Curing kinetics, and ionic interactions in layered double hydroxides-nitrile rubber Mg-Al-LDHs-XNBR composites.

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Supplementary material

The carboxylated acrylonitrile-butadiene XNBR rubber mixtures formulas are listed in Table A1. The reference S,MBT rubber mixture was prepared using: a laboratory two-roll mill (friction ratio 1:1.2, dimension of rolls: diameter 200 mm, length 450 mm) at 40°C during 15 minutes.

The compounded S,MBT mixture was vulcanized using electrically heated hydraulic press under a pressure of 5 MPa at its optimum curing time. Cured sheets were conditioned before testing (24 h maturation at room temperature).

Table A1: The carboxylated butadiene-acrylonitrile XNBR compounds formulas (per hundred rubber).

ingredients	MG5	MG30	MG63	MG70	S,MBT
XNBR Krynac X750 (Arlanxeo)	100	100	100	100	100
Pural® MG5 (Sasol)	30	-	-	-	-
Pural® MG30 (Sasol)	-	30	-	-	-
Pural® MG63 (Sasol)	-	-	30	-	-
Pural® MG70 (Sasol)	-	-	-	30	-
Sulfur	-	-	-	-	2
MBT	-	-	-	-	1
Zinc oxide	-	-	-	-	3
Stearic Acid	-	-	-	-	1

The higher agglomeration tendency of Pural MG63HT was confirmed by laser microscope study, Keyence VK-X1000 (Figure A1). Pural 63MG HT exhibited a strong tendency to aggregate due to electrostatic interactions and possibility to form hydrogen bonds. The agglomerated structure, with the size of agglomerated grains in micrometric range was observed.
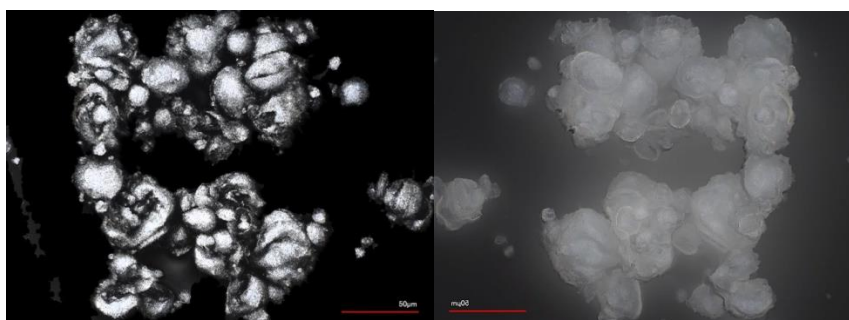

Fig. A1: Laser microscope image of Pural 63MGHT particles.

The viscoelastic properties of uncured rubber mixtures containing fillers with various Mg:Al ratios were measured as a function of angular frequency ω using 100% of oscillation strain (Fig. A2-A3). High oscillation strain led to break-up of the loosely bond filler-filler aggregates formed during storage of rubber compound and caused the decrease of the storage shear modulus comparing with the values measured at low oscillation strain (linear viscoelastic region). The slippage of weak adhered elastomer chains reduced the elasticity and promoted more viscous behavior. The hydrodynamic effect connected with the surface area and the aspect ratio of the particles was dominant. The enhancement of the storage shear modulus $G^{'}$ was in accordance with the values of the surface area, the higher surface area of incorporated filler the higher enhancement of the storage shear modulus $G^{'}$ of XNBR compound.
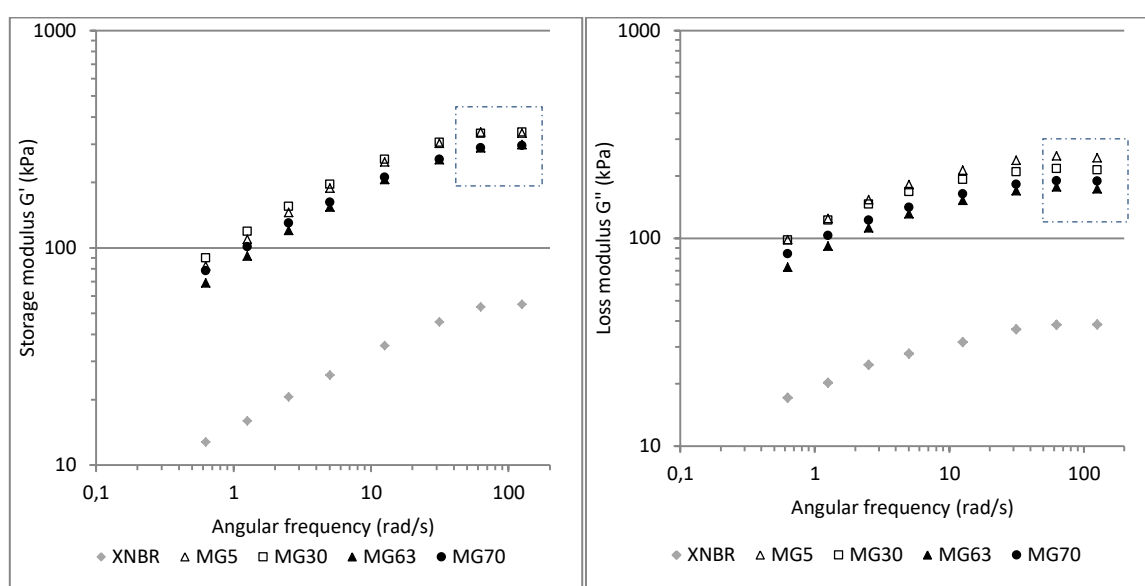

