Fractal model of imidisation in the presence of a nanofiller

L. Kh. Nafadzokova, G. V. Kozlov, and G. E. Zaikov
Kabardino-Balkarian State University, Nal‘chik
N. M. Emanuel’ Institute of Biochemical Physics, Russian Academy of Sciences, Moscow

Tyan et al. [1] investigated the process of solid-phase imidisation of polyamide acid (PAA) in the presence of a nanofiller (Na⁺-montmorillonite). It was found that increase in the content of Na⁺-montmorillonite \( W_c \) in the range 0–7 wt% and increase in imidisation temperature \( T_i \) in the range 423–523 K increase the imidisation rate. Tyan et al. [1] gave a probable chemical interpretation of this increase on the assumption that Na⁺-montmorillonite is a catalyst. However, it must be noted that the introduction of nanofiller into the reaction mixture leads to the formation of a two-phase system, where an important (or key) role will be played by interphase interactions [2]. In particular, PAA–Na⁺-montmorillonite interaction should lead to a change in the structure of the formed macromolecular coil of polyimide (PI) [3], and a similar effect is given by an increase in \( T_i \) [4]. Therefore, the aim of the present work is a structural analysis of the processes occurring in the course of solid-phase imidisation.

A study was made of the kinetics of solid-phase imidisation of PAA synthesised from 4,4′-oxydianiline and pyromellitimide anhydride both without filler and with the addition of 2.5 and 7 wt% Na⁺-montmorillonite. The degree of conversion (imidisation) \( Q \) was determined as a function of the duration of the reaction \( t \) by means of Fourier transformation of the 726 and 1014 cm⁻¹ bands of the IR spectrum. It was shown that the method used in reference [1] gives exfoliated nanocomposites. Other details of the synthesis and study of PI/Na⁺-montmorillonite nanocomposites are given in reference [1]. Solid-phase imidisation was conducted at four imidisation temperatures: 423, 473, 503, and 523 K.

We will examine the question of the interphase interactions of PI and Na⁺-montmorillonite on the surface of the nanofiller. As shown by Pfeiffer [3], the macromolecular coil on the solid surface changes its configuration (structure), which can be characterised by its fractal dimensions. This change is described by means of the following equation [3]:

\[
\frac{D_{f,\text{sol}}}{D_f} = d_n^0 \quad (1)
\]

where \( d_n \) and \( d_n^0 \) are the fractal dimensions of the surface of the nanofiller in the nanocomposite and in the initial state, \( D_{f,\text{sol}} \) and \( D_f \) are the fractal dimensions of the macromolecular coil of PI in solution (mixing of PAA and Na⁺-montmorillonite was carried out in dimethylacetamide solution [1]) and in the solid-phase state on the surface of the nanofiller respectively.

Let us examine the estimation of the parameters entering equation (1). As shown in reference [5], a polymer chain possessing finite rigidity and consisting of statistical segments of finite length is not in a position to reproduce the growing roughness of the surface as \( d_n^0 \) increases, and at \( d_n^0 > 2.5 \) the quantity \( d_n \) is defined as follows [6]:

\[
d_n = 5 - d_n^0 \quad (2)
\]

For Na⁺-montmorillonite, \( d_n^0 \) was determined experimentally and is equal to 2.78 [7]. In a first approximation, \( D_{f,\text{sol}} \) can be taken to be equal to the dimension of the macromolecular coil in good solvent \( (D_f^{\text{sol}} = 1.667 \) [8]). Then, estimation by means of equation (1) gives \( D_f = 1.33 \). It is obvious that this is
the dimension of a macromolecular coil stretched on the surface of Na⁺-montmorillonite, and below it will be denoted as $D_0$.

Calculation of the actual values of the fractal dimension $D_f$ of the macromolecular coil for a first-order reaction, which is what solid-phase imidisation is [1], can be conducted by means of the following equation [9]:

$$\rho^{1/2} = \frac{C}{k_1[1 - Q]}$$  \hspace{2cm} (3)

where $C$ is a constant equal to 0.25, and $k_1$ is the rate constant of the first-order reaction. The values of $t$ in equation (3) are in seconds. The values of $k_1$ are given in reference [1].

