Nanoindentation studies on polyurethane-hectorite/laponite elastomer nanocomposites

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Nanoindentation has been used recently to understand the mechanical behavior of polymer nanocomposites especially for coatings. In this study nanoindentation was used to understand the properties of novel polyurethane--hectorite/laponite nanocomposites. The polyurethane hectorite/laponite nanocomposites were prepared with solvent casting method. The mechanical characterization was done with nanoindentation method. The modulus values were calculated with nanoindentation. The structures of the nanocomposites were determined with transmission electron microscopy. It was observed that the maximum hardness and modulus values were achieved with 7 wt % hectorite nanocomposite. It was also demonstrated that the modulus and hardness were higher for the natural clay reinforced polyurethane than the synthetic clay reinforced polyurethane.

***Key words**: nanoindentation, nanocomposite, polyurethane, hectorite*

Badania nanoindentacyjne nanokompozytów elastomerowych poliuretan–hektoryt/laponit

Metoda nanoindentacji stosowana jest do określania właściwości mechanicznych nanokompozytów, zwłaszcza powłok ochronnych (lakierów). W prezentowanej pracy metodę tę wykorzystano w badaniach nanokompozytów poliuretan–hektoryt/laponit. Próbki wykonano wylewając roztwór na płaską, gładką powierzchnię (ang. solvent casting). Wartości modułu Younga obliczono na podstawie zebranych wyników nanoindentacyjnych. Strukturę nanokompozytów analizowano na podstawie zdjęć wykonanych z użyciem elektronowego mikroskopu transmisyjnego.

Stwierdzono, że największą twardością oraz najwyższym modułem charakteryzują się próbki zawierające 7% hektorytu. Pokazano również, że moduł i twardość próbek napełnionych materiałem pochodzenia naturalnego – hektorytem były wyższe niż próbek zawierających syntetyczny laponit.

***Słowa kluczowe:** nanoindentacja, nanokompozyt, poliuretan, hektoryt*

1. Introduction

The nanotechnology is developing with a very significant pace and many different commercial products of nanotechnology are available in the market. The polymer nanocomposites is one of the most significant areas of the nanotechnology that is commercialized and used [1]. The nanocomposites offer numerous advantages like improved toughness with improved tensile strength by adding low level of nano additives (5-7 wt %). Compared to conventional composite materials, the nanocomposites do not require 20-30 wt % of reinforcement phases and they are transparent in color [2].

There has been numerous studies on polymer nanocomposites [3-5]. The characterization of the nanocomposites is an important area to understand the properties and nano reinforcement better. Nanoindentation can be used to understand the fundamental issues of the composite materials at the nanoscale [6-8]. Nanoindentation can clarify many critical aspects of the nanocomposites with the nano particles or layers dispersed in the polymer matrices [9-10].

In this study nanoindentation was used to characterize polyurethane nanocomposites which were prepared with the novel natural clay, hectorite. The hectorite was finely dispersed with in the polyurethane structure. The mechanical properties of this exfoliated structured nanocomposite were investigated with nanoindentation in detail. The results of this study was compared with the previous study of the group [11]. In that study, the properties of these nanocomposites were investigated with conventional mechanical testing such

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as tensile testing and dynamic mechanical testing with dynamic mechanical analysis (DMA) coupled with the morphological and chemical analysis. The results were overlapping and the nanoindentation studies showed the incorporation of the clays improved the mechanical properties of the polyurethane elastomer significantly. The transmission electron microscopy study was conducted to show the fine structure of the nanocomposites. Moreover the properties of polyurethane-hectorite clay nanocomposites were compared with polyurethane-laponite nanocomposites whereby laponite is the synthetic hectorite consists of platelets of 50 nm radius and 0.92 nm thickness.

2. Materials and methods

Materials

Aromatic polyurethane (PU) was obtained by Flokser Group (Turkey) in the form PU- dimethyl formamide (DMF) solution (35 wt %). The procured polyurethane was synthesized prepared from the methyl--diphenyl-diisocyanate (MDI) and polyester polyol with 1,4-butanediol as chain extender.

