Photosensitive hybrid Titanium-containing Polymer Materials for Photonics

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Idea:

Study of photosensibility and the structural features of matrix nanostructures based on titanium-containing interpenetrating polymer networks

Methods:

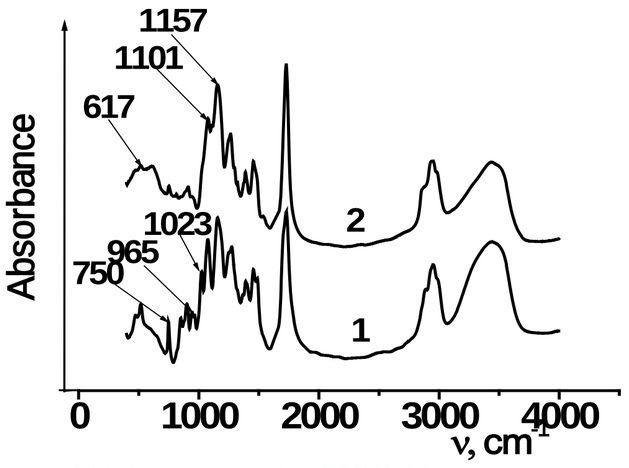
•IR-spectroscopy, differential calorimetry, optical spectrophotometry, SAXS, DSC

Titanium-containing IPNs:

Titanium-containing interpenetrating polymer networks (Ti-IPNs) based on the cross-linked polyurethane (PU) and Ti-containing copolymer (Ti-CP) based on hydroxyethyl methacrylate (HEMA) and titanium isopropoxide **(**$Ti(O^iPr)_4$**)** were obtained by simultaneous synthesis. PU/PHEMA ratio in neat and Ti-IPNs was 30/70 and 50/50 wt.%, and molar ratio HEMA/$Ti(O^iPr)_4$ was 16/1, 12/1, 8/1, and 4/1.

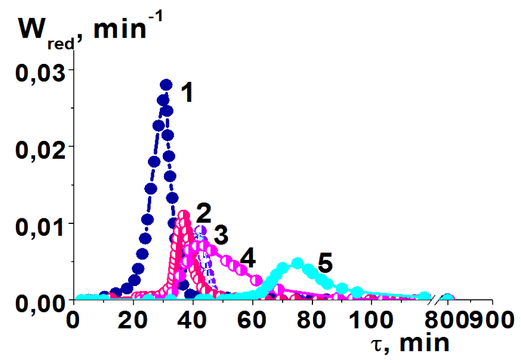
The scheme of formation of Ti-containing copolymer

IR-spectroscopy



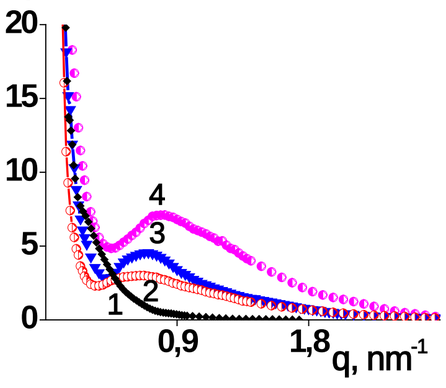
FTIR spectra : 1 – PHEMA
2 – Ti-CP based on HEMA and $Ti(O^iPr)_4$

Kinetics of Ti-CP formation



Variation of reduced rate Wred of Ti-CP and HEMA (1) polymerization at various molar ratio HEMA/$Ti(O^iPr)_4$: 16/1 (2), 12/1(3) 8/1 (4), 4/1 (5)

SAXS



Intensity SAXS for neat IPN (1) and Ti- IPN with different content of (–TiO_2–) fragments: 2 – Ti- IPN-1, 3 – Ti- IPN-2, 4 – Ti- IPN-3.

Parameters of heterogeneous structure of IPN and Ti-IPNs

Sample	PU/PHEMA/ (–TiO_2–) , wt. %	HEMA/ $Ti(O^iPr)_4$, mol	D, nm	$<\Delta\rho^2>\times10^3$, (моль)^2/см^6
IPN	50/50/0	–	–	0.445
Ti- IPN-1	48.8/48.8/2.4	12/1	9.7	0.892
Ti- IPN-2	48.3/48.3/3.4	8/1	9.0	1.070
Ti- IPN-3	47.0/47.0/6.0	4/1	7.9	2.590

Important: Analysis of the microheterogenic structure of the Ti-IPNs by the SAXS method revealed that the synthesized hybrid systems possessed nanosized regions of heterogeneity. The increase in the content of the Ti-component was accompanied by increase in the overall level of heterogeneity of the Ti-containing nanocomposite materials.

