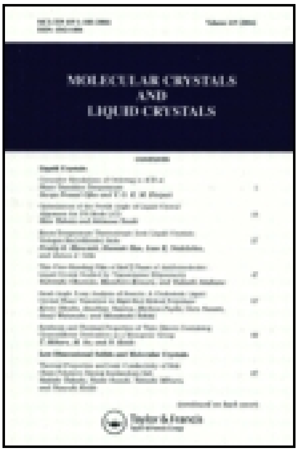

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Mechanical Evolution of the Growing Organic Solid Films of Acetyl Chloride and Diethylamine and Their Specific Interaction

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MECHANICAL EVOLUTION OF THE GROWING ORGANIC SOLID FILMS OF ACETYL CHLORIDE AND DIETHYLAMINE AND THEIR SPECIFIC INTERACTION

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Abstract A number of critical phenomena arising in the growing films of low temperature co-condensates of acetyl chloride and diethylamine has been studied. Correlation between the physico-chemical behavior of the films and the values of mechanical stresses in the samples is shown. Phenomenological model which presents a critical phenomena as a consequence of the film structure evolution during the formation process is proposed.

The method of vapour co-condensation of chemically active compounds on cold surface enables to get compounds that are difficult to prepare and materials with unusual properties.[1] However, the lack of knowledge about the nature of the specific physico-chemical phenomena of the films at low temperature co-condensates prevent a wide usage of this method.

One of such phenomena is the emerging of explosive-like exothermic processes occurring at a certain critical thickness of a growing film. These phenomena were described earlier for a number of systems and the nature of the critical behavior of co-condensates was discussed.[2] Though there was no satisfactory model proposed, the key role of the physical structure in such processes was pointed out. It is known that in the process of film growth the structure of the newly formed layers may be changed in comparison with the former layers.[3] An assumption that the emerging of critical effects coincide with the transition from one stage of structure evolution to another in the film growth can be made. The mechanical stresses arising in a co-condensate in the process of its formation may serve as an indicator for the physical structure of the films.[2] One may assume that the peculiarities of the dependence of stresses upon the growing film thickness does correlate with the values of critical thicknesses. Thus, a comparison of measurements of mechanical stresses in growing films with the proceeding of critical processes in the films may help to work out a phenomenological model for the critical behavior of co-condensates.

Thorough studies of such phenomena were performed on the acetyl chloride (AcCl) - diethylamine (DEA) system. This system is convenient for model studies because there are no chain reactions between the components. This enables to decrease the number of possible models for the critical phenomena.[4]

The co-condensation of AcCl and DEA vapours was performed under the vacuum 0.1Pa on copper surface cooled by liquid nitrogen. Films were investigated by IR-spectroscopy, thermal processes were analyzed by differential thermopair. Mechanical stresses arising in the films were measured by the console bending method.[3,5]

A description of the critical phenomena that are the fast exothermic processes is given.[4] This processes occur in the AcCl-DEA co-condensate film growing on copper surface at certain critical film thickness. L_a stands for critical thickness determined in such experiments.

Besides this, there were the other critical processes detected in the system AcCl-DEA.

There was a chemical reaction detected in the system at 80K. The reaction rate increased considerably if film thickness exceeded some critical value.[6] The critical thickness determined in these experiments was different from L_a. This critical thickness is further denoted as L_b.

Second, it was found that when the co-condensate film is formed on the layer of the same co-condensate, in which explosive processes have already occurred, the critical thickness of such film is usually different from L_a. This thickness is further denoted as L_c.[7]

Simultaneously, in all the experiments described mechanical stress measurement were done. The force F (dimension N/m) applied to film's section with the unit basis which is perpendicular to the support was experimentally determined. It is convenient to examine the dependence of the dF/dL on L for the growing film, where L stands for film thickness. It was found that changes in the value of F with time in the previously formed samples are insignificant at the low L values. In this case the value of dF/dL (dimension N/m^2 or Pa) for a particular L value has a meaning of the mechanical stress in the film layer at a distance L from the support.

Figure 1 presents a typical dependence of dF/dL and L values at 80K. One can see the regions where the function dF/dL on L increases, decreases or is kept constant.

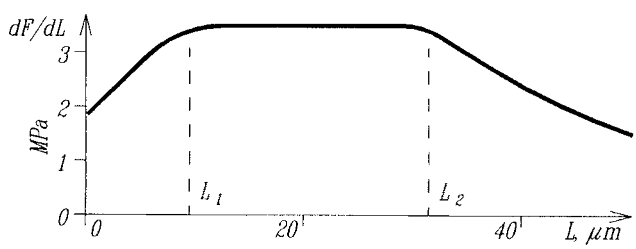

FIGURE 1 Dependence between dF/dL and L for the growing film containing 39 mol.% AcCl; condensing rate was $6.4*10^{16}$ $cm^{-2}s^{-1}$, support temperature was 80K

Thicknesses of the growing film at which the function changes its behavior are denoted as L_1 and L_2. It is interesting to compare these values with the different critical thicknesses for the AcCl-DEA co-condensates.

