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ON THERMAL CRYSTALLIZATION IN CELLULOSE TRIACETATE FILMS

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Thermomechanical analysis by extension under static and periodic impulse loads as well as the plotting of isometric heating diagrams are used for the investigation of thermally stimulated crystallization of cellulose triacetate (CTA) in unplasticized and plasticized films, the latter being known as the film base of photo and cinema materials. By introducing appropriate additives, it appeared possible to affect the crystallization process in various directions; the mechanism'of the process is discussed. The curves obtained by the techniques of thermal analysis give an individual characteristic of CTA film, reflecting the peculiarities of its production.

Cellulose triacetate (CTA) films exist in an amorphous glassy state [1]. Previous thermomechanical analysis (TMA) data indicated that elevation of the temperature leads to softening of the films and initiates crystallization of the CTA. Such a process, characteristic of various polymer glasses formed via solutions and overcooled melts [2, 3], may be called thermal crystallization.

The TMA curves recorded by extension of the CTA film under some static load exhibit a horizontal plateau [4], so the fusion temperature has the meaning of the melting point of the crystallized CTA. The action of plasticizers is rather specific. On the one hand, they produce a plasticizing effect, lowering the softening temperature (i.e. the glass-transition temperature, T_g), but on the other hand they enhance the crystallization process so that it starts at lower temperatures, T, and extension, λ, and the level of the plateau shifts downwards [4].

We set out to investigate the thermal crystallization of CTA and to search for possibilities of regulating the process by introducing suitable additives. Together with the method of TMA used before, a variant technique was developed: the film sample in the same thermal regime was extended under a periodic impulse load. This was achieved by applying an automatically programmed extending load. The

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resulting records, such as in Fig. 1, allow estimation of the values of the deformations, ε, for each loading act during the heating. This variant technique is especially sensitive to changes in the rigidity of the polymer in the course of the analysis. It may be noted that the usual TMA exhibits the cumulative elongation under a static load acting throughout the heating time.

Further, with the help of a special block incorporated in the TMA set [5], the isometric heating diagrams (IHD), i.e. the temperature-dependence of the tensions when $\Delta\lambda = 0$ [6], were automatically recorded. The instrument contains a calibrated spring and a sensitive unit which adjust the extension of the spring so as to maintain the slip of the film (20 mm in length) strictly isometric (within 0.01 mm) during its heating. The $X-Y$ plotter records the tension (computed per unit section of the film) *vs.* the temperature of the specimen.

This technique has an advantage over classical TMA, giving a direct quantitative presentation of the internal tension in the specimen, which provides an essential characteristic of a polymer film material. Film specimens prepared from industrially produced CTA were investigated.

Figure 2a shows TMA-curves for films of pure and plasticized CTA under static extension (starting load 1.0 MPa). To cast the latter, 4.8 parts of dibutyl phthalate

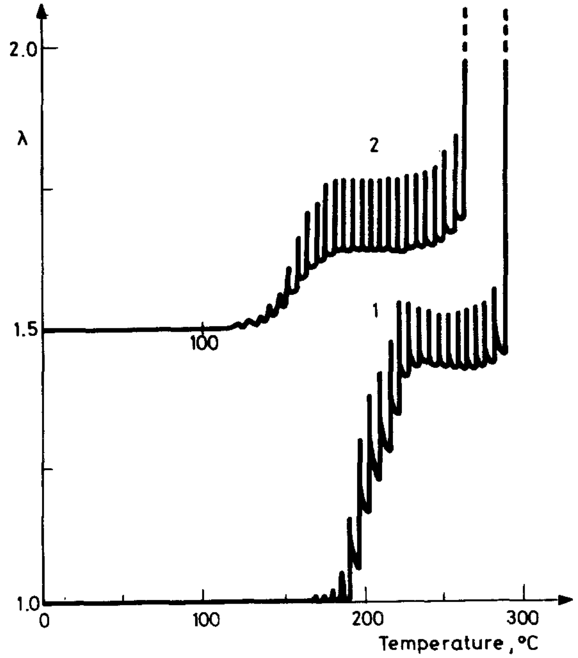

Fig. 1 Extension TMA curves, recorded under an impulse load, of CTA films: 1 – with no additives, 2 – plasticized by DBP and TPP. (Curve 2 is shifted upwards along λ axis.)