For the nanoreinforcement of the polyurethane, natural clay, hectorite (HEC) and synthetic hectorite, Laponite were used. The resource of natural clay, HEC was Eskisehir region of Turkey. The mineralogic analysis showed that HEC has 90 % purity with 5 % calcite with cation exchange capacity of 95 meq/100g. The synthetic hectorite, Laponite RD (LAP) was obtained from Southern Clay.

Nanocomposite preparation

The nanocomposites were prepared with solvent casting method. Clay was dispersed in dimethyl formamide (DMF) in the ultrasonic bath for 15 minutes. The procured polyurethane in the form of solution (35 wt % PU) was added to the clay dispersion in DMF. This solution of polyurethane-DMF-clay was stirred for 4.5 hours. Automatic solvent casting machine and adjustable solvent casting knife were used to obtain a final thickness of PU-clay nanocomposites with 100 µm. The sample codes of nanocomposites prepared in this study are given in Table 1.

Table 1. *Sample Codes*
Tabela 1. *Symbole i skład próbek*

Sample Code	Hectorite (wt %)	Laponite (wt %)	Polyurethane
PU	—	—	100
PUL5	—	5	95
PUH7	7	—	93
PUH15	15	—	85

Nanoindentation

The measurements of nanoindentation was done with Universal Nanomechanical Tester UNAT Berkovich indenter from ASMEC. All samples were attached with double-sided adhesive tape directly on metallic cylinders because any local delamination must be omitted for reliable measurements. For this reason all measurements were carried out twice and all different PU-foils (4 types) were taken into account. Each sample was measured at 3 different maximum forces of 10, 30 and 100 mN. 10 measurements in a distance of 50 µm or 100 µm were carried out at each force to reduce the measurement error and to get some statistics.

A triangular Berkovich indenter with a newly calibrated area function was used. The indentation experiments were done in fast open loop mode with a loading segment of 10 s, a creep segment of 5 s and an unloading segment of 5 s. A thermal drift correction was not necessary due to the short measurement time. The poison's ratio of the polymer was estimated to be 0.40.

Transmission electron microscopy (TEM) was operated at 200 kV and images were obtained by Gatan Model 694 Slow Scan CCD Camera system. Measurements on images were performed by Gatan Digital Micrograph software.

3. Explanation of measurement quantities

Contact depth: The contact depth is the depth at which the indenter looses the contact with the sample surface. It is given by the difference between maximum indentation depth and elastic surface deformation above contact area.

Hardness results: If not other stated the indentation or plastic hardness is given in GPa. The calculation is done according to ISO 14577 (modified Oliver & Pharr method) [12].

The projected contact area is obtained from the contact depth under consideration of the tip rounding by means of an area function. The indentation hardness (H) can be directly compared with the Vickers hardness (HV) according to:

$HV = 0.927 \cdot H$ for HV in GPa or

$HV = 94.546 \cdot H$ for HV in kp/mm^2.

HV according to this formula is designated as equivalent Vickers hardness because it is not directly obtained from the diagonal length of the impression.

In principle the tip rounding of the indenter can not be fully corrected for hardness calculations if the contact depths is below about 20-50 nm (in dependence on tip radius). Therefore hardness results are no longer depth independent in this depth range, even for homogeneous materials.

If required the Martens hardness HM is calculated according to:

$HM = F_{max}/(26.43 \cdot h_{max}^2)$

The tip rounding is not considered in this definition.

Modulus results: The indentation modulus is calculated according to ISO 14577 (modified Oliver & Pharr method) with the help of contact area and contact stiffness. It is equal to Young's modulus if no effects like pile-up or sink-in prevent a correct determination of the contact area.

Literature data or estimation values were used for the Poisson's ratios of the sample materials. For the diamond tip the elastic constants: E = 1140 GPa, n = 0.07 were used.

4. Results and Discussion

4.1. Nanoindentation Measurements

The nanoindentation studies were carried out to measure the hardness and the modulus values of the neat polymer and the nanocomposites of polyurethane with two different types of clays at various loadings. The important part of the research was the use of different forces to understand the mechanical properties of the neat polymer and the nanocomposites as well.

