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Influence of Ionizing Radiation on the Properties of Poly-N-methylallyl-5-vinyltetrazole and Energy-Rich Compositions Based on It

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Abstract

Influence of ionizing radiation on the physicochemical characteristics of poly-N-methylallyl-5-vinyltetrazole (MPVT-A) and on the rheological kinetic properties of energy-rich compositions prepared from irradiated MPVT-A samples was studied. It is established that ionizing radiation can significantly reduce the induction time of solidification of the compositions based on MPVT-A.

Keywords: radiolysis, polyvinyltetrazole derivatives, solidification induction time

INTRODUCTION

Polymers and copolymers of vinyltetrazole are efficient basis for condensed energy-rich systems. This is due to the high energy characteristics of tetrazole, low sensitivity of its derivatives to shock and friction, high thermal stability and high gas evolution [1]. A technology for obtaining poly-N-methyl-allyl-5-vinyltetrazole (MPVT-A), the promising component for energy-rich systems, was developed at the Federal Research and Production Centre “Altai” [2], and its serial production was introduced. Poly-N-methyl-allyl-5-vinyltetrazole is a copolymer of 1-methyl-5-vinyltetrazole (1,5-MVT), 2-methyl-5-vinyltetrazole (2,5-MVT), N-allyl-5-vinyltetrazole (BAT) and acrylonitrile (Fig. 1).

The problems connected with the solidification (curing) of MPVT-A in the process of obtaining condensed energy-rich systems deserve special attention [3]. It is interesting to study the effect of ionizing radiation on the major technologically significant characteristics of MPVT-A and physicochemical properties of compositions prepared on the basis of irradiated samples. These compositions include a fuel binder (FB) containing irradiated MPVT-A, nitroglycerol (NG) as a plasticizer (NG), and diphenylamine (DPA) as a stabilizer of thermal stability.

The goal of the present work was to study the effect of ionizing radiation on the characteristics of MPVT-A and to evaluate the possibility to use modern electron accelerators for the directed al-

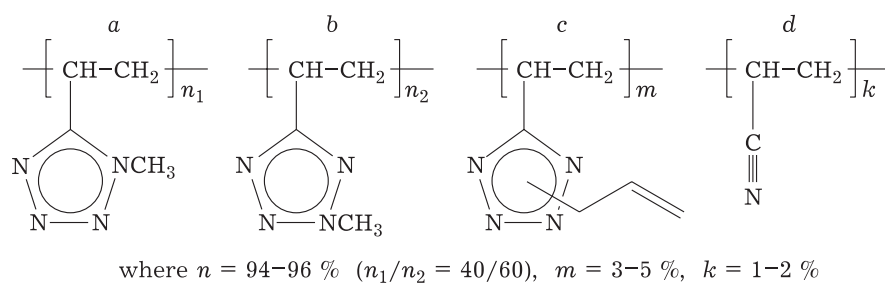


Fig. 1. Structural fragments of MPVT-A copolymers: a - 1-methyl-5-vinyltetrazole (1,5-MVT), b - 2-methyl-5-vinyltetrazole (2,5-MVT), c - N-allyl-5-vinyltetrazole (VAT); d - acrylonitrile.

teration of the properties of compositions prepared on its basis.

EXPERIMENTAL

The MPVT-A polymer was treated with a beam of accelerated electrons at the ILU-6 accelerator (BINP SB RAS, Russia) [4]. Treatment conditions were: electron energy 2.4 MeV, pulsed current 328 mA, pulse frequency 2 Hz. The absorbed radiation doses (D) were 20, 40, 60, 80 kGy. The absorbed dose was estimated using the dosimetric procedure [5].

Characteristic viscosity of MPVT-A samples was determined in the 0.1 M NaBr solution in dimethylformamide (DMFA) with the polymer concentration 0.025 g/L [6]. The content of non-alkylated fragment of the tetrazole-containing copolymer (the content of NH-acid) was determined using a method described in [6]. The amount of volatile substances was determined by means of gravimetry [6]. The volume of evolved gases (gaseous products of thermolysis, cm^3/g of polymer) at 80 °C during 72 h was determined using the ampoule chromatographic procedure (ACP) [7].

Thermal decomposition of MPVT-A samples was studied by means of synchronous thermal analysis (TGA-DTA) with the help of a thermogravimetric analyzer DTG-60 (Shimadzu, Japan) at a heating rate of 10 °C/min in nitrogen within temperature range 20–350 °C. The IR spectra of samples in KBr were recorded using an Infracum FT-801 Fourier spectrometer (Russia).

Investigation of the dynamics of FB structuring in the presence of di-N-oxide-1,3-dinitryl-2,4,6-triethylbenzene (TON-2) as a hardener was carried out with a rotation viscosimeter HBDV-II+Pro (Brookfield, USA) with the angular velocity 15 r.p.m., shear rate (SR) 5, 10 s^{-1} and temperature 25 °C. The amount of TON-2 in FB was

1 mole of TON-2 per 1.25 moles of the allyl tetrazole fragment in MPVT-A, which corresponded to 0.216 % TON-2 of the mass of FB.