Fig. A2-A3: Storage shear modulus $G^{'}$ (kPa) and loss shear modulus $G^{''}$ of uncured XNBR at 80°C as a function of angular frequency ω (rad/s), (measured at 100% oscillation strain).

Based on Fig. A4-A7 the range of curing temperatures for XNBR composites was estimated.
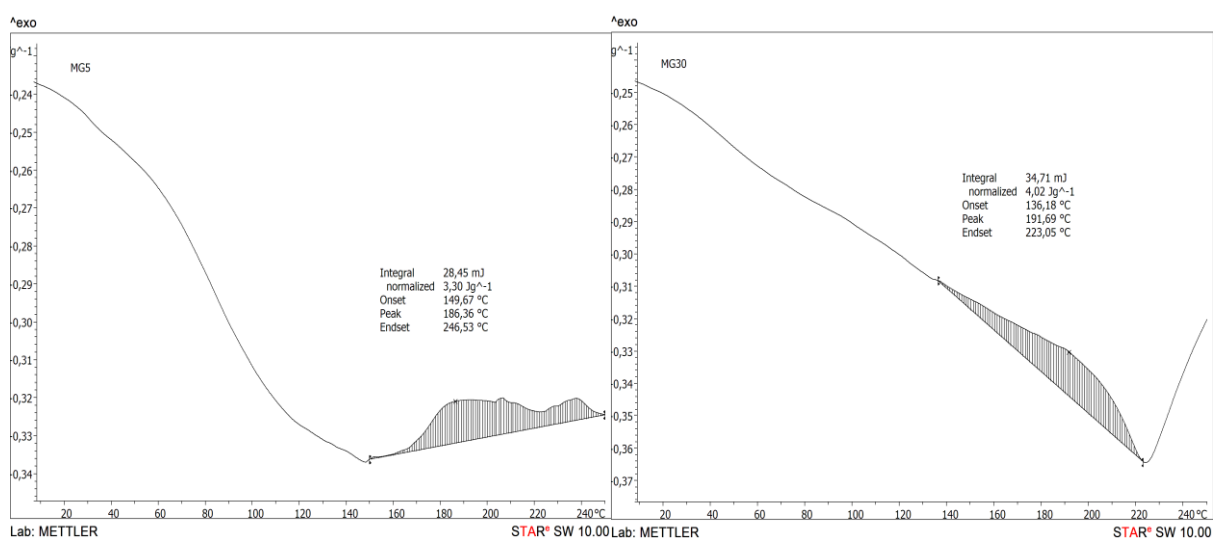

