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AN INVESTIGATION ON THE TRANSITION TEMPERATURES OF ACETYLCELLULOSE

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A method has been elaborated for the dilatometric investigation of compressed samples of acetylcellulose (AC) with the aid of the derivatograph. The determined glazing temperature shows a good coincidence with the literature T_g data for fibres and films. This allows the conclusion that orientation processes do not affect the transition. The development of crystallization has been established predominantly in heterogeneous highly esterified AC (60% CH_3COOH).

The elucidation of the transition temperatures of hard-chain polymers is frequently rendered difficult by pyrolytic processes. To determine transition temperatures simply, it is necessary to apply a combination of methods of investigation [1]; this is why transition temperatures have been studied by linear dilatometry (LD) and differential thermal analysis (DTA).

Transition temperatures are the temperatures at which changes in the mobilities of structural elements (groups, sections of macromolecules, primary and secondary supermolecular formation) take place, and are revealed on the characteristic property vs. temperature curves. Such temperatures for acetylcellulose (AC), obtained in the ordinary manner and in various ways, were described previously [2].

A method has now been elaborated for dilatometric investigations of compressed samples of AC, employing a derivatograph fitted with a special device.

Experimental

The equipment used and its principles of operation have already been described [3]. In the practice of measurements, however, a number of peculiarities must be taken into account.

The samples to be analyzed were prepared by compressing. To obtain samples of constant dimensions the material was first ground in a mill until it disintegrated into fluff. It was then allowed to stand for 24 hours in a desiccator over a saturated solution of NH_4Cl, and about 10% water was absorbed in it. This was necessary because of the strong electrostatic charging of the dry material. The powdery mass of AC produced was then compressed in a hydraulic press at 140 $kp \cdot cm^{-2}$, the special matrix of the apparatus being used for this purpose. The samples obtained, which were cylindrical in shape with 40 mm length, 16 mm OD and 8 mm ID, were dried in a vacuum oven at 10^{-1} torr and 70° for 6 hours. The original moisture content was thus restored. Investigations were carried out with 25 mm sections of the samples produced.

Calibration was performed using a material of well-known linear expansion coefficient, in this case small copper cylinders. One small division of the balance, adjusted to maximum sensitivity, was equivalent to 2.29×10^{-5} m. After contact established between the scale beam and the sample, it was loaded with 10 mg to achieve identical conditions for the dilatometric investigations. For the differential thermal analysis, a Teflon cylinder of similar dimensions to the samples investigated was employed as inert sample. The experiments were carried out in air. The dynamic heating was linear at a rate of 3° min^{-1}.

Results and discussion

The curves of change of the linear dimensions of the investigated samples are characterized by a distinct increase of slope at about 100°, due to the evaporation of the residual moisture. This is supported by the endothermic peak on the DTA curves from 35 to 115°. In this case the compressed samples are heterogeneous

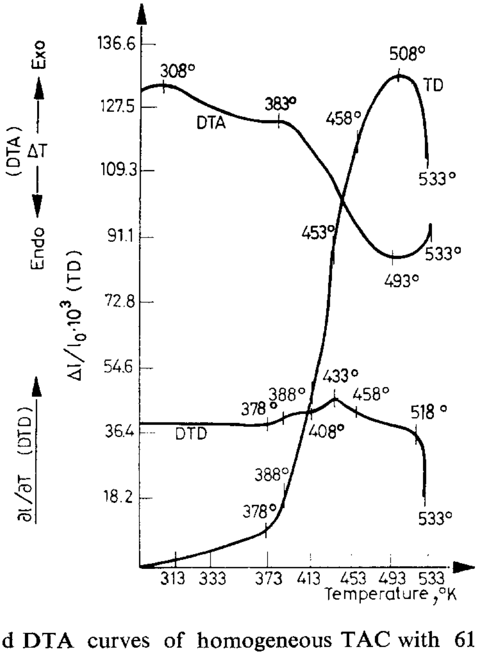

Fig. 1. DTD, TD and DTA curves of homogeneous TAC with 61.8 % fixed CH_3COOH (Sample 1, Table 1)

systems of AC, water and air. For this reason, the calculated linear expansion coefficient is obtained higher by an order of magnitude. This is of great significance in investigating the transition temperatures of polymers, and in determining glassy transition temperatures (T_g) and the main related range of relaxation (α-relaxation). The hard-chain polymers, such as derivatives of cellulose, have high T_g accompanied by decomposition; in these cases, therefore, the determination of T_g involves great difficulties.