RESULTS AND DISCUSSION

Effect of ionizing radiation on the major characteristics of MPVT-A

The major physicochemical characteristics of initial MPVT-A polymer and irradiated samples are presented in Table 1. Characteristic viscosity of MPVT-A solution decreases monotonously with an increase in irradiation dose slightly increasing at the maximal dose.

The minimal amount of volatile substances was determined at $D = 40$ kGy. The maximal gas evolution (higher by 60 % in comparison with the initial sample) as a result of polymer thermolysis corresponds to the same dose. Within the dose range 40–60 kGy, the composition of thermolysis gases changes noticeably: the maximal CO_2 content and the minimal N_2 content are observed.

MPVT-A has characteristic bands in the IR absorption spectra at 1100 and 1670 cm^{-1} ; the intensity of these bands decreases till the dose of 80 kGy, which presumably corresponds to the radiation destruction of the tetrazole cycle. The latter should be accompanied by a decrease in the degree of polymerisation and therefore by a decrease in characteristic viscosity [8], which is observed with an increase in irradiation dose.

A comparison between the IR spectra of the initial polymer and the samples irradiated with different doses does not allow us to reveal undeniable differences. So, changes taking place in the samples affect an insignificant fraction of chemical bonds (transformation degree does not exceed 1 %). At the same time, as it will be demonstrated below, changes in the reactivity pronounced as the acceleration of cross-linking with an increase

TABLE 1

Physicochemical characteristics of initial polymer MPVT-A and irradiated samples

Parameter	Absorbed radiation dose, kGy				
	0	20	40	60	80
Characteristic viscosity, dL/g	0.460	0.451	0.437	0.434	0.440
Content of allyltetrazole fragment, %	1.1	1.1	1.0	1.0	1.0
Amount of volatile substances, %	5.7	4.8	4.7	4.8	4.9
Content of NH-acid, %	1.1	0.9	0.9	0.9	0.9
Content of substances insoluble in DMFA, %	0.1	0.1	0.1	0.1	0.1
Volume of evolved gas, cm ³ /g	0.010	0.014	0.016	0.014	0.008
CO ₂ fraction, %	31	40	39	44	36
N ₂ fraction, %	69	60	61	56	64

in irradiation dose may be explained by the formation of additional centres interacting with the curing agent (TON-2).

Insignificant decrease in the characteristic viscosity of MPVT-A solutions is likely to point to the mutual compensation of differently directed changes in chain lengths (chain shortening and the formation of cross-links as a result of recombination of free radicals). It is also necessary to put attention to the fact that a part of radicals formed as a result of the rupture of macromolecules may participate in disproportionation with the formation of unsaturated carbon-carbon bonds. The latter circumstance should affect FB solidification in the presence of TON-2 [9].

Thermal stability of MPVT-A is determined by its isomer composition [10]. The thermal transformation of MPVT-A is characterised by the presence of one weak endo-effect at 134 °C and two exo-effects at 290 and 380 °C. The latter two effects correspond to the stages of thermolysis of 2,5-MPVT and 1,5-MPVT, which proceed kinetically independent of each other; the heats of the decomposition of the indicated fragments are proportional to their content in the polymers.

According to the TGA-DSC data, the behaviour of thermal decomposition of initial MPVT-A and the samples irradiated with the doses of 20–60 kGy does not change substantially. With an increase in irradiation dose to 80 kGy, both exo-effects increase substantially: the former increases from 3380 to 3670 J/g (+8.6 %), and the latter from 607 to 718 J/g (+18.3 %). It is most probable that this is connected with the radiolysis of the initial components of the copolymer (chain shortening and an increase in the amount of unsaturated bonds as a result of disproportionation of primary radicals).

Rheokinetic features of FB structuring in the presence of TON-2 depending on the dose of irradiation of initial MPVT-A

To estimate the curing capacity of MPVT-A irradiated with different doses, we prepared the samples of NG-tetrazole binder FB with the components mass ratio MPVT-A/NG/DPA = 15.0 : 85.0 : 1.5. The results of the evaluation of thermal stability of FB samples with the help of ACP are presented in Table 2. Irradiated samples release

TABLE 2

Thermal stability of FB samples (mass ratio of components: MPVT-A/NG/DPA = 15.0 : 85.0 : 1.5)

Dose of MPVT-A irradiation, kGy	Volume of evolved gas, cm ³ /g	Gas composition, %			
		NO	N ₂	CO ₂	N ₂ O
0	0.084	19	15	66	0
20	0.080	20	30	50	0
40	0.087	19	33	46	2
80	0.095	20	35	45	0

