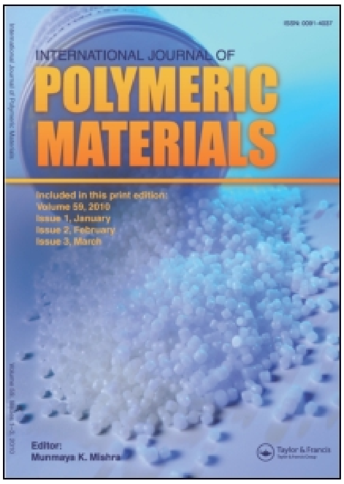

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Influence of Filler on Kinetics at Low-Temperature Conversion of Macroradicals

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In poly(methyl methacrylate) and polyvinylpirrolydone the influence of aerosil on the kinetics of macroradical transformation at 120-220 K is established. The effect of filler is explained by the changes of the structural-physical properties of the polymer binder transformed into the interface state. From the kinetic data the effective thickness of interfaces is estimated.

KEY WORDS Filler, macroradicals, kinetics.

INTRODUCTION

It seems to be generally known that in filled polymer materials interfaces are formed nearby surfaces of filler particles. This surface phase can display considerable differences in structure-physical properties as compared with those of the volume polymer phase.[1] The appearance of interfaces is discovered from the dependencies of some properties (heat capacity, specific volume, and so forth) on filler concentrations. Moreover, kinetic data of some reactions can obviously be used for similar investigations. In fact, in solid polymers the kinetics of radical reactions is connected with the physical structure of the matrix. Therefore we can judge structural modifications of polymers in interfaces by kinetic parameters of reactions.

The purpose of this work is to study, in poly(methyl methacrylate) (PMMA) and polyvinylpirrolydone (PVP), the relationship between filler availability and kinetics of macroradical conversions generated by photolysis of arid iron chloride.

EXPERIMENTAL

The aerosil is used as filler with the specific surface of 300 m^2/g and particle size of 20 nm. The filled samples of PMMA (M_v = 120000) and PVP (M_v = 30000) are prepared from 2% solutions of polymers in chloroform containing iron chloride and the warmed 400°C aerosil. After standing for a day the solutions are evaporated by the mixing, the iron chloride concentration is $2 \cdot 10^{-2}M$ in samples with any aerosil quantity. The samples are irradiated in vacuum by the filtered light of a mercury lamp with $\lambda > 320$ nm by 77 K until the iron chloride completes photoreduction. The kinetics of macroradicals thermal conversions is examined by ESR spectra.

DISCUSSION

As a consequence of photolysis of PMMA with $FeCl_3$, mainly macroradicals $\sim C(CH_3)(COOCH_3)\dot{C}HC(CH_3)(COOCH_3)\sim$ are formed.[2] The aerosil availability in PMMA does not influence the radical composition. The efficiency of the macroradicals, thermal decay, however, in the studied temperature region has shown evidence of dependence on the filler concentration. In samples containing up to 50 aerosil weight parts the kinetics of the radicals decay is practically the same. But by further growth of the aerosil quantity the decay rate essentially increases.

From the analysis of experimental dependencies one can conclude that PMMA macroradicals are kinetically inequivalent in the thermal decay reaction. This inequivalence can be characterized by the rate constants distribution $\rho(k)$. In this case for kinetics descriptions the following equation can be used[3]:

$$\frac{N}{N_0} = (1 + nk_0t)^{-1/n} \tag{1}$$

where k_0 is the average effective rate constant of the radicals' decay $k_0 = \int k\rho(k)dk$ and n is the parameter characterizing the distribution width ($n > 0$).

The anamorphoses of PMMA macroradicals decay kinetic curves in Equation (1) coordinates are shown in Figures 1a and 1b. From these anamorphoses the values of kinetic parameters k_0 and n are determined (Table I). The data in Table I show that the distribution width by rate constants of the radicals' decay is not changed by the increase in temperature. In samples containing up to 55 aerosil wt % at 200 K and to 50 wt % at 170 K, the average effective rate constants do not change. But if the aerosil quantity exceeds this value k_0 rises abruptly 15–60 fold.