In Figure 1-3, the nanoindentation test results for PU are shown. The tests were done for the neat polymer. Different graphs are plotted for different loadings. The application of different forces allows the determination of depth dependent hardness and modulus values. The deviations in the measurements (dH and dE) were obtained from the statistical error given by the scatter of the single measurements.

The graphs for the PUH7 nanocomposites are shown to be representative for the nanocomposite in

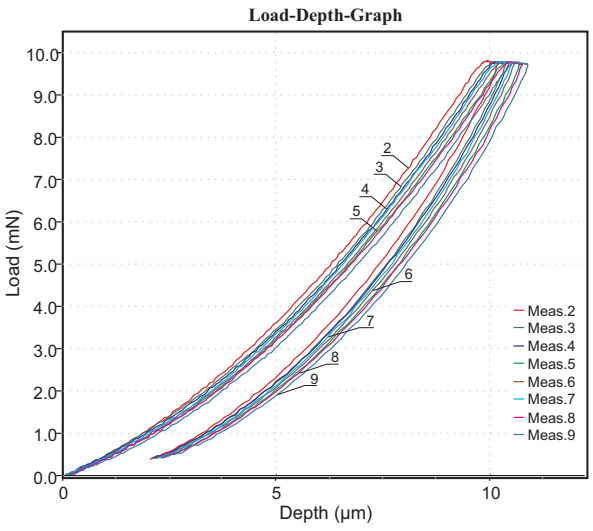

Figure 1. *Comparison of the single measurements on PU-foil for an applied maximum force of 10 mN.*
Rysunek 1. *Porównanie wyników pojedynczych pomiarów uzyskanych dla folii PU przy maksymalnej sile nacisku 10 mN*

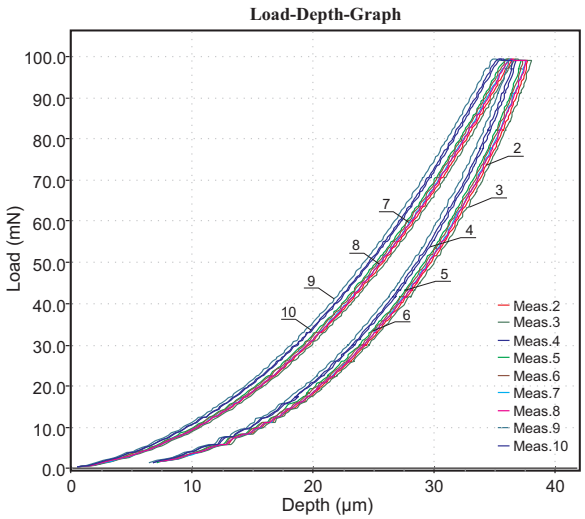

Figure 2. *Comparison of the single measurements on PU-foil for an applied maximum force of 100 mN.*
Rysunek 2. *Porównanie wyników pojedynczych pomiarów uzyskanych dla folii PU przy maksymalnej sile nacisku 100 mN*

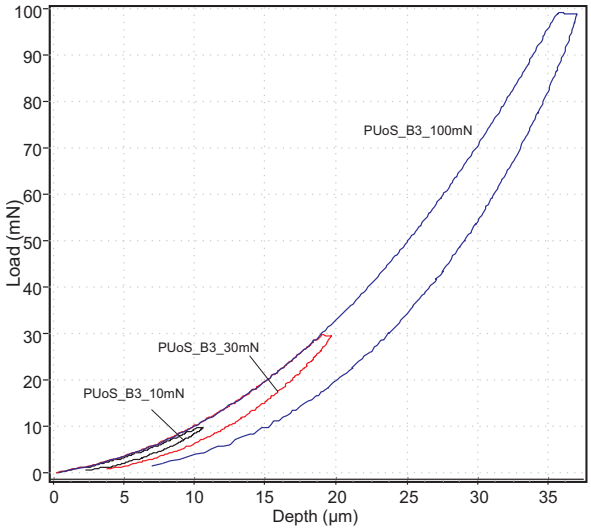

Figure 3. *Comparison of averaged load-displacement curves on PU-foil for applied forces of 10 to 100 mN.*
Rysunek 3. *Porównanie uśrednionych zależności nacisk-zagłębienie uzyskanych dla folii PU przy sile nacisku od 10 mN do 100 mN*

