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SUPPLEMENTARY MATERIAL TO

Nanocomposites made from thermoplastic linear poly(urethane-siloxane) and organoclay: Composition impact on the properties

MARIJA V. PERGAL[1]*, SANJA OSTOJIĆ[2], MILOŠ STEINHART[3], IVAN S. STEFANOVIĆ[1], LATO PEZO[2] and MILENA ŠPÍRKOVÁ[3]

[1]*University of Belgrade, Institute of Chemistry, Technology and Metallurgy, National Institute of the Republic of Serbia, Njegoševa 12, 11000 Belgrade, Serbia,* [2]*Institute of General and Physical Chemistry, University of Belgrade, Studentski trg 12–16, 11000 Belgrade, Serbia and* [3]*Institute of Macromolecular Chemistry CAS (IMC), Heyrovsky Sq. 2, 16206 Prague 6, Czech Republic*

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Preparation of TPU NCs

The TPU NCs were synthesized under the following polymerization conditions:[10] the molar ratio of NCO/OH groups was 1.05/1.0, the amount of the catalyst was 0.15 mol.% $Sn(Oct)_2$/PDMS macrodiol, and a mixture of 1/1, *V*/*V* DMAc/THF was used. For the clay dispersion in DMAc/THF, intensive mixing with a magnetic stirrer (1000 rpm) for 10 h at room temperature and for 2 h at 50 °C, followed by sonication at 25 ºC for 1 h were applied. During the first step, a predetermined amount of clay dispersion was added dropwise into the PDMS macrodiol solution of DMA_C/THF in a 100 mL flask equipped with a mechanical stirrer, an argon inlet, a dropping funnel and a reflux condenser. This reaction mixture was stirred for 1 h at room temperature under an argon atmosphere. Then MDI was added to the flask and catalyst $Sn(Oct)_2$ solution and the mixture reacted at 40 °C for 30 minutes under continuous stirring to give NCO-terminated prepolymer. During the second step, a solution of BD in DMAc/THF (1/1, *V*/*V*) was charged into the prepolymer and the reaction mixture was stirred and kept at 50 °C for 10 h. Then, sonication (30 minutes, at 25 ºC) was performed to get better dispersion of organoclay in final TPU NCs. Finally, the resultant dispersion was cast into Teflon moulds and then heated in an oven at 40 °C for 24 h. Solvent residue was evaporated by drying in a vacuum oven (66.7 Pa) at 60 °C for 24 h to constant mass. All TPU NC films were allowed to age at room temperature in desiccators for at least 2 weeks prior the characterization.

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

Surface energy calculation

The surface free energy of TPU and TPU-NCs was calculated by:[15]

$$\gamma_{LV}(1+\cos\theta) = 2\sqrt{\gamma_S^{LW}\gamma_{LV}^{LW}} + \sqrt{\gamma_S^{+}\gamma_{LV}^{-}} + \sqrt{\gamma_S^{-}\gamma_{LV}^{+}} \quad \text{(S-1)}$$

where θ is the contact angles of distilled water, formamide and diiodomethane on the surface of TPU NCs; γ_S, γ^{LW}, γ^{AB} represent the surface free energy, dispersion component and polar component, respectively; γ^{+} and γ^{-} represent the Lewis acid parameter and the Lewis base parameter of the surface free energy, respectively; γ_{LV} is the surface tension of the test liquid. Values of surface tension for distilled water, formamide and diiodomethane needed to solve these equations are listed in previously published papers.[1-3] The total surface free energy, as well as its dispersive and polar components, could be determined by solving eq. S-1, because $\gamma_{LV}{}^{LW}$, $\gamma_{LV}{}^{+}$ and $\gamma_{LV}{}^{-}$ are all available.

Water absorption calculation

The weight percent of the water absorption was calculated by:

$$\text{Water absorption} = \frac{w_W - w_{W_0}}{w_{W_0}} 100 \quad \text{(S-2)}$$

where, w_w is the weight of the fully hydrated sample and w_{W0} is the weight of the dried sample.

