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INVESTIGATION OF POLYMER SYSTEMS USING THERMOMECHANICAL ANALYSIS

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ABSTRACT

The thermomechanical analysis is a common tool used to study properties of a variety of materials at a broad temperature range. We focused our interest on that part of the temperature range in which polymers start to melt.

INTRODUCTION

The instrument employed to carry out the microthermomechanical analysis is described elsewhere [1]. Its principle is shown in Fig. 1. The space under the indentor is under a stress, which, for an axially symmetrical case, can be described by the following equations.

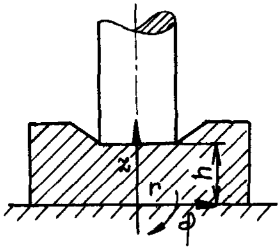

Fig. 1

If the indentor does not move the velocities are $v_z = 0$ and $\frac{\partial v_z}{\partial t} = 0$

$$\frac{\sigma_{rr}-\sigma_{\varphi\varphi}}{r} + \frac{\partial \sigma_{rr}}{\partial \vartheta} - \frac{\partial \sigma_{zr}}{\partial z} = \rho\left(\frac{\partial v_r}{\partial t} + \frac{\partial v_r}{\partial r}\cdot v_r\right) \qquad (1)$$

$$-\frac{1}{r}\frac{\partial}{\partial r}(\sigma_{rz} r) - \frac{\partial \sigma_{zz}}{\partial z} = \rho\left(\frac{\partial v_z}{\partial t} - \frac{\partial v_z}{\partial z}\cdot v_z\right) \qquad (2)$$

Then the equilibrium is given by

$$\frac{\sigma_{rr}-\sigma_{\varphi\varphi}}{r} + \frac{\partial \sigma_{rr}}{\partial r} - \frac{\partial \sigma_{zr}}{\partial z} = 0 \qquad (3)$$

$$\frac{1}{r}\frac{\partial}{\partial r}(\sigma_{rz} r) + \frac{\partial \sigma_{zz}}{\partial z} = 0 \qquad (4)$$

If we admit at the first approximation that $\sigma_{zr} = \sigma_{rz} = 0$ then we obtain

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Proceedings of ICTA 85, Bratislava

$$\frac{\sigma_{rr}-\sigma_{\varphi\varphi}}{r} = -\frac{\partial \sigma_{rr}}{\partial r} \qquad (5)$$

$$\frac{\partial \sigma_{zz}}{\partial z} = 0 \qquad (6)$$

From the equation (6) it follows that for $\sigma_{rr} > \sigma_{\varphi\varphi}$ the radial stress gradient will be negative, the largest being for r = 0. The above condition can be fulfilled provided the indentor compresses the test piece and does not rotate. However, the stress must not exceed strength of the test piece if its rupture is to be avoided. The gradient of radial stresses causes movement of the liberated liquid phase in the stress field. This phenomenon, however, can be observed in case of small radia only due to a sharp decrease in the stress gradient and owing to compensation possibilities in larger areas examined.

RESULTS AND DISCUSSION

In studying polymer melting conditions the melting process was found to proceed gradually as a function of increasing temperature. If temperature in the melting point range remains constant equilibrium is set up virtually immediately (relaxation times →0) and the indentor does not move. State of stress given by the above equations is created under the indentor. If the increase in temperature is linear the movement of the indentor corresponds to decrease of the solid phase only and fails to reflect effects of its own flow. When the temperature is increased gradually only a part of the polymer is melted and is squeezed out from the space under the indentor due to the stress. As a result the solid part of the polymer is deformed and the equilibrium between external load and internal stress at a given temperature is restored.

It is apparent from the melting process that polymeric materials contain structures of a different energy level. When heated it is always the low energy structures that are melted first. Differential record of the melting process can be considered as a manifestation of a structure distribution according to their energy level.

The behaviour described above can be illustrated by the melting process of polypropylene having different orientation (Fig.2). Structures, giving rise to sharp peaks during melting, are created

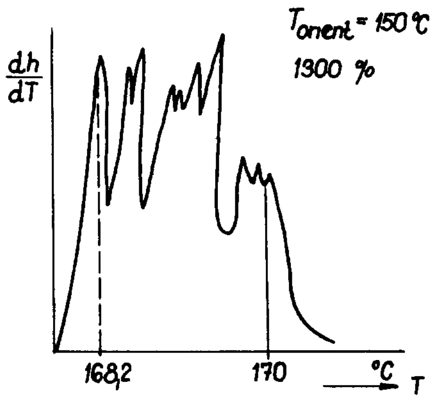

Fig. 2

according to a degree of its orientation. Fibrilation in structure results in a continuous spectrum. Structure distribution in space is apparently random. When melted under stress the melted fractions flow away while the unmelted structures are deformed. Thus a conception of a physical net permeable for the melted fractions suggests itself. In order to confirm this conception melting tests with partially chemically crosslinked low density PE were carried out. As can be seen, gradual melting of uncrosslinked portions takes place at temperatures typical for uncrosslinked low density PE.

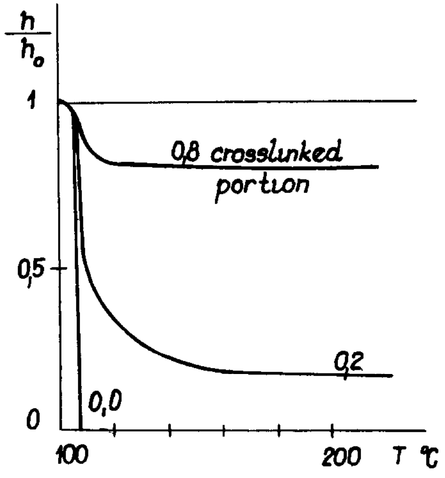

Fig. 3

Then equilibrium between external load and internal stress is independent of temperature. If this is true in case of a crosslinked net, then, analogically, it may also be true in case of a physical net. Fractions melting gradually when appropriate melting temperatures are reached can be connected with lamella thickness. The work by Illers and Hendus [2]shows that melting point depends indirectly on the lamella thickness. Hence the thinnest lamellas will be the first to melt. However, according to Mathot and Pijpers [3] there is a dependence between melting point and $\bar{M}_w$. This means that changes in melting point during melting can be used to a certain extent to derive molecular weight distribution since linear relationship exists between melting point and the reciprocal of $\bar{M}_w$[3]. In the above studies PE was employed.

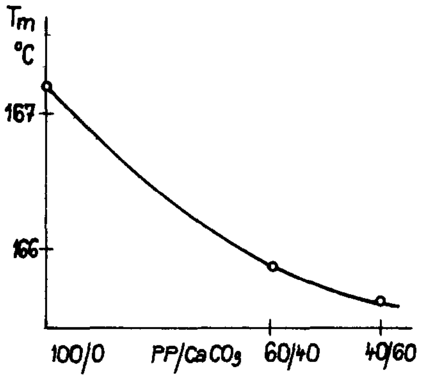

Fig. 4

Polypropylene containing fillers is a somewhat different case. As can be seen from Fig.3, melting point of the matrix shifts to lower values. If the above relationships are applied the decrease in the melting point is found to be connected with a decrease in thickness of lamellas of the crystallized matrix. On the other hand, the lamella thickness is related to molecular weight. Thus it can be deduced that filling affects the crystallized structure of the matrix as if the molecular weight of the polymer used decreased. Simultaneously, it is to be noted that the melting point obtained by TMA is a function of the load used, as shown in Fig. 4. From this respect the drop in melting point in the presence of fillers can also be attributed to internal stresses connected with primary state of stress around the filler particles.

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