In principle the increase of the radicals' decay efficiency is possible on the filler surface, but evidently this effect cannot be used to explain the observed phenomena. Actually, for k_0 and W_a the linear relation should be fulfilled: $k_0 = k_v + \alpha W_a$ (k_v is the effective rate constant of the radicals, decay in polymer). The obtained results however conform with the interfaces states,[1] as according to this conception some property changes are displayed especially strongly if all the polymer phases turn into interfaces (high-filled polymer).

The interface thickness is estimated by the average distance between filler particles:

$$e = d\left[\left(\frac{\varphi m}{\varphi}\right)^{1/3} - 1\right] \tag{2}$$

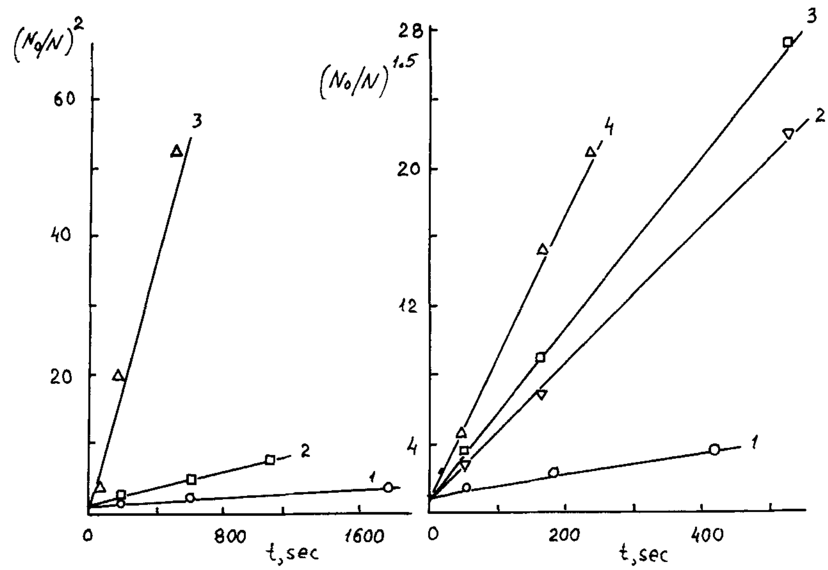

FIGURE 1 The anamorphoses of the decay kinetic curves of PMMA macroradicals in Equation (1) coordinates at (a) 170 K: (1) 0–55%, (2) 60%, (3) 70% aerosil and at (b) 200 K: (1) 0–50%, (2) 55%, (3) 60%, (4) 70% aerosil.

TABLE I

Kinetic parameters of the thermal decay of macroradicals in filled PMMA

T = 170 K			T = 200 K	
W_a, wt %	$k_0 \cdot 10^3$ sec^{-1}	n	$k_0 \cdot 10^3$ sec^{-1}	n
0	1.4	2	5	1.5
50	1.4	2	5	1.5
55	1.4	2	35	1.5
60	6.5	2	45	1.5
70	90.0	2	80	1.5

where d is the particle's diameter, $\varphi_m \simeq 0.8$ is the most possible part of filler and φ is the filler experimental volume part when an uneven change of parameter is observed.

It should be mentioned that the thickness of interfaces is the effective value differing for research methods and experimental conditions. Perhaps therefore in filled PMMA the thickness estimated by Equation (2) is approximately 8 nm at 200 K and 5.5 nm at 170 K.

