Supplementary materials

Novel polyurethane network/organoclay nanocomposites: Microstructure and physicochemical properties

Marija V. Pergal[a,*], Gordana Gojgić-Cvijović[a], Miloš Steinhart[b], Dragan Manojlović[c], Sanja Ostojić[d], Lato Pezo[d], Milena Špírková[b]

[a] *University of Belgrade, Institute of Chemistry, Technology and Metallurgy, National Institute of the Republic of Serbia, Njegoševa 12, 11000 Belgrade, Serbia*;

[b] *Institute of Macromolecular Chemistry CAS (IMC), Heyrovsky Sq. 2, 16206 Prague 6, Czech Republic*;

[c] *Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Republic of Serbia; South Ural State University, Lenin Prospekt 76, 454080 Chelyabinsk, Russia*;

[d] *Institute of General and Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia.*

* Corresponding author. E-mail: marijav@chem.bg.ac.rs

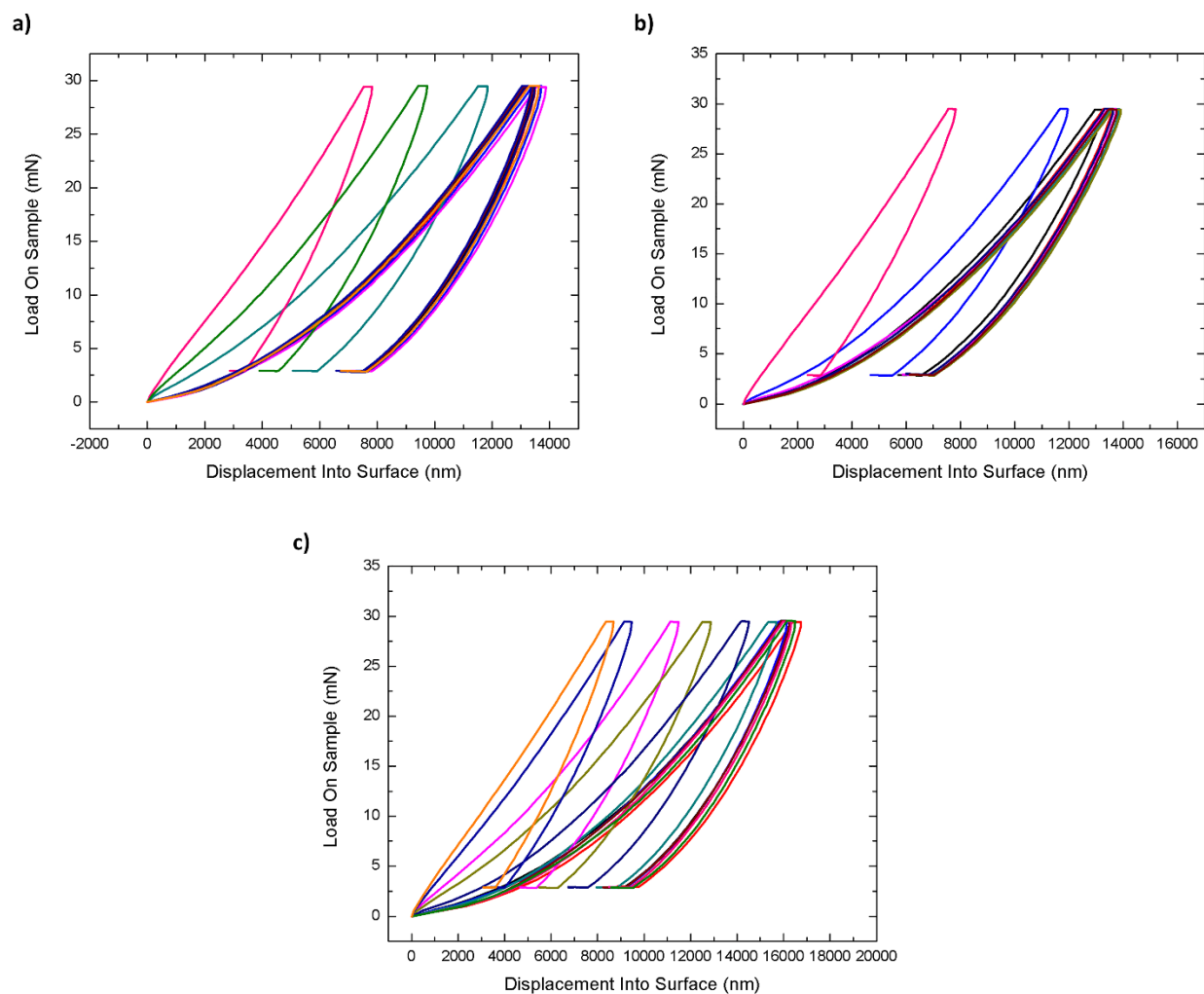**Figure 1s.** Photographs of the prepared PUN-NC materials.