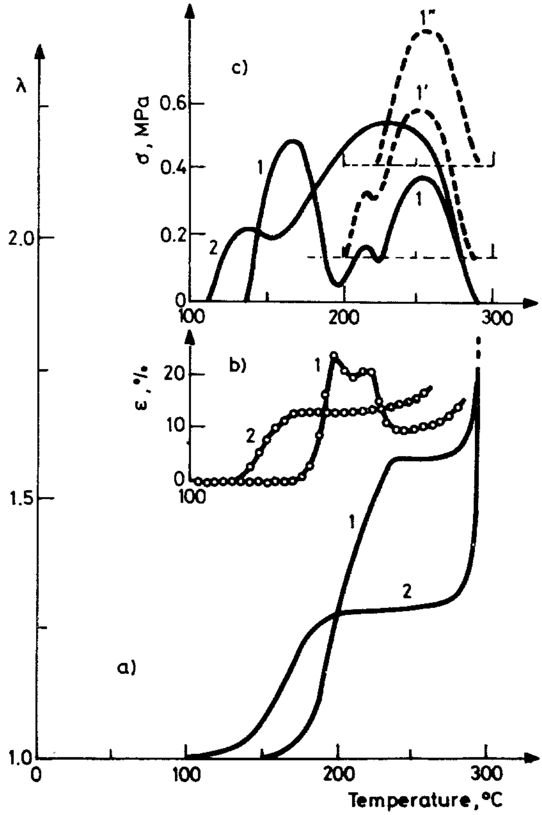

Fig. 2 Extension TMA curves, recorded under a static load of 1 MPa *(a)*, temperature-dependence of deformation amplitudes, ε, under extension by impulse load *(b)*, and isometric heating diagrams *(c)* of CTA films: 1 – with no additives, 2 – plasticized by DBP and TPP. Curves 1' and 1" – the same as 1, with pre-heating to 200 and 220°, respectively; these curves are shifted upwards along the σ axis (λ – unit elongation, σ – tensile strength at $\Delta\lambda = 0$)

(DBP) and 11.0 parts of triphenyl phosphate (TPP) were added to 100 parts of CTA. Due to planar orientation during the formation of the films, internal tensions arise, though the films have not been specially extended previously. This was shown by the IHD (Fig. 2c). It should be noted, that specimens cut out of the film in the longitudinal and lateral directions demonstrated the actual coincidence of the IHD.

For pure CTA, the diagram is rather complicated: it contains three peaks. The first one (the low temperature one) corresponds to relaxation processes in the originally amorphous polymer, while the second and third emerge due to the crystallizaton of CTA in the course of the experiment; they seem to reflect the two stages of the crystallization process, a fact often encountered in the thermal analysis of polymers [7].

The increase in density during crystallization leads to contraction of the specimen. Thus, in order to preserve its length isometric, an evern increasing tensile strength has to be applied. Hardening of the film occurs during this process, as shown by experiments on film samples previously heated to 200 and 220°. The IHD obtained (see Fig. 2c, curves 1' and 1") look as if all the low-temperature parts were cut off (i.e. the value $\sigma = 0$ is preserved below the temperatures mentioned). This can be considered to be due to the fact of "freezing" of the molecular mobility as a result of crystallization during preheating.

IHD of CTA and some of its compositions were obtained earlier [8]. However, there are substantial differences in the locations of the peaks, and the published interpretation does not fully coincide with that given here.

The two-stage run of the process may be observed in the TMA curves too (Fig. 2a, curve 1). In the rising part of the curve (above T_g), there is first a slowing-down of the rise and only then its full cessation. Earlier [4], these details were unnoticed. Very distinctly, the two-stage run of the crystallization is manifested by the TMA extention curves obtained under an impulse load (Fig. 1). When the deformation amplitudes on each impulse are plotted as a function of temperature, a bimodal curve is obtained (Fig. 2b, curve 1), which conforms well with the IHD (Fig. 2c, curve 1).

