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The Kinetics of Spontaneous Changes in the Phase Structure of Molten Two-Component Polymer Systems

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ABSTRACT

The spontaneous break-up of long threads of polymer melt suspended in the melt of the other polymer has been observed. The kinetics of this process was studied for several pairs of polymers. The possibility of description of this process by the theory of development of stationary capillary waves is demonstrated.

INTRODUCTION

The multicomponent polymer systems obtained by mixing of polymer melts are of importance and interest owing to the technical ease of mixing which consists mostly in extruding the preliminary mixed components. The blend results from two processes: forced mechanical mixing and spontaneous mixing. The former one is realized by exterior forces developing flow rate gradients. This results in a considerable increase of the free energy of the system. Thermodynamic instability of such a configuration of components causes spontaneous mixing which in the case of incompatible polymers can be observed as the change in geometry of the phase structure, previously formed.

It is known that the extrusion of the blend of two polymer melts leads to a specific configuration of thin treads of suspended component oriented along the axis of the extruded filament |1,2|. The structure of components thus formed may be fixed by quenching the extrudate. It has been also found that annealing of the extruded filament in molten state may lead to a droplet-like dispersion of the minor component |3|. The mechanism and kinetics of such dispersion changes have not been yet sufficiently studied, however, it was observed that the process consists in breaking-up of threads of molten polymer suspended in the melt of the other polymer. Qualitative analysis of this process points out its close similarity of the break-up of thin threads of low molecular weight liquids. The mechanism of the later process have been alredy reported |4,5|.

The aim of the present work was to measure the kinetics of the break-up of molten polymer threads and to

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point out the possibility of description of this process in terms of the mechanism given by Tomotika |5|.

THEORETICAL

The theory of break-up of long liquid thread immersed in another liquid is based on the assumption that this process is caused by the growth of symmetrical stationary capillary waves at the surface of the thread. The resulting disturbance of the thread shape may be expressed by the following equation,

$$e = a \sin \frac{2\Pi x}{\lambda} \qquad (1)$$

where x is the distance measured along the axis of the thread, e is the disturbance at a give point and a is the amplitude of the wave of length λ (Fig.2). The growth of the disturbance amplitude may be expressed as |4|,

$$a = a_o \exp (q\ t) \qquad (2)$$

where t is time, a_o is the amplitude at t=0, q is the rate constant of the amplitude growth. The factor q has been found assuming that the interfacial energy is dissipated as work of viscous flow |5|.

The process goes on with such a wave length for which the amplitude of disturbance has the maximum rate of growth. It is determined by the viscosity ratio of the thread to surrounding fluid and by the thread radius. Both q and λ values can be calculated on the basis of Tomotika theory |5|. The growth of the disturbance proceeds until its amplitude reaches the value,

$$a_b = \sqrt{\frac{2}{3}}\, R_o \qquad (3)$$

It takes place after the time $t_b = \frac{1}{q}\ln(\sqrt{\frac{2}{3}}\ \frac{R_o}{a_o})$. (4)

At this moment the thread breaks into drops whose dimensions may by calculated on the basis of conservation of the thread volume.

A good agreement between the theory and experiment has been shown in the case of the low molecular weight liquids |4|. This paper includes the results of examination of break-up of thin threads in the system of polymer melts.

EXPERIMENTAL

Kinetic measurements of the break-up of thin molten polymer threads were made for a series of polymer systems as specified in Table I. The observations of changes in the thread shape showed that in all cases under investigation the process is of high regularity and the changes observed are identical to those shown in Fig.1

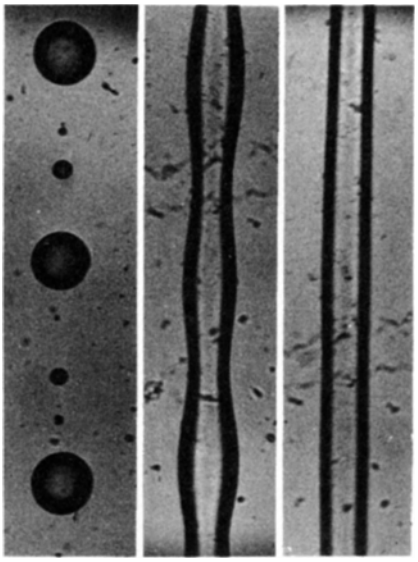

Fig.1. Succesive steps of the break-up of molten polymer thread (polyamide) in the melt of the other polymer (polystyrene).

for polyamide fiber suspended in polystyrene melt. The succesive steps of the process are shown by the microscopic photographs.

The samples for measurements of thread shape changes were prepared by placing thin polymer fiber between films of other polymer (0.8 mm in thickness) and heating them at 250°C so as to obtain thin threads of one molten polymer in the melt of the other polymer.

RESULTS AND DISCUSSION

To find the rate constant q the relationship between $\ln(a/R_o)$ and time was plotted for each pair of polymers. Examples of these are shown in Fig.2. for several systems. It can be easily noticed that all the relationships presented satisfy approximately a linear relation. It means that the exponential growth of the amplitude of thread narrowing predicted by the Eq.2 is observed. The experimentaly determined q and λ values and those calculated theoreticaly using the experimental values of surface tension and viscosity data are given in Table I. The correlations between experimental and theoretical q and λ values are illustrated in Fig.3. The results seem to confirm that the kinetics of the process may be described by the theory developed for the process taking place in low molecular weight liquid.

