

Features of Obtaining Polymer Composites Based on Dispersed Oxides and Vinyl Polymers

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The effects of dispersed oxides Fe_2O_3 , Cr_2O_3 , $\alpha\text{-PbO}$, $\beta\text{-PbO}$, PbO_2 , SiO_2 on the processes of radical polymerization of styrene are studied. It is shown that the dispersed oxides affect the polymerization rate and the response of the thermal decomposition of radical initiators. Peroxides are adsorbed on the surface of mineral oxides and decomposed into free radicals. On the surface of SiO_2 and Cr_2O_3 , a heterolytic decomposition of peroxides takes place. The oxide introduced into the polymerization system reduces the molecular weight of the polymer that forms under these conditions. The degrees of grafting macromolecules to the surface of oxides were found.

topics: polymer–mineral composites, kinetics of formation, molecular weights, growing degree

1. Introduction

Polymer–mineral composites (PMC) are widely used in electronics. The introduction of mineral oxides into the polymer provides the composites with new properties. Such materials have specific optical, magnetic, and other physico–chemical properties that allow them to be used in various devices [1–3]. However, the formation of PMC is not sufficient in current conditions, and the study of the features of obtaining such materials would allow to optimize their synthesis and manage their properties.

In our work, the results of the study on the influence of mineral dispersed oxides Fe_2O_3 , Cr_2O_3 , $\alpha\text{-PbO}$, $\beta\text{-PbO}$, PbO_2 , and SiO_2 (aerosil) on the polymerization of styrene in the mass are presented. We chose dispersed oxides for obtaining PMC is due to the fact that such composites may have promising practical uses. Lead oxides introduced into the polymer matrix can serve as radiation shielding materials.

2. Experimental

The rate of polymerization was studied by the dilatometric method in continuous mixing of the reaction medium. The mixing rate has been chosen in such a way that mineral oxide lobes were evenly distributed in the reaction medium. The rate of thermolysis of peroxide initiators was determined iodometrically. The degree of grafting of the macromolecules of the polymer to the surface of the mineral was studied by means of thermogravimetry. The molecular weights of polymers were determined viscosimetrically. Methods of measuring these parameters are given in [4].

In the study, styrene was used, and benzoyl peroxide (BP), sebacic acid oligoperoxide (OSA), *tert*-butyl hydroperoxide (HPTB), and didecanoicdiperadpinate (DP) served as initiators.

3. Results and discussion

Leading of dispersed oxide in the polymerization mixture can result in both inhibition and acceleration of the process (Table I). The rate of polymerization was determined at 333–353 K. Table I shows the results of the polymerization rate (W) at 348 K. The polymerization rate of PbO_2 content (C [%]) is affected by the nature of the peroxide initiator used in the reaction (Fig. 1). Benzoyl peroxide introduced into the polymerization system with an increase in the PbO_2 content practically does not change W , while when it is used as an HPTB initiator along with an increase in the filler content, it is used as an HPTB initiator, the polymerization rate increases by more than 6 times.

In addition to the influence on the polymerization process, dispersed oxides affect the rate of thermal decomposition of the peroxide initiator. The kinetics of the thermal decomposition of radical initiators were studied in the temperature range 333–353 K. In Fig. 2 the kinetic curves of the thermal schedule of PB and HPTB are shown. The linear coordinate dependence of $\ln(C_0/C_t)$ and t indicates the first kinetic order for peroxide. According to the tangent of the angle of the dependence, the constants of thermal destruction of peroxides (k) were found. The process of thermal decomposition of the organic peroxides in the presence of dispersed oxides and in the homogeneous system is well described by the kinetic equation of the first order reaction. Table I

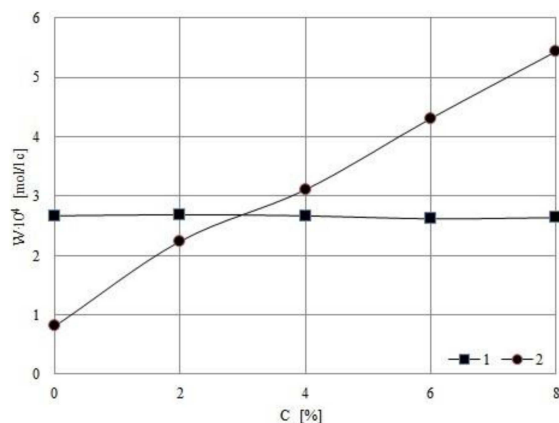


Fig. 1. Dependence of the styrene polymerization rate from the PbO_2 content. Initiator: 1 — PB ($[\text{PB}] = 0.03 \text{ mol/l}$); 2 — HPTB ($[\text{HPTB}] = 0.08 \text{ mol/l}$), $T = 348 \text{ K}$.