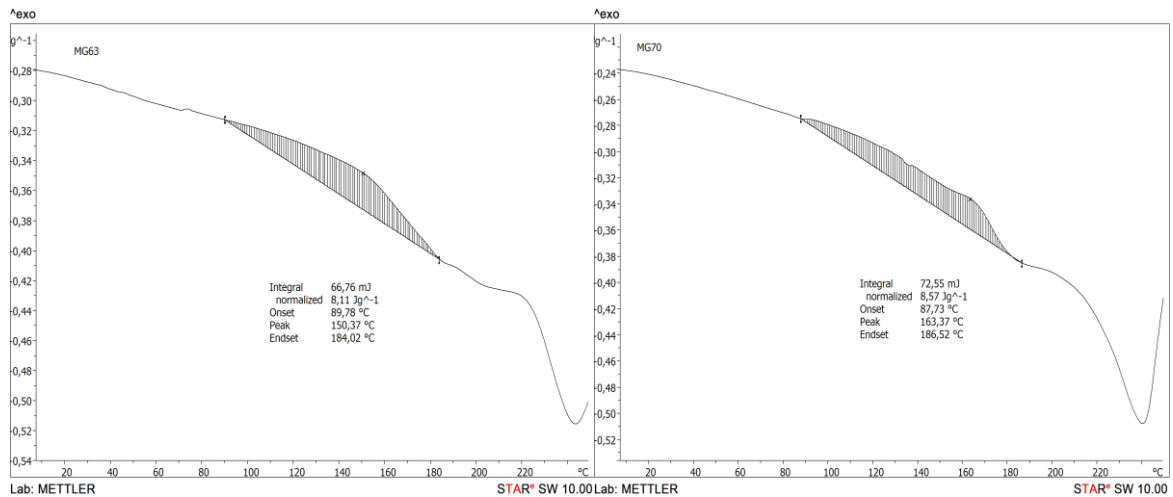Fig. A4-A5: DSC curves of curing for MG5-XNBR and MG30-XNBR.

Fig. A6-A7: DSC curves of curing for MG63-XNBR and MG70-XNBR.

The vulcanization curves, the increase of the normalized elastic component $\Delta S'$ as a function of time for the Mg-Al-LDHs-XNBR cured at the temperature of 160° and 180°C is shown at Fig. A8-A9.
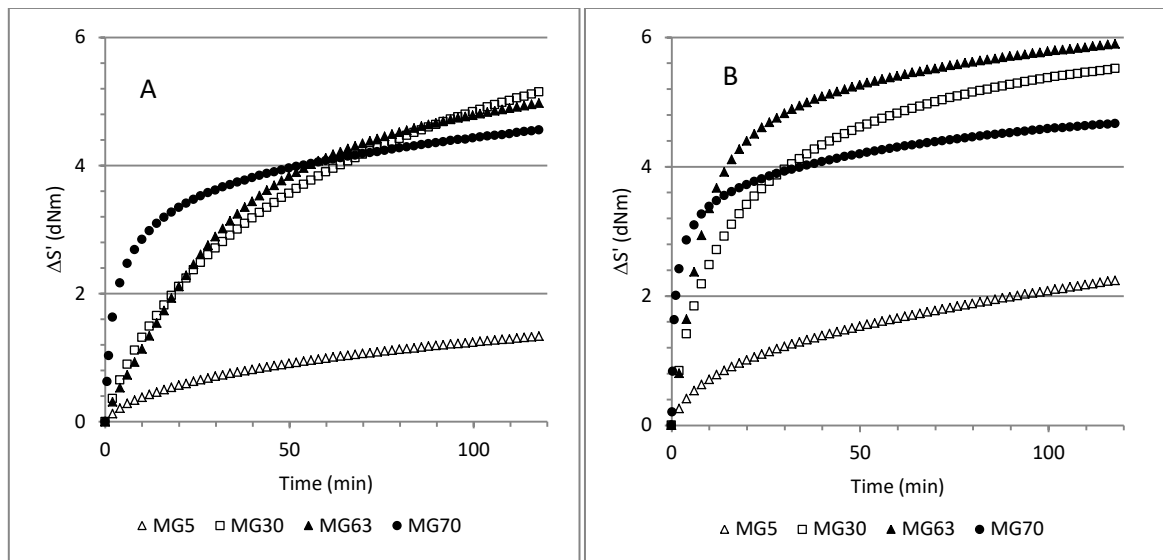

Fig, A8-A9: The increase of the normalized elastic component $\Delta S'$ as a function of time for Mg-Al-LDH-XNBR compounds at 160°C (A) and 180°C (B) calculated as $\Delta S'(t) = S'(t)-S'_{min}$