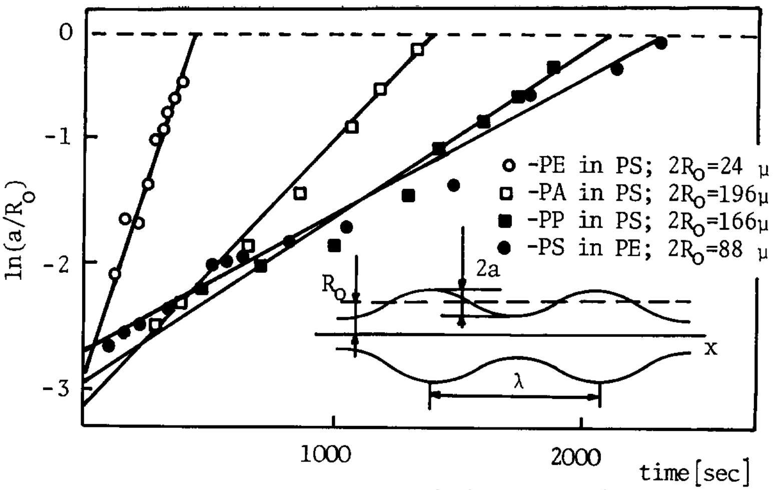

Fig. 2. Examples of plots of $ln(a/R_o)$ *vs time.*

Table I

Comparisson of the experimental and theoretical data characterising the break-up process of melt threads

Medium	Thread	Thread diameter [µm]	Viscosity ratio at shear rate 0.17 sec^{-1}	Interfacial tension [dynes/cm]	λ_{exp} [µm]	λ_{theor} [µm]	$q_{exp} \cdot 10^3$	$q_{theor} \cdot 10^3$
PS	PA	196 66 45	1.46	14.4	870 306 145	789 265 181	2.07 5.02 9.78	0.9 2.61 3.37
	PE	30 24	0.85	3.7	119 118	211 269	7.62 6.34	4.55 5.69
	PP	166 47	1.0	2.0	625 220	613 174	1.97 -	1.75 -
PE	PS	88	1.17	3.7	585	505	1.03	0.64
	PA	150	1.68	17.0	686	748	11.1	17.8
PA	PS	62	0.69	14.4	280	407	6.17	6.2
PP	PS	226	1.0	2.0	846	835	0.81	1.5
	PA	68 32	1.43	16.5	276 211	274 129	13.0 24.4	2.9 19.2

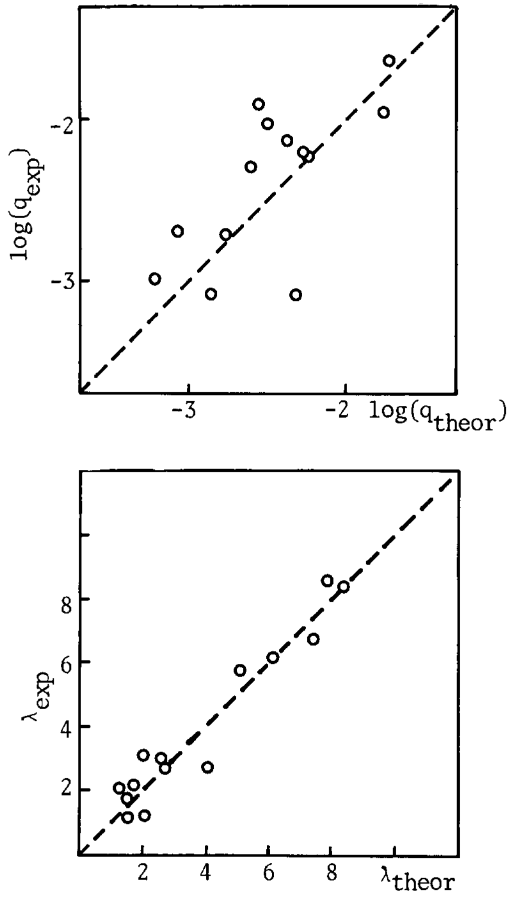

Fig. 3. Correlations between experimental and theoretical q and λ values.

The divergences in the experimental and theoretical rate constant values may be due to the fact that inertial effects connected with liquid flow have not been taken into account in the theory. It seems, however, that due to the low rate values, the necessary correction should not be high. One can also believe that the observed discrepancies of the q values are due to the use of the viscosity values corresponding to different shear rates than these in the actual process. The solution of this problem involves however further consideration on the distribution of the flow rates inside the thread during its narrowing which seem to be an extremaly difficult task.

The process of spontaneous break-up of thin threads of the molten polymer suspended in the melt of the other polymer may have an important effect on changes of the phase structure of polymer blends subjected to intensive flow as for example during extrusion. It becomes clear on the basis of the results presented that the minor component in the extruded blend will behave accordingly to the mechanism described. Long threads of this component formed during extrusion will break-up into droplets if only the blend will be kept in molten state sufficiently long time. On the other hand in blends containing comparable amounts of both components it is usually difficult to distinguish which one of the components constitute the matrix and which one is dispersed. In such a case the structure can change from place to place and each component can be treated both as the matrix or as the dispersed phase dependently on the local structure. If such a blend consisting of components A and B is extruded layers and fibrils of both components can be formed in the extrudate. Accordingly to the results presented here the rate of breaking up of threads of component A in matrix B will be different from the rate of breaking of threads B in matrix A. Due to this one component will disperse earlier than the other one. It can be supposed that this situation, if repeated many times during mixing process will influence the type of the blend structure in this way that the ratio of rates of breaking-up of threads of both components can determine the composition at which the phase inversion takes place. Further studies are,however, necessary to relate the results of this paper to the real structures of polymer blends.

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