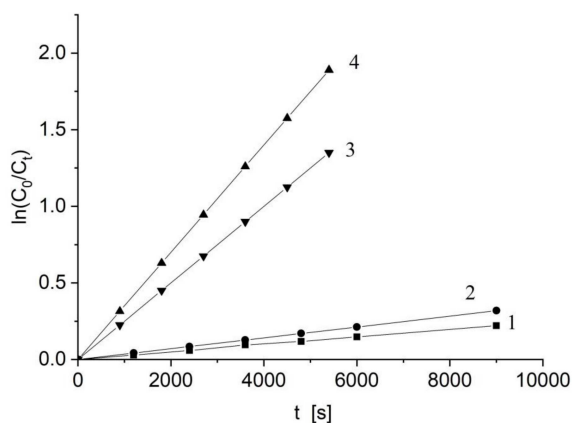


Fig. 2. Kinetic curves of the thermal destruction of PB (curves 1 and 2) and HPTB (curves 3 and 4). Oxides content: 1 — 0; 2 — 8 mass% Fe_2O_3 ; 3 — 8 mass% PbO_2 ; 4 — 4 mass% $\alpha\text{-PbO}$, $T = 333 \text{ K}$.

shows the total speed constants of thermal destruction (k) of organic peroxides in the presence of dispersed oxides, and the effective activation energy of this process (E_d). The total constant of the decay rate of the PB with an increase in Fe_2O_3 content from 0 to 15.6 increases approximately twice (Table I). In [5, 6] it is shown that the peroxide initiators of radical processes can be adsorbed on the surface of dispersed oxides. In the case of the peroxide compounds adsorbed on the surface of SiO_2 and Cr_2O_3 , they are decomposed by the heterolytic process without forming free radicals capable of initiating radical polymerization. The non-rational path of peroxides decomposition on the surface of these minerals is the result of the study on polymerization in [7, 8]. In some cases, during the polymerization of styrene in the presence of oxides, there was a change in the color of the filler, indicating a change in the valence state of oxide.

TABLE I

The rate of styrene polymerization (W) and constants of the thermolysis rate of peroxide initiators (k) in the presence of oxides (C) at 348 K, the activation energies of the polymerization reaction (E_a) and the process of peroxides destruction (E_d).

Oxide	C [%]	$W (\times 10^4)$ [mol/(l s)]	E_a [kJ/mol]	$k (\times 10^5)$ [s ⁻¹]	E_d [kJ/mol]
PB, 0.03 mol/l					
—	0	2.67	86	2.46	137
Fe_2O_3	8.0	3.30	73	3.54	98
Fe_2O_3	15.36	3.50	69	4.46	84
Cr_2O_3	4.0	3.81*	89	3.82	132
SiO_2	6.0	2.51	85	3.02	116
$\alpha\text{-PbO}$	8.0	2.80	82	2.67	130
$\beta\text{-PbO}$	4.0	2.62	84	2.65	128
PbO_2	8.0	2.64	89	2.69	110
DP, 0.03 mol/l					
—	0	2.55	92	5.25	140
Fe_2O_3	8.0	2.70	89	6.04	118
OSA, 0.03 mol/l					
—	—	5.20	87	21.7	119
Fe_2O_3	8.0	4.07	88	11.9	114
Cr_2O_3	3/0	2.68	87	11.8	117
HPTB, 0.06 mol/l					
—	—	0.81	78	—	—
Cr_2O_3	2.0	—	—	40	56
$\alpha\text{-PbO}$	4.0	1.68	59	35	50
$\beta\text{-PbO}$	4.0	1.85	54	30	40
$\beta\text{-PbO}$	8.0	1.85	58	33	42
PbO_2	8.0	3.71	52	25	60

*concentration of peroxide 0.05 mol/l

The process of peroxides decomposition on the surface of the oxides Fe_2O_3 , $\alpha\text{-PbO}$, $\beta\text{-PbO}$, PbO_2 has an oxidation-reducing character in which free radicals capable of initiating the polymerization process are formed. The oxidation-reducing reaction process indicates a significant decrease in the activation energy E_a (Table I) compared to homogeneous systems. The energy of activation of the polymerization process E_a in all cases is within the range of 52–89 kJ/mol (see Table I). Therefore, the dispersed mineral oxide affects both the polymerization process and the rate of degradation of radical polymerization initiators. In some cases, there is a change in the valence state of surface metal ions of the investigated oxides.