To confirm better activity during curing at higher temperature for MG5 and MG30 the storage shear modulus G' in function of oscillation strain at 100°C was investigated using RPA rheometer for samples cured at 140°C and 180°C (Fig. A10). As we expected curing at higher temperature 180°C significantly enhanced the values of the storage shear modulus of MG30-XNBR. The effect of temperature was not observed for MG63 and MG70-XNBR rubbers.
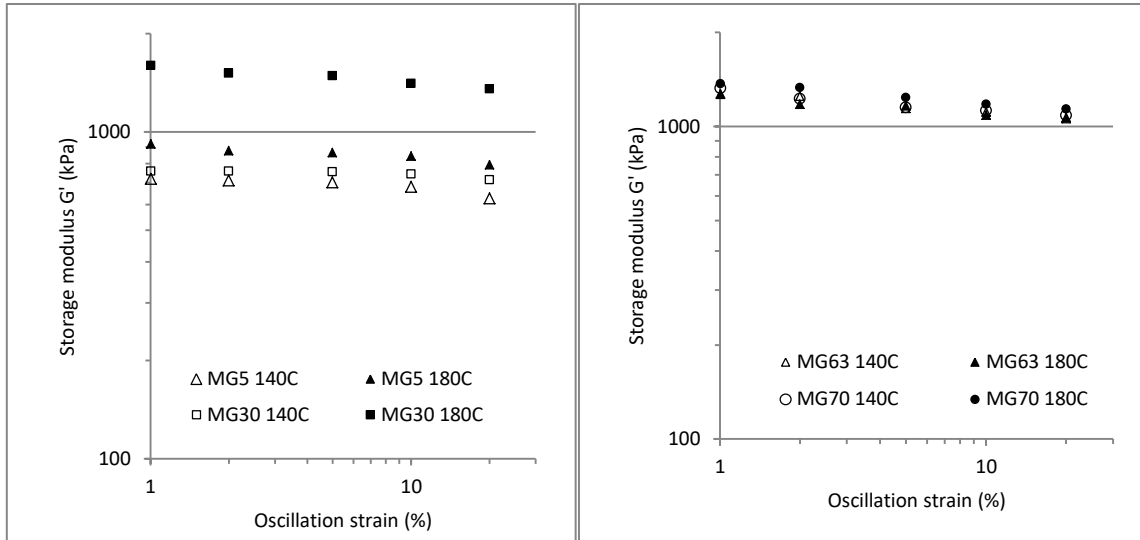
Fig. A10: The storage shear modulus G$^{'}$ at 100°C as a function of oscillation amplitude (frequency 10Hz) measured by RPA rheometer after curing (time of curing 2h, temperature of curing 140°C or 180°C)
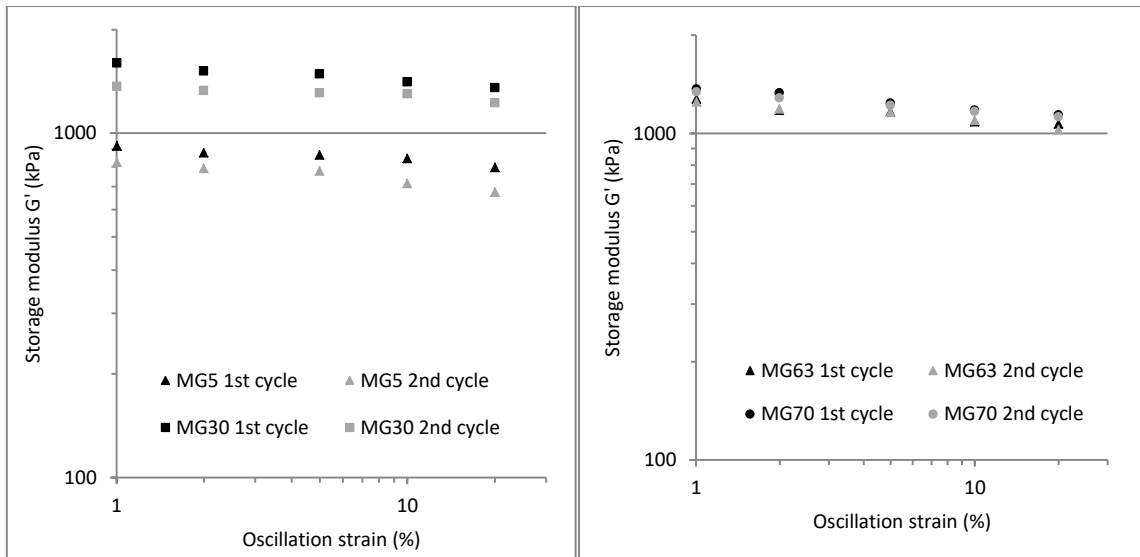

Fig. A11: The changes in value of the storage shear modulus G$^{'}$ for samples cured at 180°C after second cycle of the oscillation amplitude sweep.

