THERMAL AND HYDRATION STUDY ON HYDROPHILIC NANOCOMPOSITES BASED ON POLYMER/SILICA FOR BIOMEDICAL APPLICATIONS

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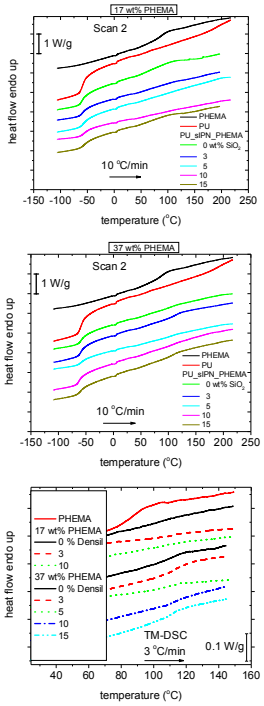
Materials and Experimental Techniques

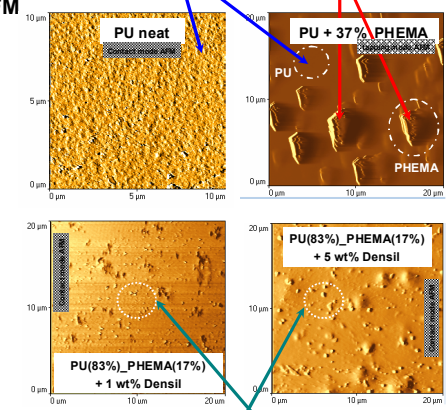
Nanocomposites based on a sequential semi – interpenetrating polymer networks (semi-IPN) of cross-linked polyurethane (PU) and linear poly(hydroxyethyl mehacrylate) (PHEMA) filled with 3 to 15 wt% nanosilica filler were prepared [1] and investigated. As nanofiller, densil was used. Densil is the product of nanosilica A-300 (specific surface area S_{bet}~300 m^2/g) modification by mechano-sorptive method [2], consisted of primary nanoparticles of about 13 nm in diameter (according to SAXS). Such modification leads to significant changes in asperity of surface and porosity of nanofiller. Different PHEMA contents (17 and 37 wt%), in the semi-IPNs, were chosen in an attempt to control the hydrophilic properties and the microphase separation of the polymer matrix. Morphology (AFM), thermal (DSC), dielectric (DRS, TSDC) and water sorption techniques (ESI, DDI) were employed for the present study, especially in the perspective of biomedical applications (e.g. controlled drug delivery).

Differential Scanning Calorimetry (Standard & Modulated Temperature)



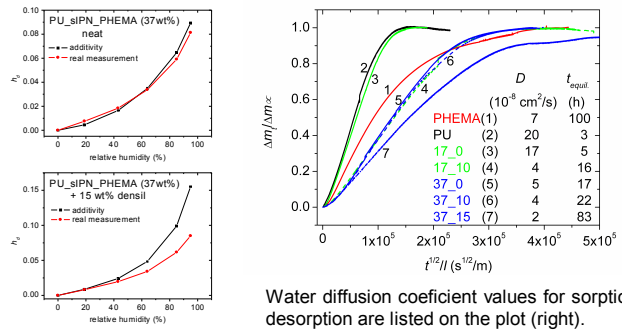
	X_{pu} (wt)	X_{phema} (wt)	X_{filler} (wt)	ΔT (°C)	T_g (°C)	ΔC_p (J/g°C)	$\Delta C_{p,norm}$ (J/g°C)	ΔT (°C)	T_g (°C)	ΔC_p (J/g°C)	$\Delta C_{p,norm}$ (J/g°C)
PHEMA	0.00	**1.00**	**0.00**	-	-	-	-	18	**88**	0.19	**0.19**
PU	1.00	**0.00**	**0.00**	13	**-58**	0.47	**0.47**	-	-	0.00	0.00
17-0	0.83	**0.17**	**0.00**	14	**-58**	0.40	**0.48**	-	-	0.00	0.00
17-3	0.81	**0.16**	**0.03**	19	**-57**	0.37	**0.46**	7	**111**	0.03	**0.03**
17-5	0.79	**0.16**	**0.05**	18	**-56**	0.36	**0.46**	-	-	0.00	0.00
17-10	0.75	**0.15**	**0.10**	19	**-54**	0.40	**0.54**	8	**107**	0.02	0.03
17-15	0.71	**0.14**	**0.15**	18	**-55**	0.30	**0.43**	3	**106**	0.02	**0.02**
37-0	0.63	**0.37**	**0.00**	13	**-58**	0.35	**0.56**	12	**112**	0.05	**0.13**
37-3	0.61	**0.36**	**0.03**	14	**-57**	0.35	**0.57**	12	**113**	0.07	**0.20**
37-5	0.60	**0.35**	**0.05**	17	**-57**	0.32	**0.53**	18	**111**	0.09	**0.24**
37-10	0.57	**0.33**	**0.10**	12	**-62**	0.33	**0.58**	11	**114**	0.04	**0.11**
37-15	0.54	**0.31**	**0.15**	16	**-58**	0.26	**0.49**	12	**110**	0.06	**0.20**

