

# Structuring and viscoelastic properties of polyurethanes, doped with aerosil nanoparticles and activated by xanthene dyes

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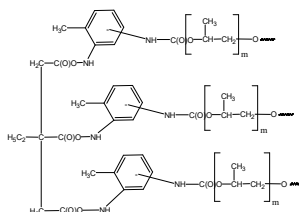
## Introduction.

Polyurethanes (PU) are long known to be a universal class of polymers, used in various industrial sectors due to their high functional chemical and mechanical properties. One of their application fields is laser techniques, in particular, development of the polyurethane-based matrices for the solid-state elements in organic dye lasers and passive Q-switches. The durability and generation efficiency of the laser elements are largely determined by the physicochemical properties of dyes and polymer matrices, in particular, their resistance to irradiation. Many various inorganic dopants and organic pigments for a use as photostabilizers were proposed.

## Motivation. Methods.

Previously, we studied how the spectral and photophysical properties of the xanthene dye Rhodamine 6G introduced into PU acrylate depended on the concentration of doping aerosil A-300 nanoparticles [1]. Larger nanofiller content (up to 8 wt.%) caused better characteristics (the monomer-dimer ratio of the dye composition in the polymer matrix and the quantum yield of luminescence increased). We considered it important to investigate the influence of the doping nanofiller amount on the photostability of the polyurethane matrix, studied previously in [2]. We used an approach of the authors [3], who showed the effectiveness of the IR-spectroscopy and dynamic mechanical analysis (DMA) methods in the study of destructive processes in polyurethanes based on polyethylene glycols of different molecular weights and diphenylmethane diisocyanate.

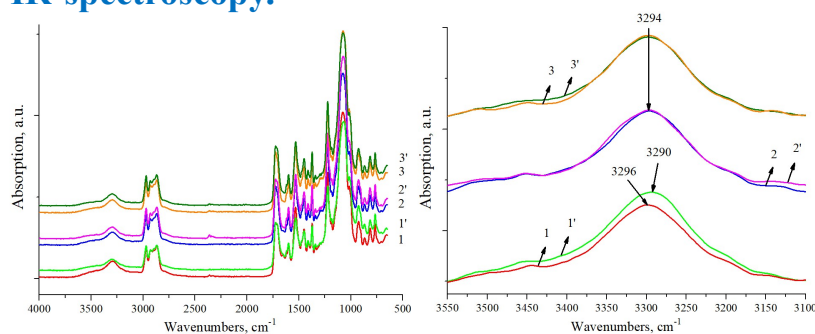
## Samples.



PU sample	A-300 content, wt.%	Irradiation
PU0	0	-
PU5	5	-
PU7	7	-
rPU0	0	+
rPU5	5	+
rPU7	7	+

## Experimental results.

### IR-spectroscopy.



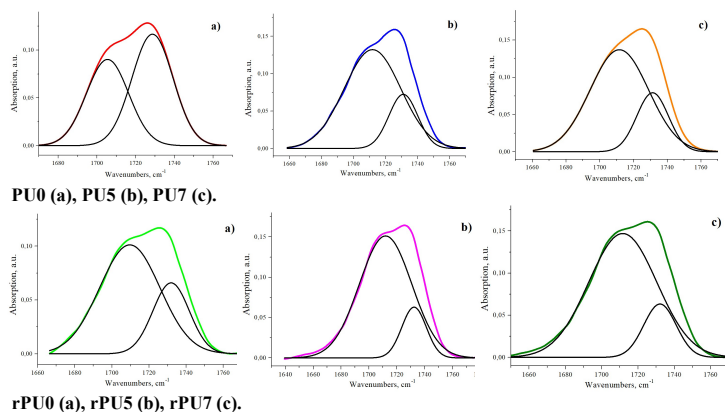
IR-spectra of the initial (1, 2, 3) and irradiated (1', 2', 3') polymer films: PU0 and rPU0 (1, 1'), PU5 and rPU5 (2, 2'), PU7 and rPU7 (3, 3').