Calculation by means of equation (3) showed that, for imidisation reactions, $D_f = 1.53 - 2.12$. In other words, for all cases of the real imidisation reaction, the condition $D_0 < D_f$ is satisfied. This relation makes it possible to assume that only some of the macromolecular coils of PI interact with the surface of the Na⁺-montmorillonite. This is confirmed by data in Figure 1, where the difference $\Delta D_f = D_f - D_0$ is plotted against the content of nanofiller $W_c$ for four imidisation temperatures. As follows from the graphs in this figure, the magnitude of $\Delta D_f$ decreases as $W_c$ increases or $D_f \rightarrow D_0$, and extrapolation of these graphs indicates that, with $W_c = 17.5$ wt%, $D_f = D_0$ or $\Delta D_f = 0$. Note that the indicated value of $W_c$ is valid only for exfoliated (non-aggregated) nanofiller.

Reduction in $\Delta D_f$ as $W_c$ increases suggests an increase in the proportion of interacting phase $\psi_{\text{interact}}$ during imidisation. Parameter $\psi_{\text{interact}}$ can be determined according to the law of mixtures from the equation

$$D_f = \psi_{\text{interact}} D_f^0 + [1 - \psi_{\text{interact}}] D_f'$$  \hspace{2cm} (4)

where $D_f'$ is the fractal dimension of the macromolecular coil in the absence of nanofiller.

Figure 2 gives the dependence $\psi_{\text{interact}}(W_c)$ for $T_1 = 423$ K. As can be seen, this correlation is linear, passes through the origin of coordinates, and is described analytically by the following empirical equation:

$$\psi_{\text{interact}} = 0.0575 W_c$$  \hspace{2cm} (5)

It is evident that, with $W_c = 17.5$ wt%, obtained by extrapolation of the graphs in Figure 1, parameter $\psi_{\text{interact}} = 1.0$, and the entire PAA–Na⁺-montmorillonite reaction system takes part in imidisation, whereas with $W_c < 17.5$ wt% imidisation proceeds partially in solid-phase PAA without the action of Na⁺-montmorillonite.

Figure 3 gives the dependence of the rate constant of the reaction $k_1$ on the relative proportion of interacting
phase $\varphi_{\text{interact}}$ which turned out to be roughly linear and showed an increase in $K_1$ as $\varphi_{\text{interact}}$ increased. This makes it possible to assume a direct dependence of the rate of solid-phase imidisation on the level of interphase interactions in the reaction system.

In reference [1], a reduction in the activation energy of imidisation $E_{\text{act}}$ was found as $W_1$ increased – from 66 to 51 kJ/mol in the range $W_1 = 0$–7 wt%. Kozlov et al. [10] proposed the following dependence of $E_{\text{act}}$ on $D_f$ in the case of the thermo-oxidative degradation of polyarylate:

$$E_{\text{act}} = 16.6D_f^2 - 2.8D_f$$

(6)

Table 1 gives a comparison of experimental activation energies ($E_{\text{act}}$) and activation energies calculated according to equation (6) ($E_{\text{tact}}$) for solid-phase imidisation. As can be seen, good agreement is obtained between the indicated activation energy values (the average divergence of $E_{\text{act}}$ and $E_{\text{tact}}$ amounts to less than 5%). This means that the activation energy (imidisation) and dissociation energy (thermo-oxidative degradation) are roughly equal, which was to be expected.

Thus, the results of the present work have shown that acceleration of imidisation as the content of nanofiller increases is caused by change in the structure of the macromolecular coil owing to interphase interactions with the surface of Na+-montmorillonite. The relative proportion of interacting phase increases as the content of nanofiller increases, and with a nanofiller content of roughly 17.5 wt% this phase occupies the entire reaction system. Reduction in the activation energy of imidisation as the nanofiller content increases is also due to structural factors, namely reduction in the fractal dimension of the macromolecular coil.

### Table 1. Comparison of experimental activation energies ($E_{\text{act}}$) and activation energies calculated according to equation (6) ($E_{\text{tact}}$) for the process of solid-phase imidisation

<table>
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<th>$W_1$, wt%</th>
<th>$E_{\text{act}}$ kJ/mol</th>
<th>$E_{\text{tact}}$ kJ/mol</th>
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### REFERENCES