Degree of phase separation calculation

The degree of phase separation (DPS) in TPU NCs can be calculated by using:[10,16]

$$\text{DPS} = \frac{A_{\text{bonded.tot}}}{A_{\text{tot}}} = \frac{A_{1703} + A_{1715}}{A_{1703} + A_{1715} + A_{1733}} \quad \text{(S-3)}$$

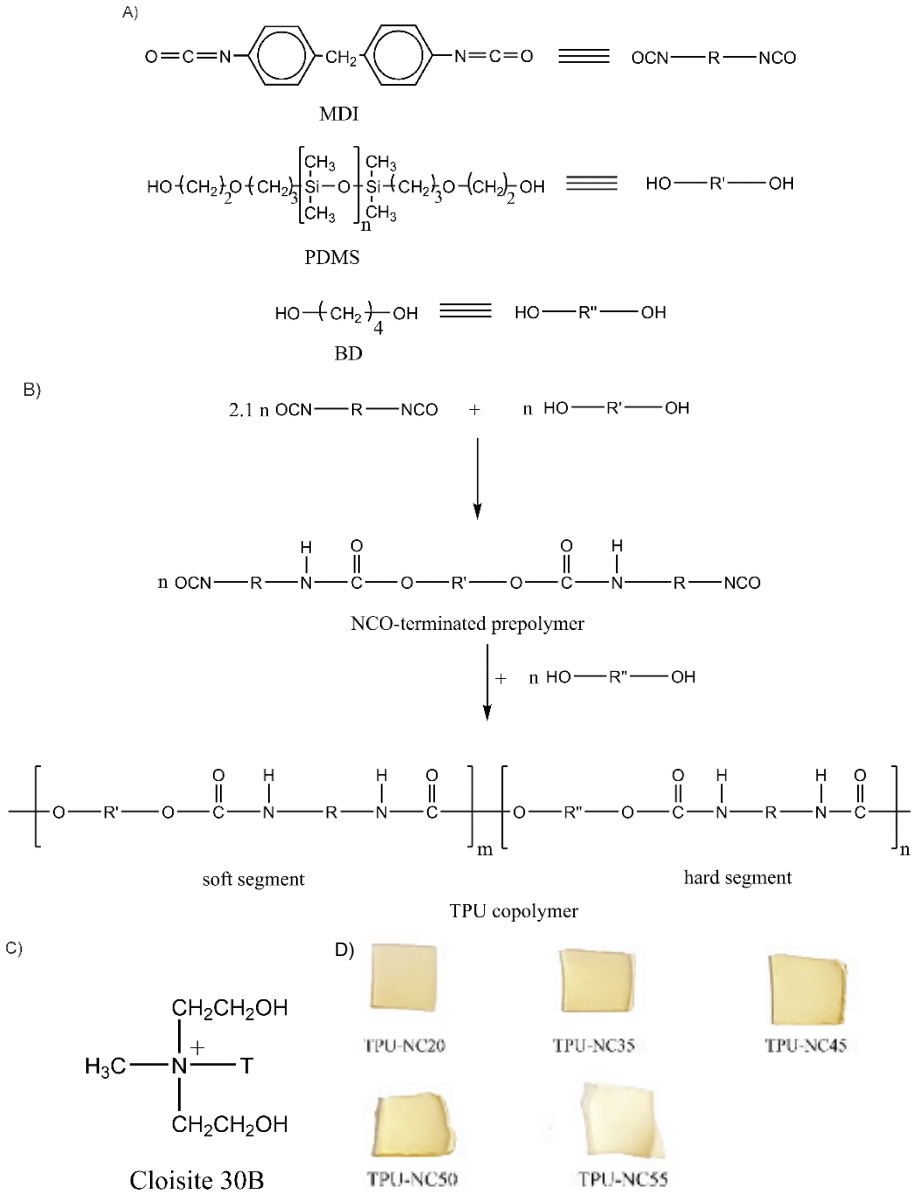

Fig. S-1. A) Chemical structures of starting reactants; B) schematic representation of synthesis of TPU based on PDMS as soft segment and MDI-BD