Additionally, the second cycle of oscillation strain sweep was applied. The oscillation amplitude higher than 20% is able to destroy the filler-filler structure formed in elastomer matrix. Stronger decrease of the storage shear modulus observed for MG5 and MG30-XNBR after second cycle of oscillation strain sweep (Fig. A11) indicated that the formation of filler-filler interactions was responsible in higher extent for the enhancement of the storage shear modulus G$^{'}$ as compared with rubber containing magnesium rich filler (MG70-XNBR).

The crosslink density for various MG-XNBR rubbers was estimated using the Flory-Rehner's equation [1], this equation (1) is commonly used to determine the crosslink density based on the amount of swelling in toluene.

$$\nu_t = -\frac{\ln(1-V_R)+V_R+\chi V_R^2}{V_S\rho_R(V_R^{\frac{1}{3}}-\frac{V_R}{2})} \quad (1)$$

where V_S is the molar volume of the solvent, χ is the Flory-Huggins polymer-solvent interaction parameter for XNBR rubber, defined as: $\mu = 0.413 + 0.434V_R$ [2] for this type of XNBR using toluene as a solvent, and $\mu = 0.483 + 0.320V_R$ for XNBR-toluene/ammonia treatment, V_R is the volume fraction of rubber in the swollen samples calculated according to the equation (3).

$$V_R = \frac{\frac{D-FH}{\rho_R}}{\frac{D-FH}{\rho_R}+\frac{A_0}{\rho_S}} \quad (3)$$

where H is initial weight of rubber sample, D is constant weight of deswollen specimen, F is weight fraction of insoluble additives such as filler, A_0 is weight of the absorbed solvent (A_0 – immediate weight after removing from solvent minus initial weight of rubber sample H), ρ_R is rubber density, ρ_S is density of solvent.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometr (Waltham, MA, USA) at room temperature with a resolution of 4 cm^{-1} and 64-scan signal from 600-4000 cm^{-1} in absorbance mode. The spectra are shown at Fig. A12 and Fig. A13. The vibrations attributed to the peaks of ATR-FTIR spectra for MG-Al-LDHs cured XNBR are compiled in Table A2.
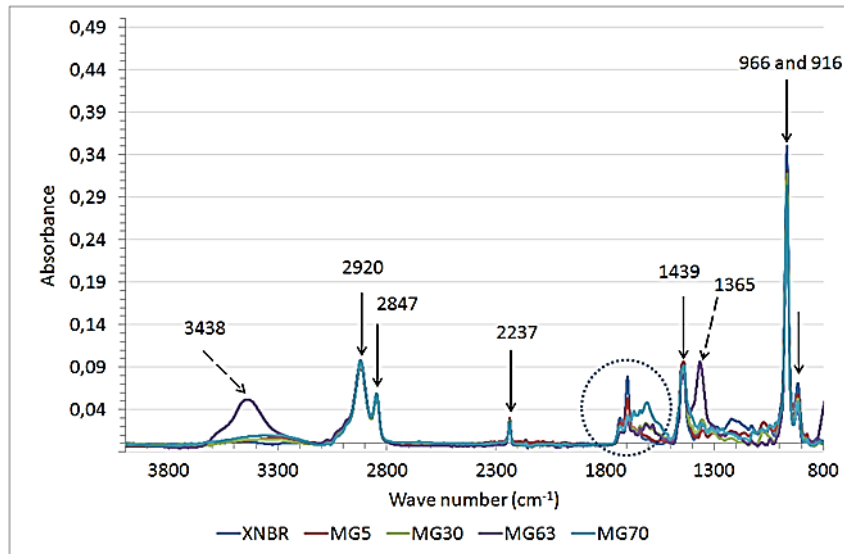