Unlike PMMA, in PVP the aerosil influence on kinetics of macroradicals reactions can be registered already in photoinitiation stages at 77 K. In this system the radicals' composition depends on aerosil quantity. ESR spectra of PVP with the different filling are shown in Figure 2. The unfilled samples have the unresolved ESR spectrum. In PVP with 15 aerosil wt % STS components of spectrum are observed and in PVP with 50 wt % the five component signal with ΔH = 1.8 mT

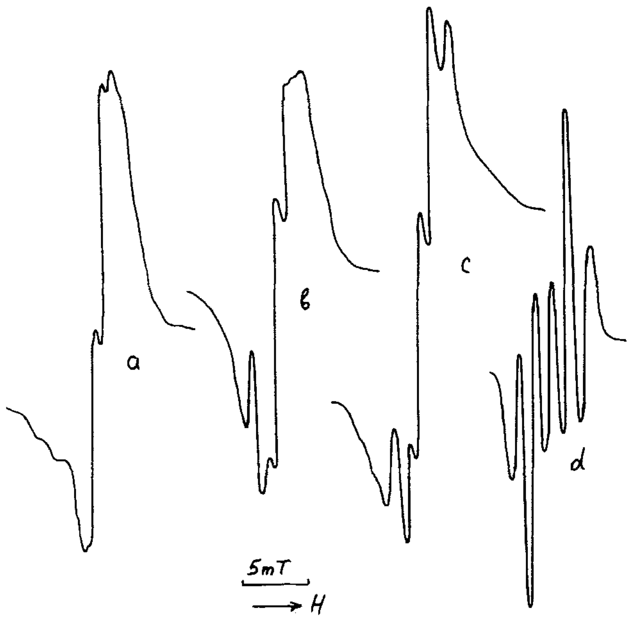

FIGURE 2 ESR spectra of PVP + $FeCl_3$ (a) without filler, (b) with 15%, (c) 50%, (d) after photolysis at 77 K and after warming of (a) at 200 K.

splitting belonging to macroradicals $\sim CH_2\dot{C}(\underline{NCH_2CH_2CH_2CO})CH_2\sim$ (I) can be distinguished.[4]

By the warming of irradiated samples the poorly resolved spectrum is transformed into the radicals I spectrum (Figure 2g). The noticeable thermal decay of the radicals I is observed by $T > 200$ K. The absence of resolved STS makes it difficult for PVP primary radicals to identify. However, taking into account the initiation mechanism by the transition metal ions photoreduction,[5] the radicals I formation can be represented by the following scheme:

$$PVP + FeCl_3 \xrightarrow{h\nu} \sim CH_2CH(\underline{\overset{+\cdot}{N}CH_2CH_2CH_2CO})CH_2\sim + FeCl_2 + Cl^- \quad (3)$$

$$\sim CH_2CH(\underline{\overset{+\cdot}{N}CH_2CH_2CH_2CO})CH_2\sim \xrightarrow{kT}$$

$$\sim CH_2\dot{C}(\underline{NCH_2CH_2CH_2CO})CH_2\sim + H^+. \quad (4)$$

On the initial photochemical stage cation-radicals II are formed. In next thermal reaction these particles are converted into radicals I. Because of small ESR spectrum resolution (Figure 2a) individual components of II cannot be separated clearly. However a common width of this spectrum approximately corresponds to that of the expected spectrum if we take into account STI constants with nucleus and protons adduced for analogous N-methylpirrolydone cation-radicals[6]:

$$a_N = 3.8\ \text{mT},\ a_H\left(\rangle\!\!-\text{CH}\right) = 3.3\ \text{mT},\ a_{H(1)}$$

$$\left(\rangle\text{CH}_2\right) = 6.2\ \text{mT},\ a_{H(2)}\left(\rangle\text{CH}_2\right) = 3.6\ \text{mT}.$$

The influence of filler on the efficiency of radicals I formation is reflected by defreezing curves that are dependencies on temperature of radicals I relative concentrations (Figure 3). These dependencies are obtained by samples standing for 5 min at fixed temperatures. The change in the concentration of radicals I is controlled by their ESR spectrum which is superimposed on signal of II.

The defreezing curves have a medium near 180–200 K. The maximum relative quantity of radicals I characterizes a share of their precursors II stabilizing at 77 K in the course of the photolysis of the samples. As Figure 3 shows in high-filled PVP (50 wt % aerosil), only 10% of cation-radicals II are stabilized while unfilled samples contain about 70% of II.