as hard segment; C) Cloisite 30B clay modifier (methyl-tallow-bis-2-hydroxyethyl quaternary ammonium salt) attached on negatively charged clay nanolayers, T is tallow (~65 % C18, ~30 % C16, ~5 % C14) and D) photographs of the prepared TPU NC films.

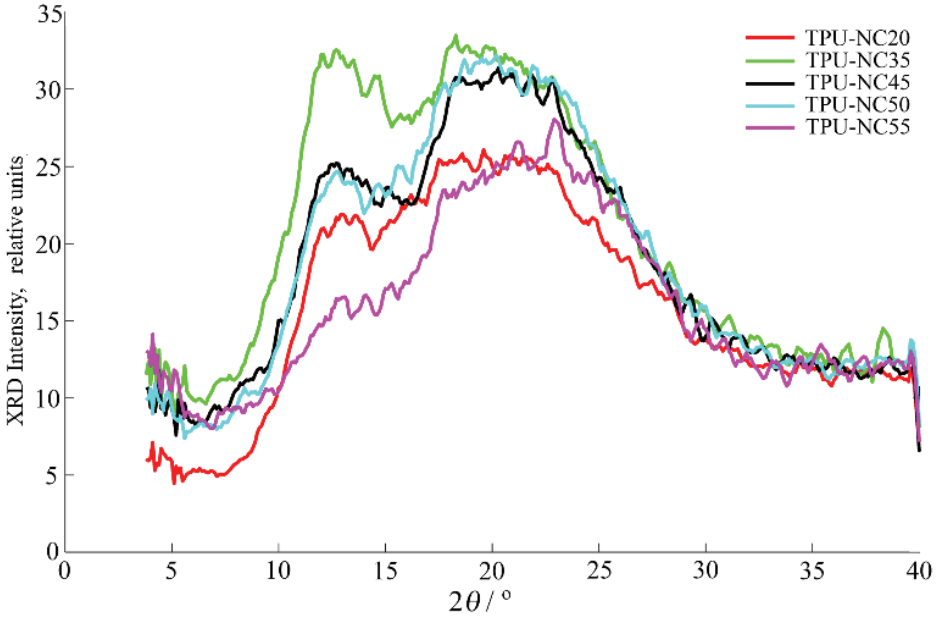

Fig. S-2. WAXS patterns of TPU NCs

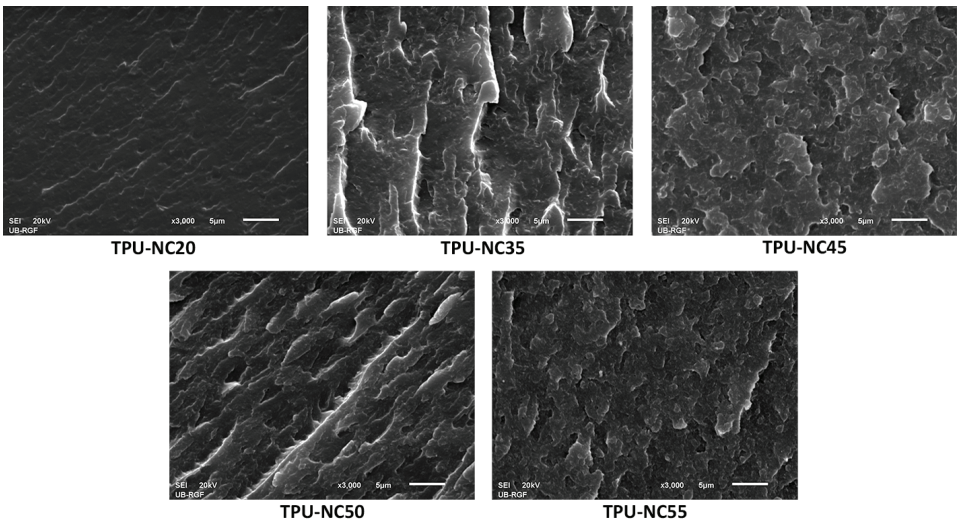

Fig. S-3. SEM images of fractured surfaces of TPU NC films at magnification ×3000.