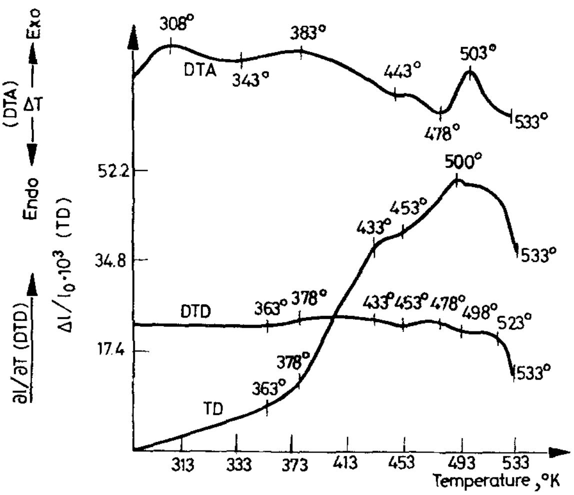

Fig. 2. DTD, TD and DTA curves of heterogeneous TAC with 62.3% fixed CH_3COOH (Sample 3, Table 1)

It is a complex process to determine transition temperatures of triacetylcellulose (TAC), for example, the correct T_g of which is about 160 – 165° [4 – 6]. The present method proved to be quite sensitive to changes in segmental mobility, permitting a comparatively easy and quick determination of this important index of polymer materials; moreover, the transition from the glassy into the highly elastic state is recorded especially distinctly in the curves of the derivative of the linear dimensions versus temperature (DTD curves).

Thermodilatometric (TD), differential thermodilatometric (DTD), and differential thermoanalytical (DTA) curves are given for homogeneous TAC with 61.8% of fixed acetic acid (Fig. 1) and heterogeneous TAC with 62.3% of fixed acetic acid (Fig. 2).

The glassy transition temperature is determined by the peak of the DTD curves. The DTD curve exhibits a maximum in this temperature interval for some samples, but not for others. This is explained by the effect of air contained in the compressed samples. At temperatures just below T_g, elastic deformation may occur due to the increased pressure in the air inclusions, leading to an increase in the linear expansion coefficient. Its decrease after transformation into the highly elastic

Table 1

No. of sample	Range of transition into highly elastic state, °C	Glassy transition temp. T_g, °C	Crystallization range determined by DTD, °C	Cristallization range determined by DTA, °C	Temperature of crystallization, °C	Temperature of disintegration °C
	1	2	3	4	5	6
1. Homogeneous TAC, 61.8% fixed CH_3COOH	145–185	160	–	–	–	240
2. Homogeneous TAC obtained by accelerated method with 62.3% fixed CH_3COOH	145–185	160	–	205–230	205	245
3. Heterogeneous TAC, 62.3% fixed CH_3COOH	160–180	160	205–225	205–245	205	250
4. Heterogeneous TAC obtained by accelerated method with 62.3% fixed CH_3COOH	160–180	160	205–225	210–245	210	250
5. Homogeneous TAC directly obtained with 60.2% fixed CH_3COOH	165–185	165	–	–	–	250
6. Homogeneous TAC homogeneously obtained with 60.1% fixed CH_3COOH	165–185	165	–	–	–	235
7. Homogeneous TAC heterogeneously saponified up to 60.3% fixed CH_3COOH	165–185	165	–	–	–	255
8. Heterogeneous TAC directly obtained up to 60.2% fixed CH_3COOH	160–170	160	210–225	210–245	210	260
9. Heterogeneous TAC heterogeneously saponified up to 60.3% fixed CH_3COOH	165–185	165	–	205–240	205	245
10. Heterogeneous TAC homogeneously saponified up to 60.9% fixed CH_3COOH	165–185	165	–	–	–	240
11. Homogeneous DAC heterogeneously saponified up to 55.6% fixed CH_3COOH	–	170	–	–	–	190
12. Heterogeneous DAC homogeneously saponified up to 55.3% fixed CH_3COOH	175–195	175	–	–	–	200

