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THERMAL AND CALORIMETRIC ANALYSIS OF CELLULOSE, ITS DERIVATIVES AND THEIR MIXTURES WITH PLASTICIZERS

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ABSTRACT

The heat capacity and physical transitions of cellulose with different crystallinity degree, its derivatives (acetates, nitrates, acetobutyrate and ethyl cellulose) as well as their mixtures with plasticizers (esters of phthalic acid, triacetin, oligoethylenebutylene glycol adipinate, castor oil and butylstearate) have been studied in the range 4 to 600 K by DTA and vacuum adiabatic calorimetry. The diagrams of physical states in binary systems polymer - plasticizer were constructed from data on concentration dependences of the temperatures of relaxation and phase transitions in the systems studied and on the solubility of plasticizer in polymer.

The heat capacity (C_p^o) and physical transitions of cellulose (in dependence on crystallinity degree), its derivatives (acetates and nitrates of different substitution degree, acetobutyrate and ethyl cellulose) and their mixtures with plasticizers (esters of phthalic acid, triacetin, oligoethylenebutylene glycol adipinate, castor oil and butylstearate) were studied between 4 and 600 K by differencial thermal analysis (DTA) [1] and vacuum adiabatic calorimetry [2].

The error of C_p^o determination below 30 and above 300 K is within 1 %, from 30 to 300 K - 0.3 %. Corundum (α-Al_2O_3) was used as a standard in DTA experiments. The rate of heating was 3 $K \cdot min^{-1}$. The weight of samples and standard was about 0.5 g. The temperature was measured with a chromel - copel thermocouple with an accuracy to ±0.5 %. The experiments were carried out in the atmosphere of dry helium.

The curves $C_p^o = f(T)$ for cellulose of variable crystallinity degree coincide essentially in the range 80 to 300 K. The transition (anormal increase in the heat capacity) observed for cellulose samples between 300 and 350 K may be attributed to the devitrification of its least ordered regions [3].

On thermograms and curves $C_p^o = f(T)$ of acetate cellulose (AC)

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containing a different amount of bound acetic acid (43.7; 54.5; 60.4 mass %) there are the following transitions: β-transition over the range 280 to 320 K (T_{β}), glass transition I between 360 and 400 K (T_{g1}), glass transition II from 390 to 440 K (T_{g2}), crystallization (T_{cr}=445-465 K) and melting (T_m=480-550 K). The heat capacity and temperatures of relaxation and phase transitions increase with growing the substitution degree of hydroxyl groips in cellulose with acetate ones. In melting range of acetates there are two endothermic peaks [4].

For nitrate cellulose (NC) with different content of nitrogen (from 8.0 to 14.1 mass %) β-transition appears on thermograms and curves $C_p^o=f(T)$ over the range 300 to 350 K. The temperature of this transition grows directly with the substitution degree of OH-groups in cellulose with ONO_2-groups that corresponds to the increase in the degree of polymer ordering on such substitution [5]. The heat capacity, entropy and enthalpy of nitrates is additive relative to the corresponding functions of cellulose and trinitrate cellulose.

For acetobutyrate cellulose with 45 and 18 mass % of bound butyric and acetic acid, respectively, and 2.43 mass % of free hydroxyl groups the thermograms show the devitrification of amorphous region (T_g=410 K), the crystallization (445 K) and melting (450-455 K) of polymer butyrate blocks as well as the crystallization (470 K) and melting (510 K) of acetate blocks in the polymer. At 525 K the polymer starts to decompose actively. Ethyl cellulose (the average substitution of hydroxyl groups is 2.3) is devitrified in the range 300 to 340 K, crystallized about 420 K and melted around 518 K.

The plasticization of AC and NC decreases relatively strongly (by 150-250 K) T_{g1} (AC) and T_g (NC) but influences slightly (5-20 K) on T_{β} and T_{g2} (AC) as well as on T_{cr} and T_m of the latter [6].

The solubility of noncrystallizable plasticizers (dibutylphthalate) in NC (the nitrogen content is 11.9 mass %) at glass transition temperature of the saturated solution was evaluated from the concentration at which the relationship $dT_g/dN_2=f(N_2)$, where N_2 is mole % of plasticizer, approaches the saturation since plasticizer as a rule no longer decreases significantly T_g of the polymer at concentrations greater than the solubility

Table The properties of plasticizers for NC and AC

Plasticizer	$T_g^{1)}$, K	$T_m^{1)}$, K	$\Delta T_g^{2)}$, K	Solubility in polymer $\lambda^{3)}$ mass %	mole %	Efficiency of plasticizer $\Delta T_g/\lambda$, $K\cdot(\text{mass }\%)^{-1}$
Nitrate cellulose (11.9 mass % of nitrogen)	420	-				
Triacetin (TA)	198	275.1	204	49±3	54±3	4.2
Dimethylphthalate (DMF)	194	272.9	230	67±1	73±1	3.1
Diethylphthalate (DEP)	180	269.9	220	61±1	65±1	3.6
Dibutylphthalate (DBP)	181	-	237	81±3	80±3	2.9
Castor oil (CO)	205	264.9	80	0.3±0.1	-	267
Butylstearate (BS)	-	299.5	45	0.75±0.1	0.6±0.1	60
Acetate cellulose (54.5 mass % of bound acetic acid)	382	500-540				
Cligoethylenebutylene glycol adipinate (OEBGA)	198	287.0	176	10±1	7±1	17.6
Diethylphthalate (DEP)	180	269.9	199	56±1	60±1	3.5
Triacetin (TA)	198	275.1	182	69±1	72±1	2.6

1) T_g, T_m is glass transition and melting temperatures, respectively. 2) ΔT_g is difference between T_g of polymer and T_g of saturated solution of plasticizer in polymer. 3) Calculation of solubility of plasticizer in polymer is described in detail in [6].

limit [6]. The solubility of crystallizable plasticizers was calorimetrically determined from the enthalpy of melting of its fraction in mixture that did not dissolve in the polymer (at melting temperature of plasticizer). Calculations of temperature dependence of amorphous plasticizer solubility in the polymer by the method of thermodynamic potentials [6] based on the calorimetric data showed that between 80 and 350 K the solubility changes only slightly (5-10 %) with temperature.

Efficiencies of the studied plasticizers (depression in T_g of polymer on adding of the same amount of plasticizer referred to unit mass of the latter) were evaluated and correlated from the data on relation $T_g=f(N_2)$ in binary mixtures polymer-plasticizer and on the solubility of plasticizers in polymers (Table). As seen from Table castor oil and butylstearate proved to be the most efficient plasticizer for NC but their solubility in the polymer is much too small (0.3 and 0.75 mass %, respectively). Among the plasticizers readily soluble in NC triacetin is the most efficient but DBP exhibits the greatest solubility. OEBGA is more effective also for AC but slightly soluble in it.

From the obtained results the diagrams of physical states of the above systems were constructed which make possible to determine temperature and concentration regions of glassy and high-elasticity states of polymer mixtures with plasticizers as well as their regions of homogeneity and heterogeneity.

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