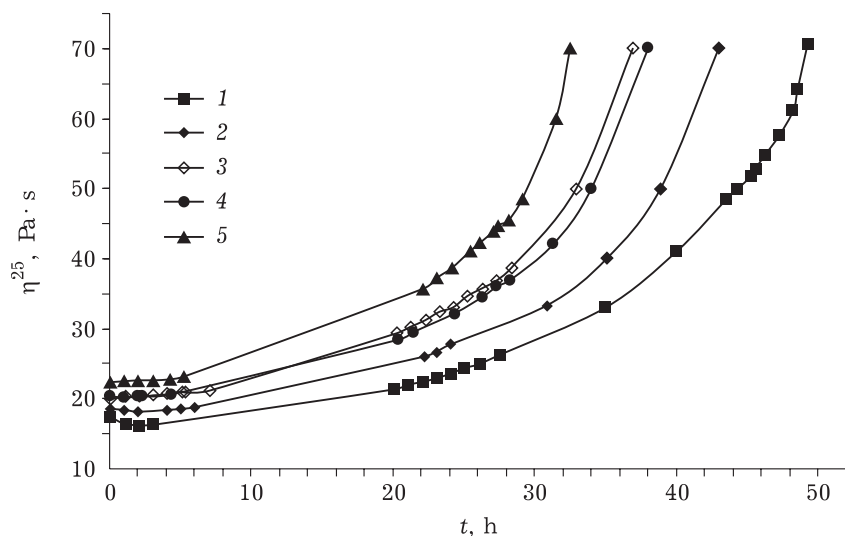


Fig. 2. Rheokinetics of FB with TON-2 as curing agent depending on the dose of MPVT-A irradiation, kGy: 1 - 0 (initial), 2 - 20, 3 - 40, 4 - 60, 5 - 80.

TABLE 3

Initial dynamic viscosity of FB in the presence of TON-2 depending on the absorbed dose of MPVT-A irradiation

D , kGy	0	20	40	60	80
η^{25} , Pa·s	16.21	17.25	18.58	18.51	19.92

less CO_2 and almost two times larger amount of N_2 . It should be stressed that for MPVT-A samples, unlike for compositions, a reverse situation is observed (see Table 1).

The values of the initial (at the moment of preparation) dynamic viscosity (η^{25}) of FB in the presence of the curing agent TON-2 depending on the absorbed irradiation dose were obtained (Table 3). One can see that in the presence of TON-2 dynamic viscosity increases with an increase in the dose of MPVT-A irradiation from 16.21 Pa·s (0 kGy) to 19.92 Pa·s (80 kGy).

Rheokinetic curves of structuring (curing) of FB in the presence of TON-2 for initial MPVT-A and irradiated samples were plotted (Fig. 2). The first stage of curing is characterised by the induction time of structuring (τ_{str}) and is likely to be connected with an increase in the length of molecular chains as a result of the interaction with the molecules of the curing agent. The time within which dynamic viscosity increases to 40 Pa·s (an increase in viscosity by a factor of 2 in comparison with initial sample) was accepted as τ_{str} . The second stage of curing is the formation of gel (the beginning of the formation of a weak spatial

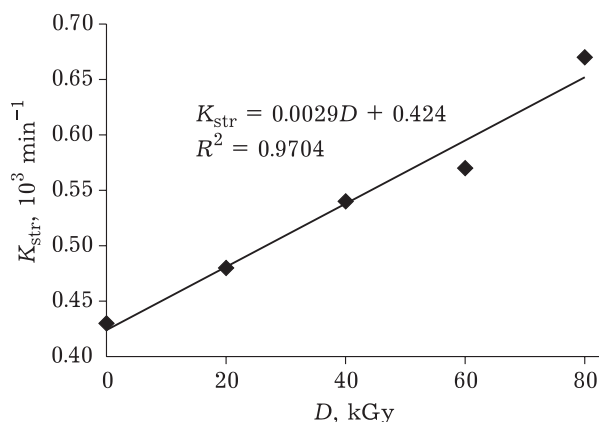


Fig. 3. Dependence of the rate constant (K_{str}) of FB structuring in the presence of TON-2 on the dose (D) of irradiation of MPVT-A polymer.

three-dimensional network), when the dynamic viscosity increases sharply.

The value $1/\tau_{\text{str}}$ corresponds to the rate constant of structuring (K_{str}); its dependence on the absorbed radiation dose is presented in Fig. 3. One can see that K_{str} increases monotonously with an increase in the dose of MPVT-A irradiation. Therefore, the rate of structuring of irradiated polymer is proportional to the irradiation dose and increases by a factor of 1.56 (80 kGy) in comparison with the initial polymer. Analysis of the curves of dynamic viscosity shows that gel formation proceeds at a rate which is approximately the same for all samples. So, MPVT-A irradiation has a strong ef-

fect on τ_{str} of FB in the presence of TON-2 but only weakly affects the rate of gel formation.

CONCLUSION

The effect of ionizing radiation within the dose range 0–80 kGy on the major characteristics of MPVT-A was established. It was demonstrated that the irradiation of MPVT-A only slightly affects its physicochemical properties, with the exception of thermal decomposition for which a noticeable increase in the exothermal effects connected with the destruction of the main components of the polymer was observed. Preliminary irradiation of MPVT-A allows a substantial decrease in the induction time of structuring for the compositions based on this material in the presence of TON-2 as a curing agent.

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