Improvement of mechanical properties and self-healing efficiency by \textit{ex-situ} incorporation of TiO$_2$ nanoparticles to a waterborne poly(urethane-urea)

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Abstract

This research work was focused on the incorporation of TiO$_2$ nanoparticles into synthesized solvent-free waterborne poly(urethane-urea) based on hydrophilic poly(ethylene oxide) (PU0) in order to improve both mechanical properties and self-healing effectiveness of polymer matrix. The incorporation of TiO$_2$ nanoparticles resulted in a successful enhancement of mechanical properties of nanocomposite films if compare to PU0. Simultaneously, obtained nanocomposite films did not only maintain the self-healing ability of PU0 film, measured by means of mechanical properties after successive cutting/recovery cycles, but also showed higher self-healing efficiency than the PU0 film. Moreover, well-dispersed TiO$_2$ nanoparticles, visualized by atomic force microscopy (AFM), kept their electrical conductive properties when embedded in the PU0 matrix, as was confirmed by electrostatic force microscopy (EFM). This research work described a simple and industrially appealing way to control the dispersion of commercially available TiO$_2$ nanoparticles in waterborne poly(urethane-urea) for the designing of inorganic/organic hybrid nanocomposites with enhanced mechanical properties and self-healing efficiency in which TiO$_2$ nanoparticles preserved their conductive properties within the polymer matrix.
Keywords: waterborne polyurethanes; titanium dioxide nanoparticles; nanocomposites; self-healing; conductive properties; mechanical properties
1. Introduction

Nanocomposites (NC), consisting on a nanometric size inorganic phase distributed in a polymer matrix[1], have attracted great attention by virtue of their multiple fields of application. They can be used in a broad range of applications such as biomedicine, solar cells, sensors, batteries, photocatalysis, display panels, gas separation, water purification and transistors[1–3].

In the case of waterborne polyurethanes (WPU), the addition of inorganic nanoparticles can enhance the properties of these polymers[4–6]. This is the consequence of the combination of the properties of the inorganic nanoparticles with the properties of the polymers[4,7] leading to better thermal[4,7] and mechanical properties[4,8,9]. Different types of inorganic nanosized fillers have been incorporated to WPU, such as Au[10], Ag[6,11], graphene[11,12], different kind of silica clays[7,13,14], CaCO₃[15], ZnO[5], Fe₃O₄[16] and TiO₂[8,9,17]. Titanium dioxide (TiO₂) is one of the most interesting inorganic nanoparticle given its environmentally friendly nature, being chemically inert and showing high photostability and, also, photocatalytic activity[9,17]. In behalf of its photocatalysis, which can be used for photodegradation of organic compounds[17], TiO₂ displays self-cleaning[17,18] and also antibacterial activity[17], which are appealing for a potential industrial application in paints and coatings. Furthermore, TiO₂ improves the UV-resistance[19] and mechanical properties[20] of the polymer matrix. Additionally, due to the n-type semiconducting nature of TiO₂[4,21], it can even confer conductivity[3] to the nanocomposite.

In order to obtain satisfactory nanocomposites, a proper dispersion of the nanoparticles in the polymer matrix must be achieved. Nonetheless, nanoparticles tend to aggregate forming clusters[15,17]. This happens due to their large surface-area/particle-size ratio[15,17], high surface tension[15] and/or incompatibility with the organic polymer matrix[15]. This puts in evidence the importance of the approach taken for the dispersion of the nanoparticles. Sol-gel process[4,7] and physical mixing by ultrasonication[17] are widely used methods to obtain a
good dispersion. Nevertheless, from an industrial point of view a mechanical stirring would be more suitable. This approach has been employed even for TiO$_2$ nanoparticles dispersion\cite{8,17}, though in an inferior extent. Nonetheless, usually, a better dispersion can be achieved by \textit{in-situ} incorporation during the polymer synthesis\cite{8,17}.

WPU, alike other polymers and materials, may suffer physical damage leading to scratches, microcracks and larger cracks\cite{22}. This damage affects their lifetime, however it could be extended if the WPU had the ability to repair itself. Self-healing is the ability of the materials to partially or completely repair itself, recovering from the properties deterioration caused by the suffered damage\cite{23}. There are mainly two approaches to self-healing: extrinsic and intrinsic. The first one consists on intentionally adding a healing agent, generally microencapsulated\cite{24–27}. The second, intrinsic self-healing, is achieved thanks to the physical interaction between the damaged interfaces\cite{26} and to the autonomous reversibility of covalent and non-covalent bonding in the polymer matrix\cite{23–26}. These reversible interactions can be due to Diels-Alder reaction\cite{28}, disulfide bonds\cite{22}, alkoxyamines moieties\cite{25}, van der Waals\cite{29}, π-π stacking\cite{30}, ionic\cite{26} and hydrogen bonding interactions\cite{26,29,30}, among others.