AFM



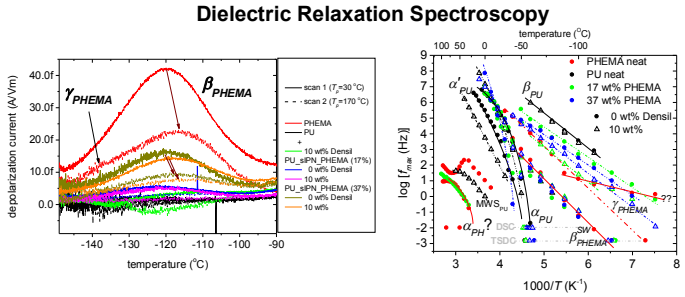
Densil aggregates (100-300 nm in diameter)

Equilibrium water Sorption and Dynamic water Desorption Isotherms



Water diffusion coeficient values for sorption and desorption are listed on the plot (right).

Dielectric Relaxation Spectroscopy



TSDC thermograms (left) and Activation Diagrams (Arrhenius plots, right) for PU semi-IPNS with PHEMA filled with Densil [2] nanoparticles.

Results and discussion

Morphological (AFM, SAXS) results showed partial separation of the two polymer phases in addition to good polymer filler distribution. Additional support to that is given by DSC results, in which two glass transitions are observed, both for PU and PHEMA. The aggregation of filler is increasing with densil content, especially above 3 wt% (in agreement with SAXS results).

In the nanocomposites the glass transition of PHEMA immigrated towards higher temperatures, as compared to initial PHEMA, simultaneously with a ΔC_p reduction. The above facts suggest constrained dynamics of PHEMA phase in the IPNs.

Non additive hydration behaviour was obtained for the nanocomposites, as compared to the unfilled polymer matrices and the initial silica. The good hydration properties (ESI) of the semi-IPN matrix are preserved in the nanocomposites, although the hydrophilicity of silica (densil) was suppressed, most probably due to the engagement of surface silanol groups (–Si-OH) by polymer chains. These endgroups of densil are most responsible for the hydration of the systems. The water diffusion coefficient, *D*, decreases with PHEMA, monitoring the deplasticization of PHEMA phase during its dehydration, while the matrix (of PHEMA) changes from the elastic to the glassy state. *D* decreases, also, with the addition of densil, suggesting that the diffusion of water molecules is restricted from the –Si-OH attraction.

TSDC and DRS results showed, in agreement with each other, that glass transition and segmental dynamics of the two phases were practically not affected by the presence of the nanoparticles. On the other hand, local dynamics, varried systematically on the amount of PHEMA and water content.

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