Figure 4-6. The measurements show that the curves are quite similar with decreased depth with the nanocomposites showing the effect of the nanocomposite. The application of different forces allows the determination of depth dependent hardness and modulus values. The deviations in the measurements (dH and dE) were obtained from the statistical error given by the scatter of the single measurements.

For comparison all depth-dependent graphs are shown in a single chart for hardness and elastic modulus. The results are tabulated in Table 2.

The scatter of the single measurements is relatively low which indicates a good homogeneity of the

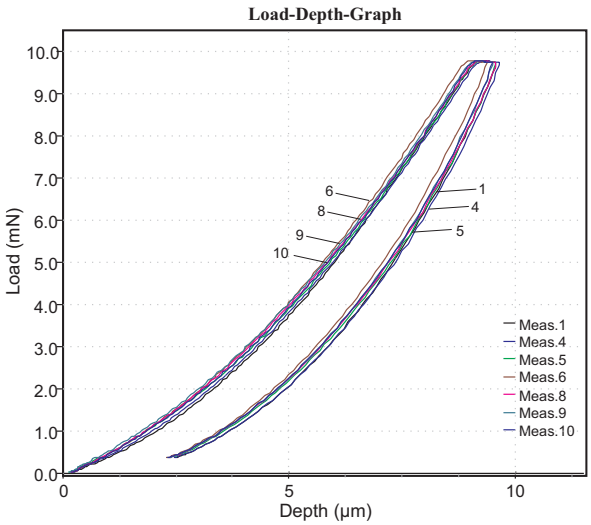

Figure 4. *Comparison of the single measurements on PUH7-foil for an applied maximum force of 10 mN*
Rysunek 4. *Porównanie wyników pojedynczych pomiarów uzyskanych dla folii PUH7 przy maksymalnej sile nacisku 10 mN*

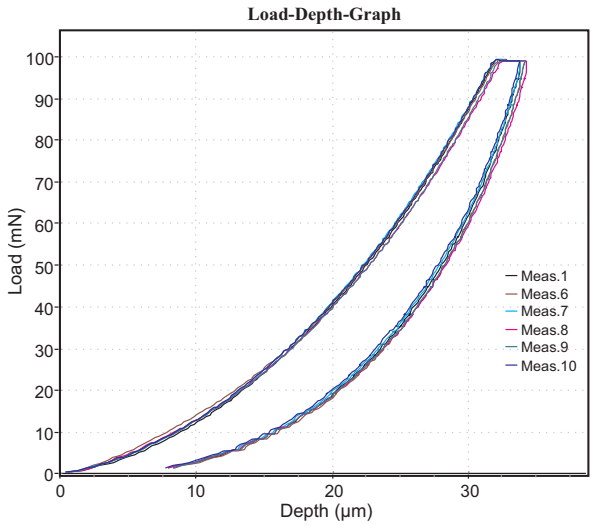

Figure 5. *Comparison of the single measurements on PUH7-foil for an applied maximum force of 100 mN*
Rysunek 5. *Porównanie wyników pojedynczych pomiarów uzyskanych dla folii PUH7 przy maksymalnej sile nacisku 100 mN*

PU-foils. The loading curves agree very well – also an indication of a low measurement error and a good homogeneity of the foils.