condition can be explained by the existence of unbalanced stretched structures which, under the conditions of increased mobility of the structural elements, assume a stable conformation state. It is known [6, 7] that the stable state of the acetylcellulosic macromolecule is the stretched one, characterized by a higher degree of arrangement and consequently a denser packing of the macromolecules;

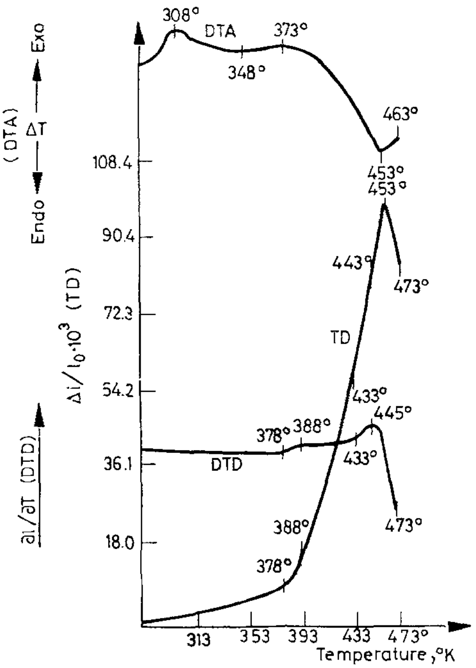

Fig. 3. DTD, TD and DTA curves of homogeneous DAC heterogeneously saponified up to 55.6% fixed CH_3COOH (Sample 11, Table 1)

thus, the observed decrease in the linear expansion coefficient immediately after T_g is quite obvious. The glassy transition temperatures of all investigated TAC samples are in the range 160–165°. The method of obtaining TAC (Table 1) and the degree of orientation have no essential effect on the transition temperature from the glassy into the highly elastic state.

The DTA curve shows an endothermic change above 120° extending up to 200°. In all probability, this is due to the over-all effect of splitting and formation of intermolecular bonds under the effect of heat, the former being predominant. In addition, the endothermic character of the curves below T_g can be attributed to the various conformational alterations of the acetylcellulose macromolecules, i.e. to the movement of atomic groups of the basic polymer chain, as well as to β, γ [8] relaxation of side atomic groups.

Homogeneous and heterogeneous diacetylcelluloses (DAC) were also analyzed, with T_g values of 170 and 175°, respectively (Figs 3, 4). The higher transition temperature compared with that of TAC correlates well with the higher hardness of the macromolecular chains of DAC.

Acetylation of cellulose leads to an increase in the flexibility of the macromolecules; for this reason, parallel with the increase in fixed acetic acid content, i.e. with the decrease in the amount of free hydroxyl groups, the transition temperature from the glassy into the highly elastic state is lower in the case of DAC, where the fixed acetic acid content of about 55% completely supports the higher T_g.

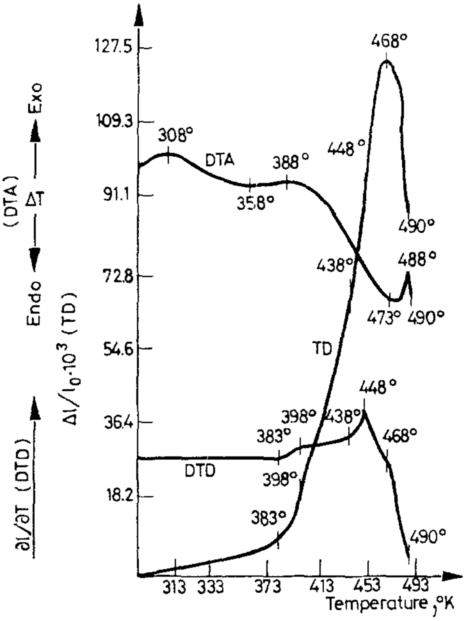

Fig. 4. DTD, TD and DTA curves of heterogeneous DAC homogeneously saponified up to 55.3% fixed CH_3COOH (Sample 12, Table 1)