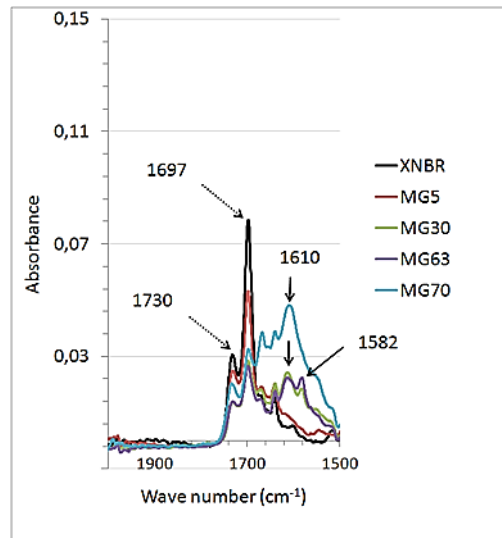Figure A12: ATR spectra of XNBR composites containing various Mg-Al-LDHs.

Figure A13: ATR spectra of XNBR composites containing various Mg-Al-LDHs.

Table A2: Vibrations attributed to peaks of ATR-FTIR spectra for Mg-Al-LDHs-XNBR composites.

Wave number (cm^{-1})	Vibrations
3200 – 3700	symmetric stretching (v_s O-H) in hydroxyl groups
2920	asymmetric stretching (v_{as}C-H) in methyl (-CH$_3$) and methylene (-CH$_2$) groups
2847	symmetric stretching (v_sC-H) in methyl (-CH$_3$) and methylene (-CH$_2$)groups
2237	stretching of nitrile triple bonds in the –CN groups present in acrylonitrile unit of XNBR
1730	carbonyl stretching of monocarboxylic acid
1697	stretching vibration of hydrogen bonded acid dimmers of carboxylic acid groups
1610	stretching vibration of >C=O in carboxylate ions (-CO-O$^-$)
	carbonyl stretching vibration of magnesium hydroxycarboxylate salt
1582	stretching vibration of >C=O in carboxylate ions (-CO-O$^-$)
	asymmetric carbonyl stretching vibration of magnesium carboxylate salt
1439	in-plane -C-H deformations in methylene groups (CH$_2$)
1365	indicating the presence of interlayer carbonate anion in LDHs
966	out of plane -CH=CH-deformation
916	out of plane –CH=CH$_2$ deformations

The oscillation sweep tests at -5°C at an oscillation strain range from 0.1% to 100% and constant angular frequency of 10 rad·s^{-1} were performed to determine the changes in mechanical loss tan δ as a function of applied deformation (Fig. A12).
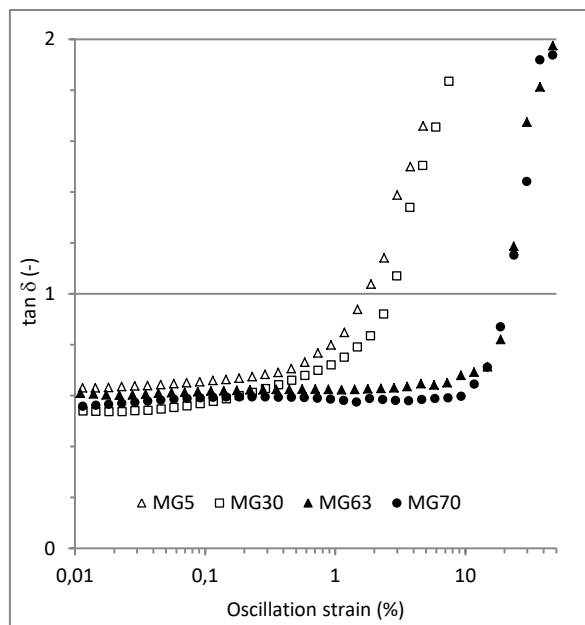
Fig. A12: Loss factor tan δ measured at -5°C as a function of oscillation strain (angular frequency 10 rad·s^{-1}).

References

[1] Flory P.J., Rehner J.: Statistical mechanics of cross-linked polymer networks . II Swelling, The Journal of Chemical Physics, **11**, 521-526 (1943). DOI:10.1063/1.1723792

[2] Gaca M., Pietrasik J., Zaborski M., Okrasa L., Boiteux G., Gain O.: Effect of zinc oxide modified silica particles on the molecular dynamics of carboxylated acrylonitrile-butadiene rubber composites. Polymers, **9**, 645 (2019). DOI:10.3390/polym9120645