It was observed that the modulus values increase with the nanoclays. The interesting observation was the maximum value obtained with the 7 wt % hectorite loading (The other wt % data is not shown to draw a more clear picture to understand the fundamentals of the nanocomposites with nanoindentation). The clay layers are agglomerated after certain level. The clay layers at 15 wt % still increase the modulus and hardness of the neat polyurethane but they are not that effective as 7 wt %. The findings show that the modulus values and hardness values can be measured with the nanoindentation confirming other measurements [11]. In previous studies, it was also demonstrated that the there is maximum point to achieve in nanocomposites [13, 14]. This also shows the effectiveness of the nanocomposites as the 7 wt % is well dispersed. This dispersion is well shown and discussed in Transmission Electron Microscopy part. The individual clay layers are very critical for the polymeric materials and elastomers. They enhance the properties of the elastomers significantly enabling them to have additional properties. Moreover the percent elongation (data not shown here) of these polyurethane materials increase with the clay

Table 2. *Summary of Results*
Tabela 2. *Zestawienie wyników badań*

Sample	F	hc	H	dH	E	dE
	mN	m	Gpa	GPa	GPa	GPa
PU	9.7	7.103	0.008156	0.000739	0.04213	0.00410
PU	29.5	13.830	0.006503	0.000543	0.03931	0.00383
PU	99.0	27.691	0.005413	0.000386	0.04057	0.00366
PUH7	9.7	6.706	0.009101	0.000576	0.05488	0.00425
PUH7	29.5	13.227	0.007069	0.000705	0.05003	0.00606
PUH7	99.0	27.835	0.005304	0.000497	0.05506	0.00758
PUL5	9.7	7.264	0.007792	0.001330	0.04063	0.00691
PUL5	29.4	14.572	0.005842	0.000458	0.03694	0.00357
PUL5	98.9	29.211	0.004846	0.000239	0.04009	0.00293
PUH15	9.7	6.716	0.009093	0.001770	0.05123	0.00985
PUH15	29.4	14.969	0.005495	0.000668	0.04204	0.00646
PUH15	99.0	30.085	0.004519	0.000173	0.05561	0.00471

F – Load, h_c – Contact depth, E – Young's modulus, H – Hardness;
F – siła nacisku, h_c – zagłębienie indentora, E – moduł Younga, H – twardość

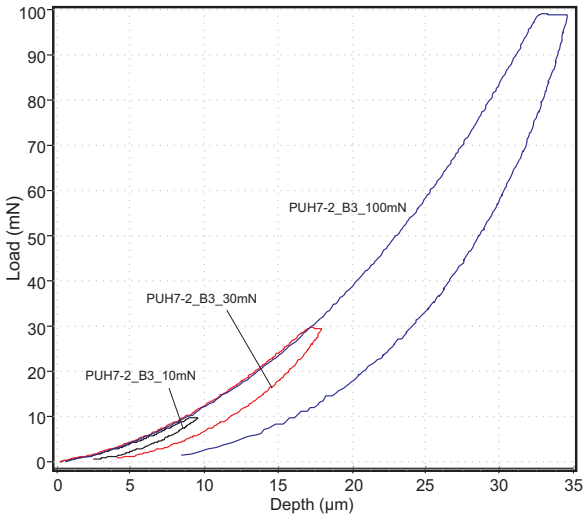

Figure 6. *Comparison of averaged load-displacement curves on PUH7-foil for applied forces of 10 to 100 mN*
Rysunek 6. *Porównanie uśrednionych zależności nacisk-zagłębienie uzyskanych dla folii PUH7 przy sile nacisku od 10 mN do 100 mN*

addition like many other polymer nanocomposites [15]. So the nanocomposites increase the modulus and elongation at the same time showing their superiority compared to the micron scale composites. The clays being abundant in nature are very important building block materials for ceramic materials but also they are gaining much more importance for the polymeric materials as well making them as composite material. The hectorite being a special type of clay as already shown in previous studies, is very critical for the polyurethane.