The comparison of L_1, L_2, L_a, L_b and L_c obtained for the comparable conditions is given in Figures 2 and 3.

L_1, L_2 and L_b were determined with significant errors. Because of that, L_1 and L_2 are marked with a single hatching and L_b with double hatching. L_1 is in a good agreement with the L_b and L_c and L_2 is in a good agreement with L_a for a wide range of reagents ratio. Quick growth of L_a and L_c for the compositions that differ significantly

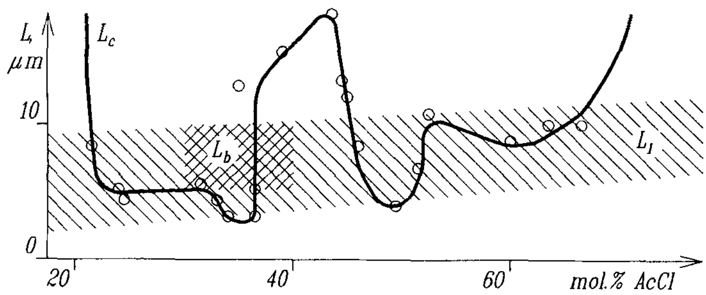

FIGURE 2 L_b values and dependence L_1 and L_c on the film composition; condensing rate was $7*10^{16}$ $cm^{-2}s^{-1}$, support temperature was 80K.

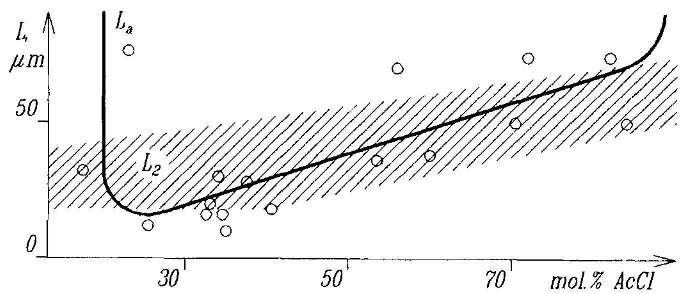

FIGURE 3 Dependence L_2 and L_a on the film composition; condensing rate was $7*10^{16}$ $cm^{-2}s^{-1}$, support temperature was 80K.

from the equimolar ratio of the reagents is evidently caused by the low chemical activity of such samples. A decrease in the activity brings difficulties in proceeding of the critical processes.

Such agreement can be explained with the help of the following assumptions dealing with the nature of the mechanical stresses evolution in growing film. When $L>L_2$ the dependence of F on L is frequently uneven, sharp jumps are observed and a net of cracks becomes visible on the film. Probably in this thickness range the mechanical destruction caused by the stresses takes place on the film surface. It is also confirmed by the decrease in the dF/dL values which correspond to the stress relaxation.

The material destruction caused by stresses is often preceded by the, more or less, extended region of the sample plastic deformation. This region is characterized by a practically constant stress value. It is reasonable to assume that in the thickness region between L_1 and L_2 the growing film undergoes plastic deformations under the influence of the condensing layers. It is known that the stresses in the condensed films that are characterized by high strength, often reach the values of dozens and hundreds MPa.[3]

In the AcCl-DEA films the stress magnitude is most likely limited by the low strength. The occurring processes that generate high stresses in strong films may cause plastic deformation and then destruction.

We can assume that the thickness L_2 corresponds to the beginning of an active process of the crack formation. If this is the case, a good agreement between L_a and L_2 has a natural explanation in that the explosion processes are initiated by the crack emerging. Analogous mechanisms involving the mechano-chemical initiation were proposed for the fast processes in a number of low temperature systems.[8]

According to the assumptions which were made, thickness L_1 corresponds to the beginning of the plastic deformation in the film which should lead to a sharp increase of the molecular mobility. This evidently causes a sharp growth of the chemical reaction rate in the reactive sample. The agreement between L_1 and L_b values is explained by this assumption.

From this point of view one can interpret a good coincidence of L_1 and L_c values. After the explosion the film probably contains grains of a new phase which under favorable conditions initiates the fast spreading of the post-explosion phase in a forming co-condensate.[7] The increase in the molecular mobility may belong to those favorable conditions.

Probably in the beginning of the film growth up to thickness L_1 the influence of the support is strong and the film structure differs from the structure in the bulk. The last consequence may account for the difference between properties of growing film with thicknesses lower and higher L_1.

Thus, in this work a phenomenological model based on consideration of the structure evolution of the growing films was derived. This model describes a number of critical effects which follow the formation of the reactive low temperature co-condensates.

The film growth proceeds from the phase of strong support influence to the phase of the plastic deformation followed by the phase of crack formation. Transitions between these phases cause a generation of the explosive-like processes and a sharp growth of the chemical reaction rate in films.

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