For some of the investigated samples, the DTA curves exhibit an exothermic peak above 200°. This is illustrated in Figs 2 and 5 for two specially characteristic samples: heterogeneous, directly obtained TAC with 60.1% of fixed acetic acid (Fig. 5) and heterogeneous TAC, heterogeneously saponified up to 60.3% of fixed acetic acid (Fig. 6). It is seen from the DTA and TD curves that the above exothermic effect is generally preceded by a reduction in the rate of change of the linear dimensions of the samples. This shows that conditions of crystallization are created at this temperature.

It has been considered until recently that only TAC (62.5% of fixed acetic acid) can crystallize because its molecules possess the maximum possible flexibility compared with those of other AC's. The remaining AC's can crystallize under special conditions satisfying the structural and the conformational factors.

The present investigations show that, under the conditions of the higher conformational mobility of the macromolecules, when the temperature increases above TG, AC's containing about 60.0% of fixed acetic acid can crystallize without any preliminary processing such as relieved crystallization, filming and spinning.

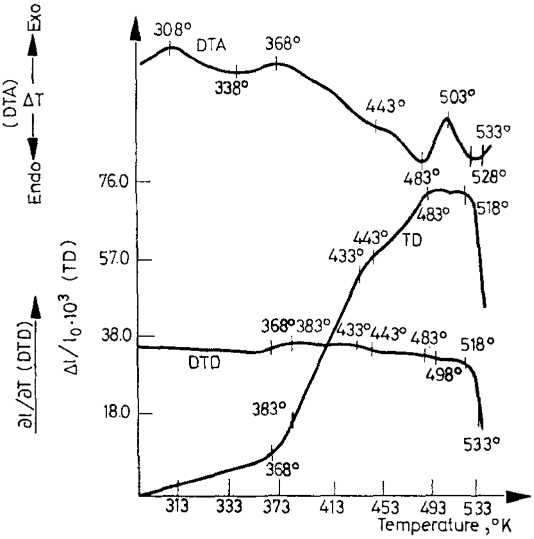

Fig. 5. DTD, TD and DTA curves of heterogeneous TAC, directly obtained up to 60.2% fixed CH_3COOH (Sample 8, Table 1)

Table 1 shows that an AC crystallization peak is observed only for the heterogeneously obtained highly esterified AC's (HEAC) and TAC, and one sample of homogeneous TAC with 62.3% of fixed acetic acid, which is close to the theoretical maximum (62.5%).

Using the standard method of differential thermal analysis combined with thermogravimetric analysis by the derivatograph, the development of a crystallization process was observed in the temperature interval only for the heterogeneous AC. The method of measurement therefore has an essential effect on the susceptibility of AC towards crystallization. This interesting fact needs elaboration. In the homogeneous method of acetylation a uniform distribution is achieved between esterified and non-esterified hydroxyl groups. In the case of heterogeneously obtained AC, as a result of the constancy of the structure of the cellulose, the accessible sections of the macromolecules and the accessible macromolecules are completely acetylated; in HEAC obtained in this way, therefore, submicroscopic regions arise wherein completely esterified fundamental parts are present. Due to this, they have sufficient flexibility for crystallization only with some difficulty under the conditions employed. This assumption is also confirmed by the fact that AC No. 10 (Table 1), obtained by heterogeneous acetylation and homogeneous saponification, does not crystallize. This is probably due to the phenomenon that in saponification a statistical distribution is attained between free and acetylated hydroxyl groups. Similar reasons cause the fact that AC No. 7 (Table 1) does not crystallize. Its acetylation is carried out homogeneously yielding a compact structure; even heterogeneous saponification, therefore, does not lead to conditions favourable to crystallization. The determined temperature of crystallization (T_c) is about 20° higher than that found by linear dilatometry of membranes. This is not unexpected, bearing in mind that in film formation certain conditions of arrangement exist which relieve the process of crystallization. Further, under the conditions investigated, the hardness of the AC macromolecular sections renders their arrangement considerably more difficult than that in the films, where a certain prearrangement occurs under the conditions of the liquid phase. With further increase of the temperature over 240° for TAC and 200° for