Figure 2s. Curves obtained from nanoindentation measurements for PUN-NC films with 60 wt% of soft segment and different organoclay contents: a) 0.5 wt%; b) 1 wt% and c) 2 wt%.
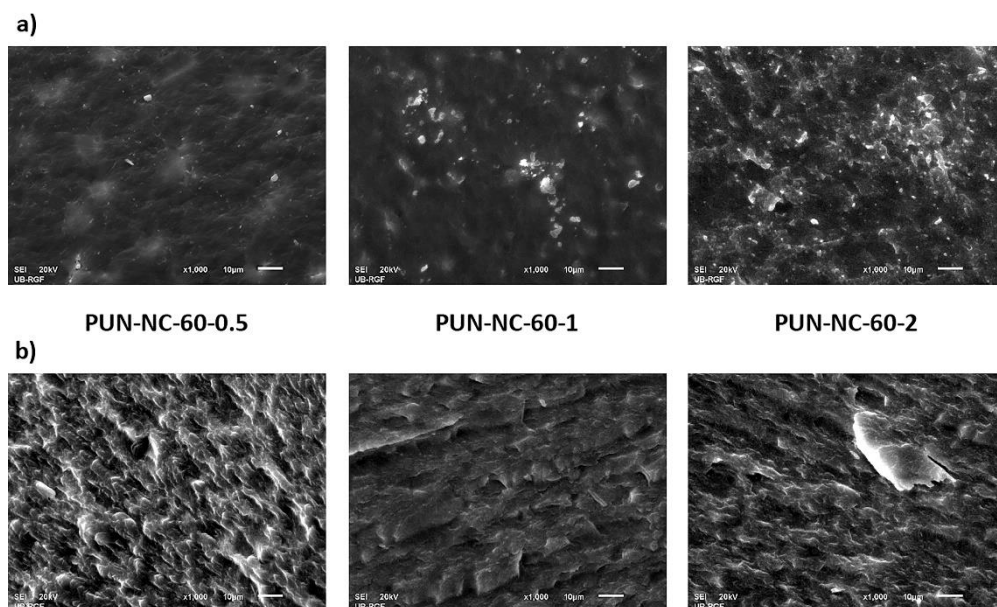
PUN-NC-60-0.5   **PUN-NC-60-1**   **PUN-NC-60-2**

Figure 3s. SEM micrographs of (a) surface and (b) fractured surface PUN-NCs based on different organoclay contents (0.5, 1 and 2 wt%) and with 60 wt% of soft segment at magnification x1000.
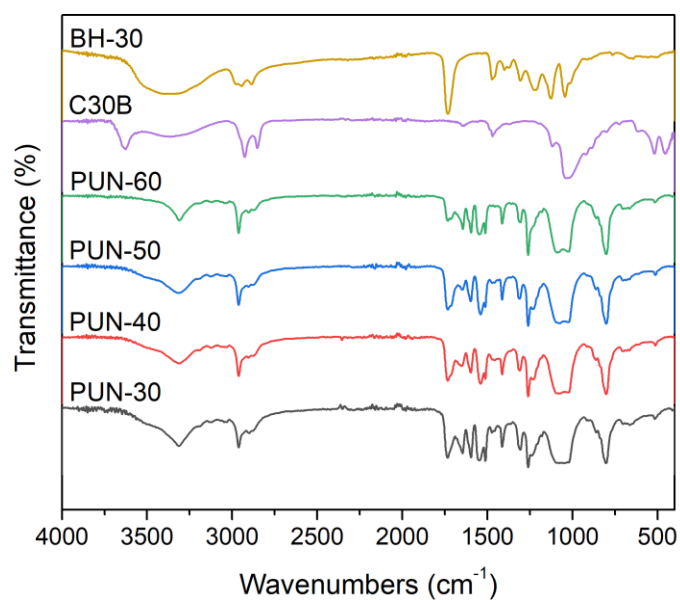