The TMA curves and also the IHD for the plasticized CTA film (curves 2 in Fig. 2a, b and c) show no signs of the two stages of crystallization. The two peaks of the IHD due to the crystallization of pure CTA seem to unite in one broad maximum*. The maximum values of the internal tensions ($\sigma_{\max}$) are markedly increased. Everything said above supports the conclusion that the presence of plasticizers intensifies the crystallization process. As for the plasticizing effect proper, it not only lowers T_g, but also diminishes the internal tension in the original state of the film (i.e. the low-temperature peak of the IHD) as compared with the unplasticized film (cf. curves 2 and 1 in Fig. 2a and c).

The run of the thermal crystallization depends on the character of the nucleation, i.e. on the presence of athermal (heterogeneous) nuclei, such as structural inhomogeneities and particles of foreign admixtures, or only of thermal nuclei which spontaneously arise in the crystallizable polymer due to fluctuations [9]. The two-stage run of the crystallization process in the CTA may be considered to be due to the consecutive action of the two mechanisms of crystal growth, first controlled by a limited number of athermal nuclei, and then by thermal nuclei, which arise in growing number during heating.

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* However, especially at higher heating rates, a slight shoulder was sometimes observed on the left side of the IHD, which may be considered to be a remnant of the second peak for unplasticized CTA.

In view of what has been said above, it is worth emphasizing the importance of such "preparative" factors as the quality of the original polymer, the purity of the solution, the casting and drying conditions, which the nucleation and subsequent crystal growth may depend on.

The resolution of the two peaks corresponding to the crystallization is due to the existence of a certain temperature interval in which the value of σ diminishes. Such a diminition may be attributed to partial melting of the crystals formed in the first stage; this is followed by re-crystallization. The interpretation given for the run of the crystallization process shows the trends for searching for additives which would affect the process. Nucleation and/or the crystal growth in the polymer have to be regulated by means of the additives.

Some compounds which affect the crystallization process in quite opposite directions have been found in this work. Figure 3 shows the results obtained with a phosphorus-containing surfactant, which represents a mixture of acidic and neutral

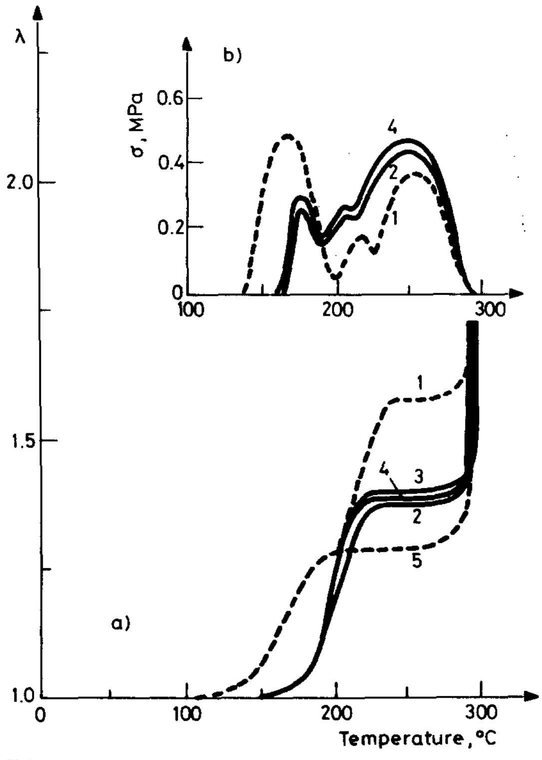

Fig. 3 Extension TMA curves *(a)* and isometric heating diagrams *(b)* of unplasticized CTA films containing I in amounts (mass %) of: 1 – 0 (cf. Fig. 1a, curve 1); 2 – 0.3; 3 – 0.5; and 4 – 1.0. Dashed curve 5 for a plasticized film (cf. Fig. 1a, curve 2) is given as a reference

salts of esterophosphates with long oxyethyl and alkyl chains (I). The TMA curves show that this admixture, at least in the concentrations used, does not produce any marked plasticizing effect, but contributes as a plasticizer to the intensification of crystallization: the level of the plateau drops; it is practically the same for different concentrations of I.