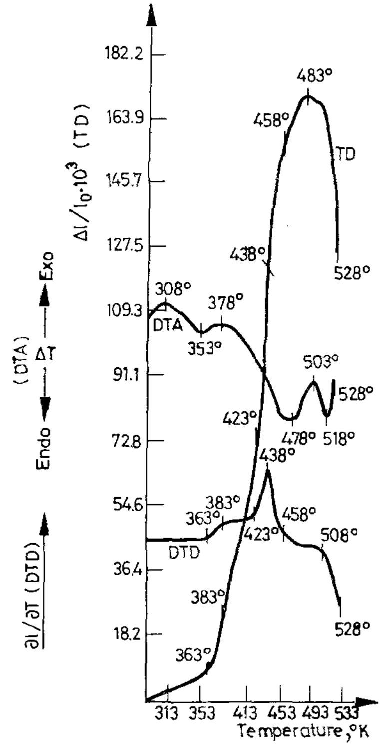

Fig. 6. DTD, TD and DTA curves of heterogeneous TAC heterogeneously saponified up to 60.3% fixed CH_3COOH (Sample 9, Table 1)

DAC (Table 1, column 6) all samples investigated were observed to undergo a strong packing, appearing as negative values of the linear expansion coefficient. This was due to the melting of the crystal formations, associated with strong pyrolytic processes. Recording of the melting temperature (T_m) of AC by DTA and LD traces should be carried out in an inert medium with effective exclusion of oxygen. This could not be achieved with an unmodified derivatograph.

Conclusions

A method was developed for the dilatometric investigation of compressed samples of AC with a derivatograph.

T_g values of the investigated samples were determined and found to be in good agreement with the literature data for AC fibres and films.

In the case of the secondary AC (55% of fixed CH_3COOH), the transition from the glassy into the highly elastic state proceeds at a higher temperature than that of TAC.

A crystallization process was established in the heterogeneous HEAC (about 60% of fixed CH_3COOH). The determined temperature of crystallization is about 20° higher than that determined by linear dilatometry of membranes.

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Résumé — On a mis au point une méthode pour l'étude dilatométrique d'échantillons comprimés d'acétylcellulose à l'aide d'un "Derivatograph". La température trouvée pour la vitrification est en bon accord avec les données de la littérature pour les fibres et les films. Ceci permet de conclure que les processus d'orientation n'influencent pas la transition. On a établi que le développement de la cristallisation s'effectuait en majorité dans l'acétylcellulose hétérogène fortement estérifiée (60 % CH_3COOH).

Zusammenfassung — Es wurde eine Methode zur dilatometrischen Untersuchung von Acetylcellulose-Preßlingen mit Hilfe des Derivatographen ausgearbeitet. Die bestimmte Verglasungstemperatur ist in guter Übereinstimmung mit den der Literatur entnommenen ähnlichen Temperaturen bei Fasern und Filmen. Die Orientierungsvorgänge üben folglich keinen Einfluß auf den Übergang aus. Man stellte fest, daß die Kristallisation hauptsächlich in heterogener, hochveresterter Acetylcellulose erfolgt (60% CH_3COOH).

Резюме — Разработан метод дилатометрического изучения прессованных образцов ацетилцеллюлозы (АЦ) с помощью дериватографа. Определяемая температура стеклования хорошо совпадает с литературными данными. Это позволяет сделать вывод, что ориентационные процессы не оказывают на переход никакого влияния. Установлено, что развитие кристаллизации преобладает в гетерогенной, высокоэтерифицированной АЦ (60% CH_3COOH).