Polymerization of styrene in the presence of the dispersed oxides passes at high speed up to 10% degree of the monomer to polymer conversion. Polymerization in systems containing dispersed oxides passes both with the participation of the surface and in the monomer solution. After the conversion is reached, the polymerization rate value falls to 10% since the surface of dispersed oxide of the macromolecules formed by the macromolecules is blocked. Subsequently, the polymerization process continues

TABLE II

Molecular weights (M) and grafting of macromolecules (g) to the surface of dispersed oxides.

Oxide	C [%]	M ($\times 10^{-3}$)	g [%]	Oxide	C [%]	M ($\times 10^{-3}$)	g [%]
PB, 0.03 mol/l				HPTB, 0.06 mol/l			
–	–	50	–	–	–	135	–
Fe ₂ O ₃	8.0	39	4.5	α -PbO	4.0	80	4.1
Fe ₂ O ₃	12.2	36	4.1	α -PbO	8.0	75	4.6
Cr ₂ O ₃	3.0	48	1.0	β -PbO	4.0	74	4.4
α -PbO	4.0	47	3.5	β -PbO	8.0	73	4.5
β -PbO	8.0	45	3.4	PbO ₂	4.0	68	4.6
PbO ₂	8.0	49	3.4	PbO ₂	8.0	60	4.8
SiO ₂	4.0	49	2.1	Cr ₂ O ₃	3.0	76	6.0
DP, 0.03 mol/l				OSA, 0.03 mol/l			
–	–	68	–	–	–	40	–
Fe ₂ O ₃	4.0	65	3.8	Fe ₂ O ₃	4.0	40	4.6
Fe ₂ O ₃	12.2	56	4.2	Fe ₂ O ₃	12.2	72	4.6
Cr ₂ O ₃	3.0	64	1.3	Cr ₂ O ₃	3.0	45	1.2

only in solution and at 100% of the transformation formed by a polystyrene composite with a dispersed oxide, which is evenly distributed by the polymer volume.

Mineral dispersed oxide introduced into the polymerization system reduces the molecular weight (M) of the polystyrene (Table II). The reduction of M shows that the surface participates in breaking the polymer chains. Part of the macromolecules in the polymerization in the presence of oxides is attracted to the surface. The degree of grafting (g) is low and lies within the range of 1.0–6.0%. Moreover, grafting of polystyrene macromolecules changes the surface properties of the investigated oxides. Thermogravimetric studies of miner-polymer composites indicate that the beginning of the destruction of the system filled with polymer oxides begins from 20 to 30° less than for unfilled polystyrene.

Investigation of the molecular weight distribution (MWD) of polystyrene has shown that the formed polymer filled with oxides of polymerization systems is bimodal. In homogeneous systems, a polymer with a unimodal MWD is formed. The thermo-mechanical studies of polystyrene and polymer containing inorganic oxides practically do not differ.

4. Conclusions

The dispersed oxides introduced into the polymerization system are used in the production of PMC with different physical properties. Moreover, oxides influence both the physical and chemical parameters of the polymer formation and its molecular weights.

References

- [1] A. Berlin, *Polymer Composite Materials: Structure, Properties, Technology* Profession, St. Petersburg 2011.
- [2] S.G. Nedilko, *Acta Phys. Pol. A* **133**, 829 (2018).
- [3] C.V. Volkov, E.P. Kovalchuk, V.M. Ogenko, O.V. Reshetnyak, *Nanochemistry. Nanosystems. Nanomatyr-ial*, Nauk. Dumka, Kiev 2008.
- [4] V. Dutka, Ya. Kovalskyi, O. Aksimentyeva, N. Oshchapovska, *Adv. Chem. Eng. Sci.* **11**, 18 (2021).
- [5] V. Dutka, O. Aksimentyeva, N. Oshchapovska, Ya. Kovalskyi, H. Halechko, *Colloids Interfaces* **3**, 13 (2019).
- [6] V.S. Dutka, Ya.P. Kovalskii, Yu.V. Dutka, *Colloid J.* **75**, 649 (2013).
- [7] V.S. Dutka, Ya.P. Kovalskii, Yu.V. Dutka, *Ukr. Chem. J.* **82**, 122 (2016).
- [8] V.S. Dutka, Ya.P. Kovalskii, Yu.V. Dutka, *UkrPolymer* **36**, 207 (2014).