Figure 4s. FTIR spectra of Cloisite 30B, BH-30 and pure PU networks (PUN) with different soft segment contents.
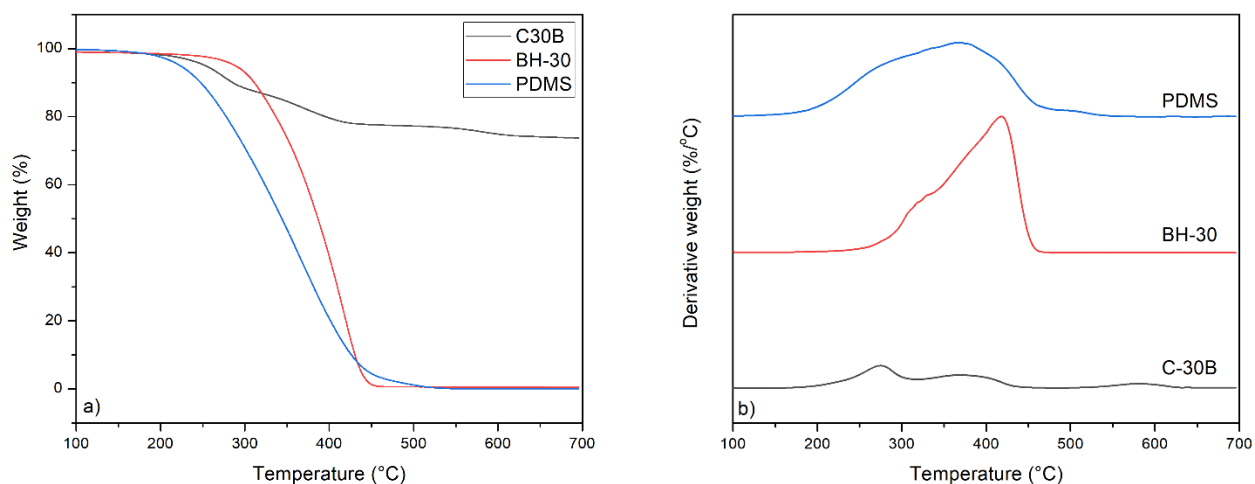
Figure 5s. (a) TGA and (b) DTG thermograms of PDMS, BH-30 and Cloisite 30B determined at a heating rate of 5 °C/min, in nitrogen atmosphere.
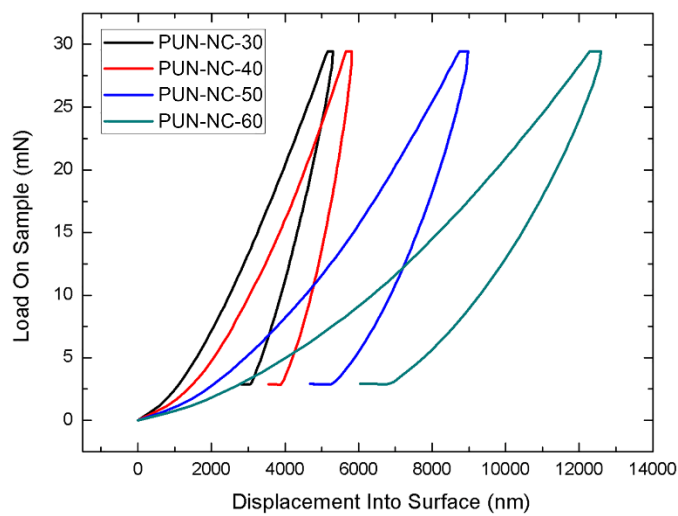

Figure 6s. Typical indentation load-displacement curves for PUN-NC films with different soft segment contents.

Table 1s

Nanoindentation measurements for PUN-NC with 60 wt% of soft segment and different organoclay contents (0.5, 1 and 2 wt%)

Material	Young modulus (MPa)	Hardness (MPa)	Plasticity (ductility index)
PUN-NC-60-0.5	119 ± 39	14 ± 9	8.5
PUN-NC-60-1	103 ± 39	15 ± 10	6.9
PUN-NC-60-2	94 ± 37	12 ± 9	7.8

Table 2s

Mass loss values after in *vitro* biodegradation process of the prepared nanocomposites (PUN-NC) and pure PU networks (PUN).

Material	Mass loss after three months (wt%)	Mass loss after six months (wt%)
PUN-NC-30	7.01	7.53
PUN-NC-40	7.42	7.80
PUN-NC-50	8.65	14.78
PUN-NC-60	3.88	14.48
PUN-30	1.44	1.44
PUN-40	5.91	18.35
PUN-50	Broke apart	Broke apart
PUN-60	6.90	18.66

Surface free energy calculation

Physical parameters of the surface free energy of a solid (γ_S) were found based on the Owens-Wendt method. The method assumes that the surface free energy (γ_S) can be presented as a sum of two components according to equation 1s [48]:

$$\gamma_S = \gamma_S^d + \gamma_S^p \qquad \text{(Eq. 1s)}$$

where:
γ_S^d - surface energy connected with dispersion interactions,
γ_S^p - surface energy connected with polar interactions.

The surface free energy for solids (S) and liquids (L) interacting with those solids should fulfill the Owens-Wendt equation (2s):

$$\gamma_L \cdot \frac{1 + cos\theta}{2} = \sqrt{\gamma_S^d \cdot \gamma_L^d} + \sqrt{\gamma_S^p \cdot \gamma_L^p} \qquad \text{(Eq. 2s)}$$

where θ is the experimentally found contact angle between a liquid drop and a solid surface under investigation; γ_L is the surface tension of the test liquid. Therefore, the wetting angles θ were first measured for the surfaces of PUN-NC films with the use of model liquids (water and diiodomethane) with the known parameters: $\gamma_L = 72.8$; $\gamma_L^d = 21.8$; $\gamma_L^p = 51.0$ mJ/m^2 (for water) and $\gamma_L = 50.8$; $\gamma_L^d = 48.5$; $\gamma_L^p = 2.3$ mJ/m^2 (diiodomethane).

Then, Eq. (2s) was used to calculate the values γ_S^p and γ_S^d for the prepared PUN-NC films. The γ_S values were calculated from Eq. (1s).