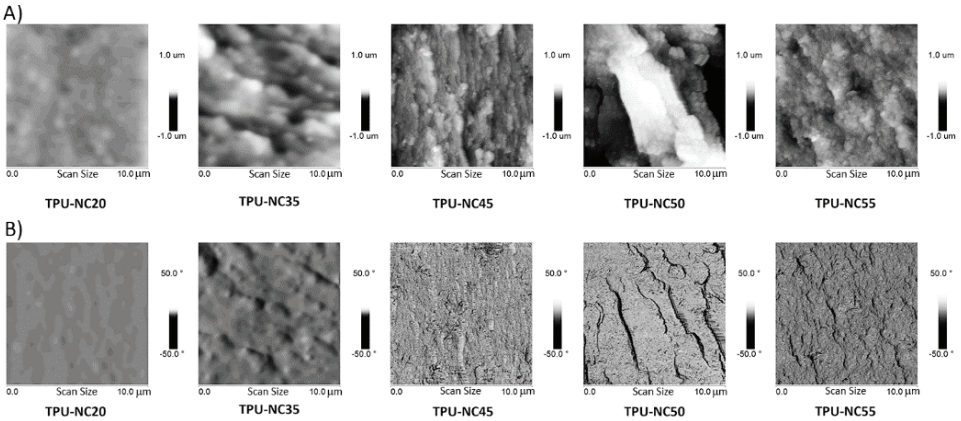

Fig. S-4. (a) 2D height and (b) 2D phase AFM images of TPU NCs at 10 × 10 μm^2.

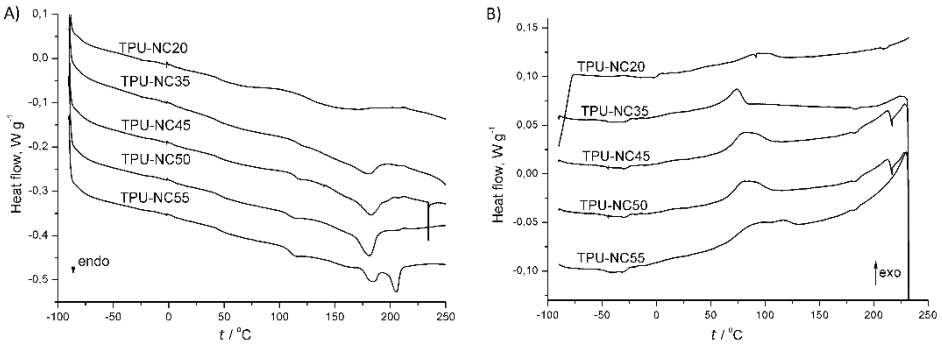

Fig. S-5. DSC curves of TPU NCs obtained during the second heating (a) and cooling (b) run.

Table S-I. Band assignments in the FTIR spectra of TPU NCs

ν / cm^{-1}	Band assignments
3310	stretching vibrations of hydrogen-bonded urethane N-H groups
2960	asymmetric stretching vibrations of CH_2 groups
2900	symmetric stretching vibrations of CH_2 groups
1735	stretching vibrations of free urethane C=O groups
1720	stretching vibrations of disordered urethane C=O groups
1705	stretching vibrations of hydrogen-bonded urethane C=O groups in hard domains
1590	C=C stretching vibrations in the aromatic rings
1530	amide II vibrations
1230	amide III vibrations
1105	stretching vibrations of C-O-C and Si-O-Si bands
1010	stretching vibrations of C-O-C and Si-O-Si bands
800	rocking vibration of C-H in $SiCH_3$
523	bending vibration of Si–O–Al
461	rocking vibration of Si–O–Si