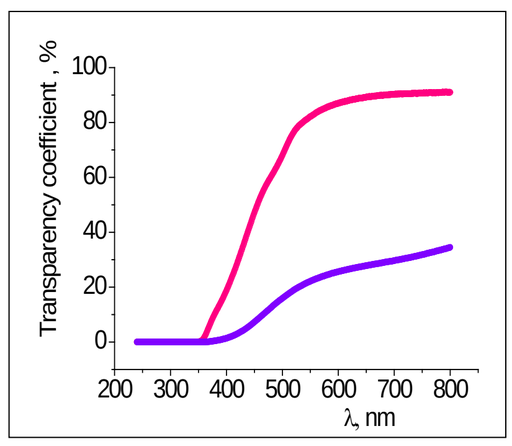
DSC

Sample	HEMA/ $Ti(O^iPr)_4$, mol	PU/PHEMA/ (–TiO_2–), wt. %	T_{g1}, °C	ΔC_{p1}	T_{g2}, °C	ΔC_{p2}
IPN	–	30/70/0	-23.0	0.27	73.7	0.34
Ti- IPN -4	16/1	29.3/68.3/2.4	-13.8	0.21	79.6	0.29
Ti- IPN -5	12/1	29.0/67.7/3.3	-14.3	0.20	82.4	0.28
Ti- IPN-6	8/1	28.6/66.8/4.6	-14.6	0.23	85.8	0.25
Ti- IPN-**7**	4/1	27.7/64.3/8.0	-15.5	0.24	100.2	0.12

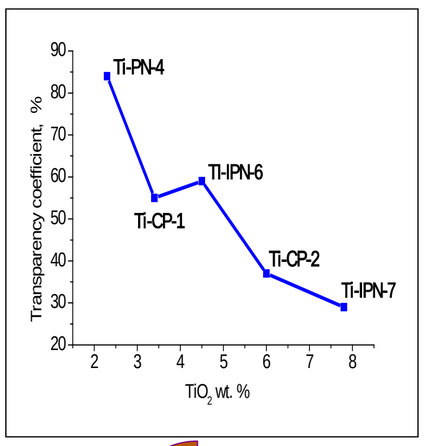
Important: Study by DSC method showed that increase of the (–TiO_2–) fragments content in IPNs led to essential increase of T_{g2} of the Ti-CP component and decreases ΔC_{p2}. This can be caused by an increase in the cross-linking density as a result of an increase in the number of fragments (–TiO_2–) in the resulting spatial network of the Ti-CP .

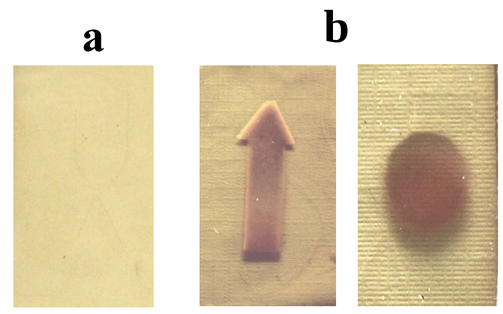
Optical spectrophotometry

Sample	HEMA/ $Ti(O^iPr)_4$, mol	PU/PHEMA/ (–TiO_2–), wt.%	T, % at 650 nm	
			before UV-irradiation	after UV-irradiation
Ti-CP-1	16/1	0/96.6/3.4	90.85	55.0
Ti-CP -2	8/1	0/94.0/6.0	89.24	37.0
Ti- IPN-4	16/1	29.2/68.4/2.4	91.11	84.0
Ti- IPN-6	8/1	28.7/66.8/4.6	90.31	59.0
Ti- IPN-7	4/1	27.7/64.3/8.0	90.26	29.0



Ti- IPN-7 before UV- irradiation
Ti- IPN-7 after UV- irradiation





Ti-IPNs before (a) and after (b) UV- irradiation

Important: The values of light transmission coefficients (T, %) for Ti-CP and Ti-IPNs series of samples show that the ability for UV-induced optical absorption of polymeric Ti-containing materials increases with the increasing of Ti-component content.

Summary:

•At synthesis of simultaneous Ti-IPNs based on PU and Ti-CP three-dimensional cross-linked structures with including (–TiO_2–) fragments in a polymer chain of PHEMA are formed.

• Titanium-containing interpenetrating polymer networks are optically transparent with the optical transparency coefficient value up to 90-91 % at 650 nm. It has been shown that for Ti-IPNs the reverse visible darkening at UV-irradiation was observed, due to formation of paramagnetic ions of Ti^{3+} as a result of electron transition $Ti^{4+} + e \leftrightarrow Ti^{3+}$.