The good interaction of the polyurethane and the hectorite was provided with the new preparation technique discovered during this study showing the importance of the swelling of clays in the organic solvent dimethyl formamide (DMF), being partially intercalated even before interacting with the polyurethane. Another critical parameter for the good nanocomposite preparation was the processing clays with the polyurethane-DMF solution. It was determined that the optimum stirring was 4.5 hours of mixing for the solution casting method of polyurethane-hectorite nanocomposite preparation. The dispersion of clay layers in the polyurethane takes certain time. The third reason for successful nanocomposite was the hydrophilicity of the polyurethane unlike the polyolefins. As the clays are hydrophilic by their nature, the compatibility of the clay and the polyurethane is quite well resulting in good properties of nanocomposites as measured by the nanoindentation.

It was observed it was not possible to disperse the nano layers of hectorite at 15 wt % as good as 7 wt %. It was agglomerated and the resultant properties of the nanocomposite was inferior compared to 7 wt % as demonstrated by nanoindentation studies. The nanoindentation is a very important tool showing the difference between these two different nanocomposites with different layers of clays. The nanoindentation is indenting the material with certain loading at specific intervals. So the changes in the structure and morphology of the nanocomposites were easily distinguished by the nanoindentation studies. The nanoindentation can be easily used to understand the nano layer reinforcement of the nano particles in the polymer matrices.

Other important finding was the comparison of the hectorite and laponite. Hectorite and laponite have similar chemical structures with Li content and higher Mg content compared to the montmorillonite clays. These chemical differences in hectorite and laponite make them much better clay materials than the other natural and synthetic clay types. So in this study, it was also possible to understand the differences of the natural and synthetic form of hectorite.

Firstly, it was not easy to prepare polyurethane-laponite nanocomposite elastomers above 5 wt % due to the agglomeration of the laponite nano particles. The processing conditions were changed but it did not make any difference in the preparation. So the samples with the laponite were prepared with the same method as the polyurethane-hectorite nanocomposites were prepared. The maximum loading achieved was 5 wt % of the laponite.

When the results of hectorite and laponite (with their best composition) were compared, it was observed that the hectorite improves the properties of the polyurethane much better. Although the laponite is more pure than natural clay laponite, the interaction of the laponite and polyurethane was inferior compared to the hectorite nanocomposites. The better interaction of hectorite was understood from the nanoindentation measurements. The reason for better interaction was the good dispersion of the hectorite compared to laponite dispersion. It was not possible to prepare more than 5 wt % the laponite nanocomposites. The dispersion of the nano layers of the laponite was not very well done. The surface chemistry was not compatible with polyurethane as hectorite. Surface treatments are required for the polyurethane laponite nanocomposites.

The nanoindentation tool was very useful to understand the differences between different dispersions of different materials. The nanoindentation could detect the changes in the modulus values and change in microstructure very easily [16]. The nanoindentation was also helpful to understand the differences in the chemical differences of the natural and synthetic in the same polymeric materials. The laponite increased the modulus and hardness compared to the neat polyurethane elastomer but it was still inferior to the polyurethane-hectorite nanocomposite. TEM pictures of different nanocomposites are also shown and they are discussed in the next section.

4.2. Transmission Electron Microscopy (TEM)

With transmission electron microscopy, the nano layersof clay was confirmed and the fine dispersion of