In Fig. 3b, IHD for some films containing I are compared with those of pure CTA. The much smaller size of the first peak is evident for the lower anisotropy of the amorphous film formed in the presence of the surfactant I. This is probably connected with the adsorption of I during casting on the interface between the solution and the hard underlayer; thus, adhesion to it is weakened and, as a result, the planar orientation of the CTA molecules is weakened as well. Meanwhile, the crystallization of CTA in the presence of I commences earlier and leads to higher values of σ in the temperature range of the crystallization process. Micelles of the surfactant in this case may be considered to take part as complementary

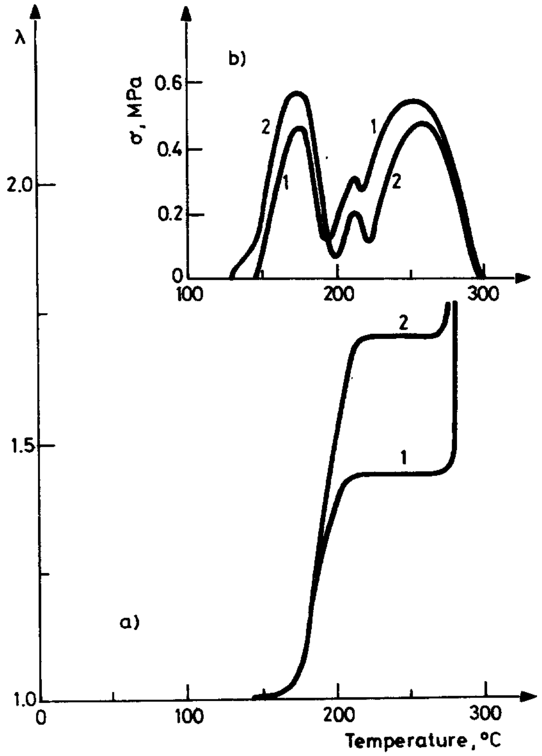

Fig. 4 Extension TMA curves *(a)* and isometric heating diagrams *(b)* of CTA films without additives (1) and containing 1.0 mass % of II (2)

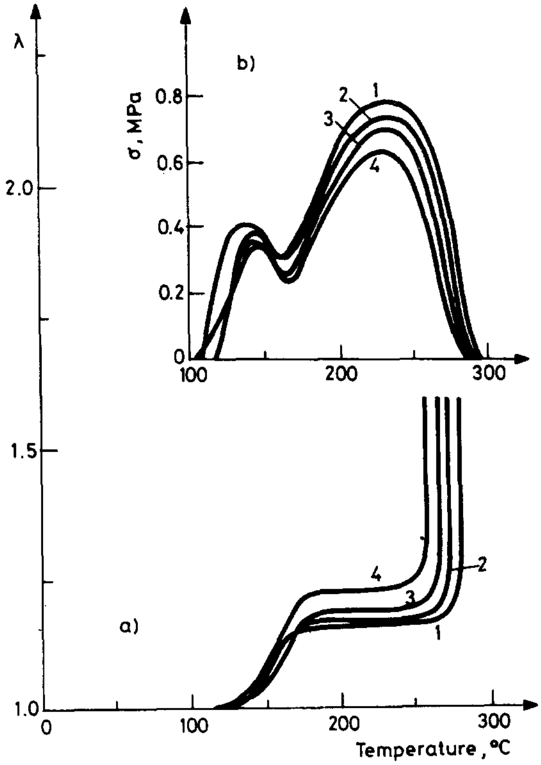

Fig. 5 Extension TMA curves *(a)* and isometric heating diagrams *(b)* of plasticized CTA films containing II in amounts (mass %) of: 1 – 0; 2 – 0.5; 3 – 1.0; 4 – 2.0

heterogeneous nuclei in CTA crystallization. A similar effect is shown by the admixture of I in CTA films containing plasticizers.

The effect of another additive studied, 3-aminopropyltriethoxysilane (II), is quite different. This compound is not a surfactant and, in our opinion, exists in a molecular-dispersed state in the film-forming solution. The results shown in Fig. 4 suggest that, which a small admixture of II, the height of the plateau of the MTA curve becomes much larger than that for the pure CTA film. The IHD show a redistribution of the intensities of the peaks, which testifies to some rise in the internal tensions in the original state of the film and to its crystallizability becoming lower.