Table S-II. Deconvolution results of TPU NCs, determined from FTIR spectra

Material	Fraction, %					DPS, %
	$(C=O)_{free}$	$(C=O)_{HB\text{-}disordered}$	$(C=O)_{HB\text{-}ordered}$	NH_{HB}	NH_{free}	
TPU-NC20	14.5	15.1	70.4	84.3	15.7	85.5
TPU-NC35	13.2	10.6	76.2	88.9	11.1	86.8
TPU-NC45	8.1	9.4	82.5	92.4	7.6	91.9
TPU-NC50	6.9	9.1	84.0	94.5	5.5	93.1
TPU-NC55	6.1	7.2	86.7	94.9	5.1	93.9

Table S-III. Integral intensities of the three peaks into which the XRD data could be decomposed

Material	Integral intensity, arbitrary units			Amorphous ratio, %
	Peak 1-12.22°	Peak 2-17.6°	Peak 3-21.9°	
TPU-NC20	44.0	107.9	521.0	16
TPU-NC35	54.6	192.5	269.8	37
TPU-NC45	51.8	88.4	395.7	17
TPU-NC50	48.2	113.7	493.4	17
TPU-NC55	10.5	3.46	192.6	2

Table S-IV. Surface roughness determined by AFM and water absorption values of TPU NCs

Material	Surface area, μm^2	R_q^* / nm	R_a^{**} / nm	R_{max}^{***} / nm	Water absorption, wt.%
TPU-NC20	100	14.4	10.8	105	0.52±0.02
TPU-NC35	101	47.1	35.8	340	0.69±0.03
TPU-NC45	106	56.6	42.8	505	0.70±0.02
TPU-NC50	113	255	210	1629	0.97±0.02
TPU-NC55	107	59.9	46.2	558	1.11±0.03

Surface area: the total area of examined sample surface (the three-dimensioned area of a given region expressed as the sum of the area of all the triangles formed by three adjacent data points); R_q^*(rms): the standard deviation of the Z values for height images are nm and degrees for phase images within the given area; R_a^{**} (mean roughness): the mean value of the surface relative to the center place; R_{max}^{***} (max height): the difference in height between the highest and lowest points on the surface relative to the mean plane; mean: the average of all Z values within the enclosed area; Water absorption values are given with their standard deviations.

Table S-V. TGA and DSC results of the prepared TPU NCs

Material	t / °C				Residue yield at 650 °C, %	t / °C		ΔH_m / J g^{-1}	t_{cHS} / °C	ΔH_c / J g^{-1}	X_c / %
	$t_{5\%}$	$t_{10\%}$	$t_{50\%}$	t_{max}		t_{rel}	t_{mHS}				
TPU-NC20	295	305	344	328/406/422	4.9	60	153	4.2	94	3.0	4.6
TPU-NC35	295	306	341	329/460	5.5	109	180	6.2	101	3.4	6.8
TPU-NC45	293	306	339	330/435	8.5	110	183	8.3	107	5.8	9.1
TPU-NC50	289	306	341	332/463	9.0	110	182	8.6	115	6.7	9.4
TPU-NC55	288	304	339	330/506	11.7	112	184/206	8.4	119	7.5	9.2

Table S-VI. Storage modulus and phase transitions of TPU NCs

Material	G' at 25 °C / MPa	$t_{gPDMS}^{\tan\delta}$ / °C	$t_2^{\tan\delta}$ / °C	$t_{HBD}^{\tan\delta}$ / °C
TPU-NC20	67	-102	5	75
TPU-NC35	100	-104	1	82
TPU-NC45	180	-109	-3	97
TPU-NC50	340	-112	-5	112