The polyurethane structure was determined to consist of flexible and rigid segments (blocks) and the band Amide I ( $\nu_{C=O}$ ) splits into two components, ascribed to different types of associates: The high-frequency component ( $1730\text{ cm}^{-1}$ ) with the peak position, which is insensitive to the diisocyanate type and concentration, corresponds to the absorption by the urethane NH-groups, hydrogen bonded to the oxygen of the polyester chains. Contrary to this, the maximum of the low-frequency component ( $1705\text{ cm}^{-1}$ ) depends on the diisocyanate type and refers to the absorption of self-associated urethane groups, and therefore, characterizes urethane groups, located inside polymer rigid domains. The interactions between the urethane NH-groups and oxygen of the oligoester part prevail in the initial PU film. During the aerosil introduction there are predominant interactions of urethane groups inside the rigid segments due to the steric restrictions, and the formation of hydrogen bonds between the aerosil Si-OH groups and C=O groups of the PU is also possible.

The analysis of the IR-spectra shows that in the irradiated films, a significant part of the associated C=O groups is inside the hard domains. Changes in the shape and intensity of the Amide I band after irradiation are associated with an increased amount of the C=O groups as a result of possible oxidation processes.

Graphical separation parameters for the spectral band of the C=O stretching vibrations in the pure and doped polyurethanes after irradiation.

Sample	Integral intensity of the low-frequency component, %	Integral intensity of the high-frequency component, %	Intensity low/high-frequency component ratio
PU0	44	56	0.79
PU5	78	22	3.55
PU7	76	24	3.17
rPU0	72	28	2.57
rPU5	84	16	5.25
rPU7	83	17	4.88



rPU0 (a), rPU5 (b), rPU7 (c).

## Viscoelastic properties.

Samples	$T_g, ^\circ\text{C}$	$\tan\delta_{\max}$	$E'_{T=25^\circ\text{C}}$ MPa	$E'_{T=80^\circ\text{C}}$ MPa
PU0	17	1.032	17.18	3.11
rPU0	12	1.001	7.82	3.55
PU5	14	0.867	17.36	3.69
rPU5	12	0.913	10.37	4.06
PU7	14	0.848	24.20	6.01
rPU7	11	0.902	10.28	1.91

Aerosil doping of the polyurethane matrix causes a slight decrease of a temperature  $T_g$ , which indicates the appearance of some defects in the material structure due to the filler presence. At the same time, in the case of the PU7 film, the value of  $E'$  grows significantly due to the formation of a filler spatial alignment within the system. However, after irradiation, the  $E'$  of this sample considerably decreases. Thus, the assumption can be made that irradiation of the PU7 matrix destroys the structural network of the filler. Such an effect is not observed for the irradiated polyurethanes with a lower concentration or absence of aerosil.

Therefore, the analysis of viscoelastic properties showed a slight destructive effect of UV radiation on the PU structure, which was determined by decreased values of the glass transition temperature and the elastic modulus. Aerosil doping of the PU matrix caused larger structural heterogeneity of the material after irradiation. As the aerosil content was increased to 7 wt.%, irradiation of the corresponding polymer destroyed partially a spatial network of the filler.

## Conclusions.

Effects of the inorganic nanofiller on the photooxidative processes in the polyurethanes have been investigated by an analysis of the spectral characteristics for the aerosil-filled PU films under irradiation. The aerosil incorporation has been shown to slow considerably these processes. This effect has been seen the most for the filler larger concentration of 7 wt.%. A possible reason for the slowdown of photooxidative and photochemical processes in the doped polymers is the dissipation of irradiation energy by the nanofiller. According to the dynamic mechanical data, irradiation of the aerosil-filled PU polymers has been found out to cause larger structural heterogeneity of the material and a decrease in its modulus of elasticity. Irradiation of the PU matrix, doped with 7 wt.% aerosil, partially destructs the spatial network of the nanofiller due to dissipation of the irradiation energy by inorganic nanoparticles.

The obtained results evidence the stabilizing effect of the aerosil nanofiller on the polyurethane resistance to the irradiation with an ultrahigh pressure mercury lamp.

Taking into account the results of our work [1] on the aerosil positive effect on the stability and efficiency of laser dye elements for a polyurethane acrylate matrix, we can predict further improvements in the development of the aerosil-doped transparent optical materials for both laser technology and photonics.

## References.

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