This additive behaves similarly in relation to plasticized films as well (Fig. 5). When the content of II increases, the curves obtained regularly shift in the directions which correspond to lower crystallization intensity (the plateau of the TMA curves goes up, while the IHD maxima go down). Shifts in the hightemperature branches of the curves to the low-temperature side, amounting to 20–30 deg, have been observed, too. This is evidence of the fact that, in the presence of II, the crystals are formed not merely in a lesser amount, but also with lesser perfection. It may be assumed that in this case the effect of the admixture is exerted not on the nucleation, but on the crystal growth. Evidently, in contrast with the liquids used as plasticizers, which are soluble only in amorphous CTA and do not penetrate into the crystal formations, the molecules of II are to a certain extent soluble in the crystal phase of CTA.

It is impossible to overlook that in Figs 4 and 5 the TMA curves and the IHD for the films containing no admixture of II (the unplasticized as well as the plasticized ones) do not coincide with the corresponding curves in Fig. 2. This is easy to explain, because another series of CTA was used, to obtain these films, the crystallizability of which turned out to be somewhat different. This confirms the known fact that the properties of CTA films vary markedly, depending on the peculiarities of their production, and especially on the actual content of bound acetic acid in the polymer.

CTA films recovered by washing off the emulsion layers from photo materials if different firms have been investigated as well. It was shown that, while the general character of the curves is preserved, they differ essentially by their display of crystallization. Figure 6 shows striking differences in the IHD for some such films.

Thus the techniques of thermal analysis used afford valuable individual characteristics of the polymer material, and permit assessment of the run of the crystallization process.

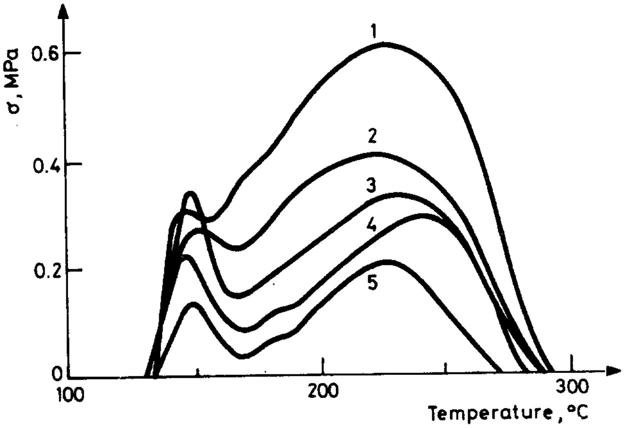

Fig. 6 Isometric heating diagrams of plasticized CTA films recovered by washing off the photographic layers from different photo materials: 1 – Tasma; 2 – Svema; 3 – Kodak; 4 – Agfa; 5 – Orwo (1–4 – colour positive; 5 – X-ray film)

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Zusammenfassung — Zur Untersuchung der thermisch stimulierten Kristallisierung von Cellulosetriacetat (CTA) in unplastifizierten und plastifizierten (letztere bekannt als Filmgrundlage für Foto- und Kinomaterial) Filmen wurden thermomechanische Analyse durch Ausdehnung unter statischen und periodisch-impulsförmigen Belastungen sowie die Aufnahme von isometrischen Aufheizdiagrammen verwendet. Durch Einbringung entsprechender Zusatzstoffe erschien es möglich, den Kristallisationsprozeß in verschiedenen Richtungen zu beeinflussen; der Mechanismus dieses Vorganges wird besprochen. Die bei den verschiedenen Thermoanalysetechniken erhaltenen Diagramme stellen eine individuelle Charakteristik der CTA-Filme dar, in der sich die Besonderheiten ihrer Produktion wiederspiegeln.

Резюме — Термомеханический анализ при растяжении под действием как статической, так и периодической импульсной нагрузок, а также построение диаграмм изометрического нагрева, использованы для исследования термостимулированной кристаллизации триацетата целлюлозы (ТАЦ) в плёнках — непластифицированной и пластифицированных — известных в качестве плёночной основы кинофотоматериалов. Показана возможность разносторонних влияний на кристаллизационный процесс путём введения подходящих добавок; обсуждается механизм процесса. Кривые, полученные использованными методами термического анализа, дают индивидуальную характеристику ТАЦ-плёнок, отражающую особенности её производства.