for the sample with mass fraction $x_{wC1}=0.600$ stored 11 days in 293 K after preparation is presented in Fig. 4. No melting process of C1 indicates that this component occurs in amorphous form in the sample. The DSC curve of the sample with mole fraction $x_{wC1}=0.512$ recorded 170 days after sample preparing is presented in Fig. 5. The C1 in this case appears in two

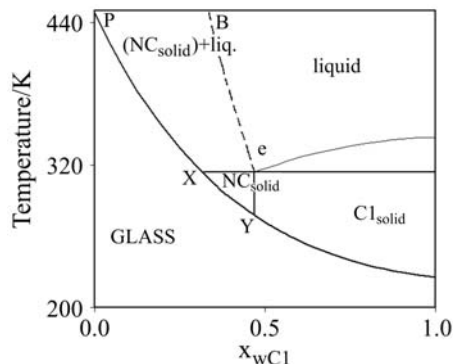


Fig. 3 Phase diagram with predicted glass transition temperature T_{g12} dependence (line PQ); The co-ordinates of eutectic point e: $x_{wC1}^e=0.47$, $T_e=313.8$ K

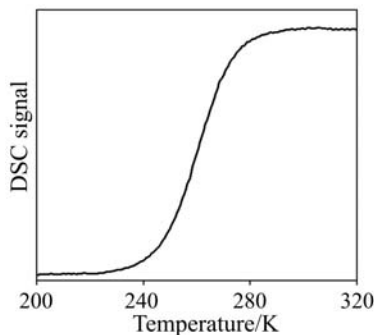


Fig. 4 Typical DSC curve of glass transition for the sample with $x_{wC1}=0.600$

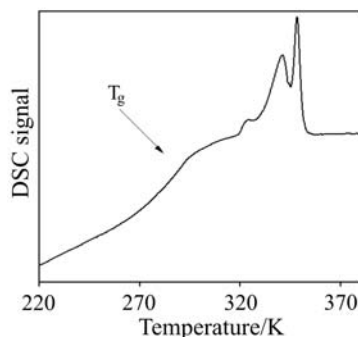


Fig. 5 DSC curve for sample with $x_{wCl}=0.512$. Glass transition and melting are presented

phases: in the amorphous one, which exists in lower temperature range, and in crystalline one, which melts in complex way in the higher temperature range. There are three endothermic peaks in the C1 melting region. The peak that occurs in the higher temperature corresponds to melting of C1, in unrestricted spaces. The two peaks visible in lower temperatures can be assigned to the melting process that proceeds in restricted spaces (pores). The composition of amorphous phase used in the calculations took into account that some part of C1 exists in crystalline form. It was assumed that crystalline phase of C1 is formed by C1 molecules only.

The glass transition temperatures were estimated basing on calculated interaction parameter values χ . The Lu and Weiss model [10] was applied, that connects glass transition temperature of polymer – low molecular compound mixture T_{g12} with mass fraction of components x_{wCl} , x_{wNC} , and interaction parameter χ by equations:

$$T_{g12} = \frac{x_{wNC}T_{gNC} + Kx_{wCl}T_{gCl}}{x_{wNC} + Kx_{wCl}} + \frac{Ax_{wCl}x_{wCl}}{(x_{wNC} + Kx_{wCl})(x_{wNC} + bx_{wCl})(x_{wNC} + cx_{wCl})^2} \quad (4)$$

where

$$A = \frac{-\chi R(T_{gNC} - T_{gCl})c}{M_{NC}\Delta C_{pCl}}, \quad K = \frac{\Delta C_{pCl}}{\Delta C_{pNC}}, \quad c = \frac{\rho_{NC}}{\rho_{Cl}}, \quad b = \frac{M_{Cl}}{M_{NC}}$$

and T_{gCl} , T_{gNC} – pure components glass transition temperatures, ΔC_{pCl} , ΔC_{pNC} – heat capacity change during glass transition of pure components, M_{Cl} – molecular mass of low molecular compound, M_{NC} – molecular mass of polymer unit, ρ_{Cl} and ρ_{NC} – densities of pure components. The value of $T_g=449$ K for NC given by Zhanning [11] was used in our calculations.

The curve of concentration dependence T_{g12} (line PQ) is put together with curves of liquid–solid equilibrium in Fig. 3. The $T_{g12}=f(x_{wCl})$ curve intersects the NC solubility curve (line B-e) at point $x_{wCl}=0.53$, $T=266.1$ K, and the curve of liquid – solid equilibrium for C1 (line A-e) at point $x_{wCl}=0.365$, $T=300.7$ K. Consider cooling of the system for $x_{wCl}<0.365$ starting from high temperature (region of liquid solution NC–C1). The crystallisation of NC should be observed after intersecting of NC solubility curve (line B-e). This process in reality is very slow and the system undergoes

overcooling. Further cooling of the mixture causes its vitrification. The crystallisation of C1 does not occur in this region. If the mass fraction of C1 is between 0.365 and 0.47 the first process that should proceed during cooling of the system is crystallisation of NC. As previously noted, the system is overcooled. Subsequent cooling of the system can lead to C1 crystallisation before the sample is vitrified.

Similar behaviour of the system will be observed for higher concentration of C1. For mass fraction above $x_{wC1}=0.53$ the NC crystallisation will not occur. In this region of compositions the crystallisation of C1 and vitrification of mixtures are the only possible processes in the system.

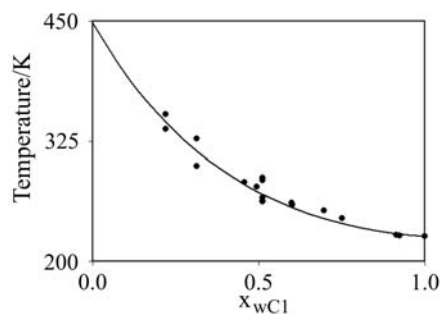


Fig. 6 Comparison of Lu Weiss models results (line) with experimental values of glass transition temperatures (points) for NC–C1 system

The curve obtained using Lu and Weiss model was set up with experimental glass transition temperatures of NC–C1 (points) mixtures, from DSC measurements, in Fig. 6. It can be seen that results arising from the model are in good agreement with the measured values. The highest value of glass transition temperature, 353.1 K, was recorded for the sample with $x_{wC1}=0.22$.

Conclusions

The method of estimation of χ and T_{g12} described in this work gave satisfactory results. The cooling rate was high enough to disable crystallisation of any component and the composition of vitrified phase was the same as composition of the mixture therefore. The results obtained from the model are consistent with experimental one's, which proves that method taken for heat of mixing determination [1] is correct. The process of components mixing in this system runs sufficiently fast to be finished during the first calorimetric measurement. The mixture formed in this way is homogenous enough to obtain reliable values of mixing enthalpy H^M , and predict other characteristics of the system.

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