The nonlinear dependence of the composition of the radicals on filling degree (Figure 4) allows us to propose PVP physical structure modifications affecting radical conversion efficiency as the calculation by Equation (2) shows, which is

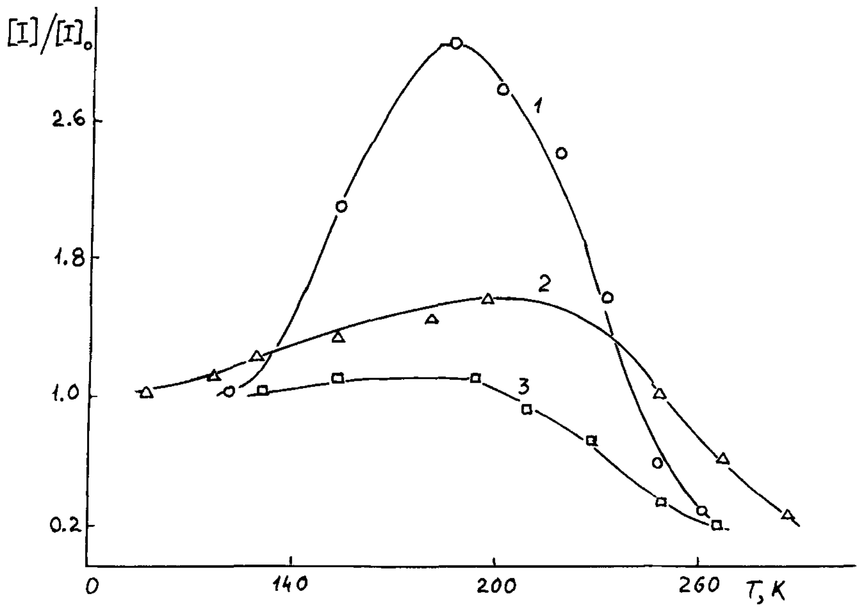

FIGURE 3 The change in concentration of radicals I during warming of irradiated PVP + $FeCl_3$ at 77 K: (1) without aerosil; (2) 15%, (3) 50% aerosil.

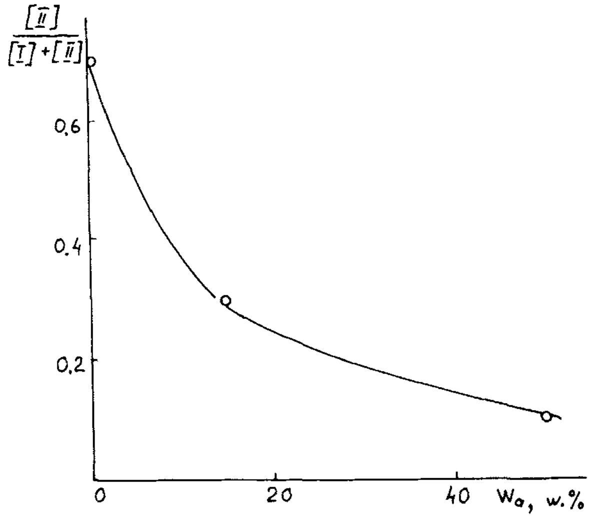

FIGURE 4 The dependence of the relative concentration of radicals II by photolysis of PVP + $FECl_3$ at 77 K on aerosil quantity.

especially strong if the distance between filler particles is about 25 nm. This distance can be considered as the effective interface thickness of filled PVP.

The results obtained do not presently permit us to draw conclusions about the specific nature of the structural reorganizations by interface shaping that influence the kinetics of the considered radical processes. One can assume that the reason for the observed effect is the friabler molecular packing in interfaces as compared with that in volume due to the difficulty of relaxation processes at the filled polymer forming from solutions.

The decreasing of molecular packing density can promote the energetical barrier diminution of rehybridization in main chain carbon atoms of radicals I and consequently increase the reaction (4) rate at 77 K. The lower packing density can make easier the local neighborhood reorganization to create favorable mutual orientations of PMMA macroradicals by their recombination. In conclusion it should be noted that the dimensions of interfaces estimated by means of kinetic data do not contradict those obtained by measurements of heat capacity and density.[7] Therefore low-temperature radicals' reactions can obviously be used for the investigation of structural organization of filled polymers.

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