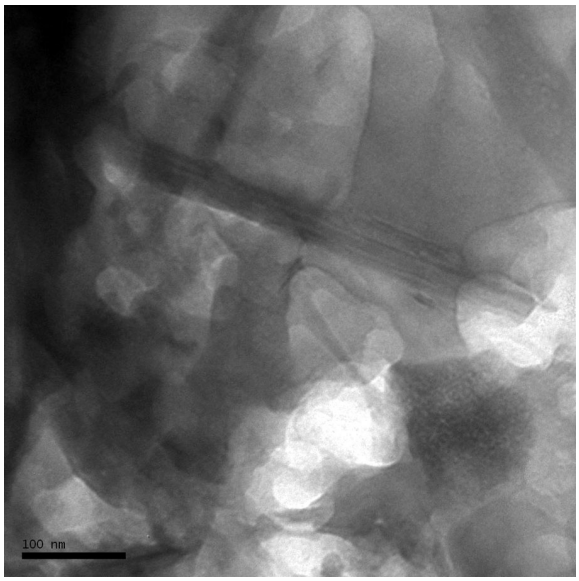

Figure 7. *TEM picture of PUH7*
Rysunek 7. *Obraz TEM próbki PUH7*

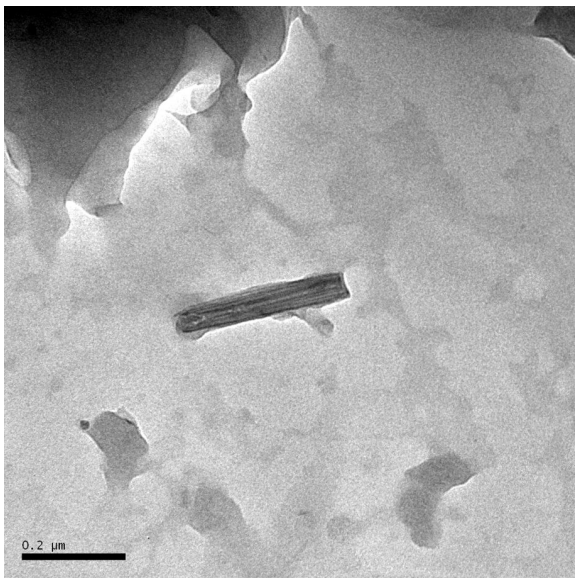

Figure 8. *TEM picture of PUH15*
Rysunek 8. *Obraz TEM próbki PUH15*

the PUH7 was confirmed. The results of the nanoindentation were also confirmed with the transmission electron microscope. The effect of the fine dispersion of the clay platelets and the reinforcement effect was confirmed with the nanoindentation measurements. When the structures of 7 wt % (Figure 7) and 15 wt % (Figure 8) nanocomposites were compared the agglomeration of the clay layers can be easily seen in TEM pictures. Furthermore differences between the polyurethane–hectorite and polyurethane–laponite nanocomposites were shown by demonstrating inferior laponite dispersion in the polyurethane material shown in Figure 9.

These differences in the nanocomposite structures are reflected in the measurements of the nanoindentation. The accurate profile mechanical measurements

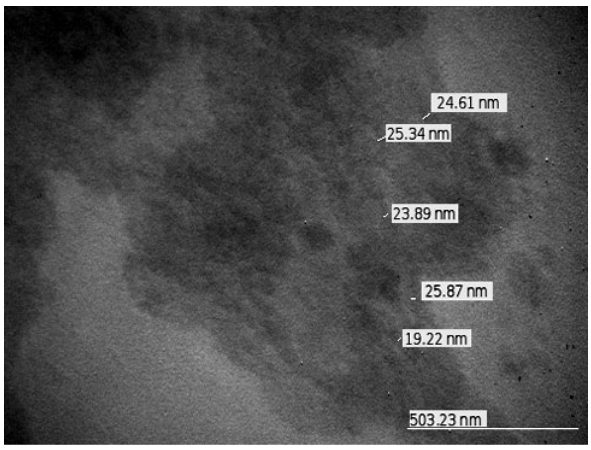

Figure 9. *TEM picture of PUL5*
Rysunek 9. *Obraz TEM próbki PUL5*

were done with nanoindentation. The measurements did not take so much time. Contrary to nanoindentation, transmission electron microscopy measurements take long time and it is quite tedious work. Nanoindentation helps to characterize the materials quite easily and characterize the properties. It is very helpful for the nanocomposites.

5. Conclusion

In this study, nanoindentation was used to characterize the properties of the polyurethane nanocomposites prepared with different clays with different percentages. By nanoindentation it was understood that the natural clay was better than the synthetic clay in terms of better reinforcement. It was shown that there was a certain threshold for the maximum loading of the natural clay which was at 7 wt %. By TEM and nanoindentation studies it was shown that, the optimum clay loading was around 7 wt %. This study will help to understand the importance of nanoindentation measurements in the nanocomposites approving other mechanical measurements like tensile and dynamic mechanical analysis. Nanoindentation gives information on a very small area. By this method, very small samples and particles can be easily characterized for nanocomposites.

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