Since the inception of self-healing concepts and theory\cite{31,32}, considerable research attention has been put into this topic given the benefits of extending the service life of materials. In the case of polyurethanes there is some research on their self-healing from different approaches\cite{25,33,34}, however still there is little research on the self-healing of WPU\cite{22,26,35}. Taking into consideration the hydrogen bonding between urethane groups\cite{24,26}, polyurethanes are of great interest for the development of novel self-healable polymers. Furthermore, poly(urethane-urea)s (WPUU) are even more appealing due to the presence of urea groups, which provide a reinforcement concerning hydrogen bonding sites\cite{26}, as there is one more N-H group than in urethane.
In our previous work, the synthesis of a waterborne poly(urethane-urea) (WPUU) dispersion based on poly(ethylene oxide) (PEO) as macrodiol was reported[36]. The aim of the present work was the fabrication of nanocomposites using commercial aqueous solution of TiO$_2$ nanoparticles by their *ex-situ* dispersion in WPUU containing hydrophilic PEO segment, which could interact with the TiO$_2$ nanoparticles[3] modulating the matrix self-healing properties. This WPUU possessed sulfonate groups, which can play the role of ionic internal emulsifier. Additionally, these ionic groups may contribute to the self-healing process as a reversible interaction[26] together with the previously mentioned hydrogen bonding. Considering all the above, this work also focused on studying the self-healing ability of the prepared WPUU and NC films.

In the present work, the chemical structure of WPUU and NC films was studied by Fourier transform infrared spectroscopy (FTIR). The thermal behavior was analyzed using differential scanning calorimetry (DSC) while thermal stability was determined by thermogravimetric analysis (TGA). Morphology of the nanocomposite films was studied by atomic force microscopy (AFM) and optical microscopy (OM). Self-healing ability was investigated by means of mechanical properties using an Instron tensile testing machine. Furthermore, electrical properties of TiO$_2$ nanoparticles embedded in the polymer matrix were studied by means of electrostatic force microscopy (EFM).

2. Experimental

2.1. Materials

The employed diisocyanate was diphenylmethane diisocyanate (MDI), provided gently by Covestro, whereas as chain extender and internal emulsifier 2,4-diamino-benzenesulfonic acid (DBSA) supplied by Sigma Aldrich neutralized with NaOH was used[37]. The soft segment of the synthesized waterborne poly(urethane-urea) dispersion was formed by poly(ethylene oxide)
(PEO) with a molecular weight of \(\approx 1000 \text{ g mol}^{-1}\), as indicated by Sigma Aldrich. TiO\textsubscript{2} nanoparticles, mixture of rutile and anatase (particle size <150 nm), were supplied by Sigma-Aldrich. Table S1 in Supplementary Information displays more details of the reagents.

### 2.2. Synthesis of the waterborne poly(urethane-urea)

Waterborne poly(urethane-urea) dispersion was synthesized as previously reported by us[36]. Briefly, MDI and PEO were left reacting for 2 h at 80 \(^\circ\)C before cooling down to room temperature and adding the chain extender in water and, afterwards, more water for a proper dispersion.

### 2.3. Preparation of nanocomposites films

Once the WPUU dispersion was synthesized, solid content was calculated in order to prepare nanocomposites by \textit{ex-situ} physical mixing of commercial aqueous solution of TiO\textsubscript{2} nanoparticles in WPUU dispersion (Figure 1). Density and solid content of commercial aqueous solution of TiO\textsubscript{2} nanoparticles were taking into account for the preparation of the nanocomposites. Three different TiO\textsubscript{2} weight content nanocomposites (10, 20 and 40 wt%) were prepared, regarding solid content of WPUU dispersion and aqueous solution of TiO\textsubscript{2}. WPUU film without TiO\textsubscript{2} was also prepared as reference. The samples were denoted as PU0, for the matrix without inorganic nanoparticles, and XTiO\textsubscript{2}-PU0 for the nanocomposites, where the X stood for the TiO\textsubscript{2} wt% content.

For the physical mixing of PU0 and TiO\textsubscript{2} nanoparticles in the commercial aqueous solution a magnetic stirrer was used to keep the mixtures mechanically stirring for 24 h at 500 rpm (Figure 1). White homogeneous dispersions were obtained.
For the preparation of the nanocomposite films, 8 mL of each mixture were poured into glass surfaces covered with Teflon (Figure 1). In order to remove any air bubble that could disrupt the surface of the films, they were kept for 5 days under vacuum. After this, they were left drying at room conditions one day, and then kept under vacuum at 60 ºC to prevent water absorption by investigated PU0 and NC films. Along whole preparation process, both mixtures and NC films were protected from light exposure.

2.4. Characterization techniques

2.4.1 Solid content

Solid content was calculated by drying a volume of PU0 in an oven at 105 ºC for 3 h. It was calculated in the same way as reported before by us [36].

2.4.2. Fourier transform infrared spectroscopy

A Nicolet Nexus 670 spectrometer provided with a MKII Golden Gate accessory (Specac) with a diamond crystal at a nominal incidence angle of 45º and ZnSe lens was used to characterized the functional groups of PU0 and TiO2-PU0 nanocomposite films by Fourier transform infrared spectroscopy (FTIR). The range was between 4000 and 650 cm⁻¹, with a resolution of 8 cm⁻¹ and averaging 32 scans.
2.4.3. Differential scanning calorimetry

To determine the thermal properties of PU0 and TiO$_2$-PU0 nanocomposite films a DSC 3+ Mettler Toledo equipment provided with an autosampler and an electric intracooler as refrigerator unit was employed. Differential scanning calorimetry (DSC) scans were carried out from -90 to 200 ºC by heating the weighted sample, between 5 to 8 mg, encapsulated in an aluminium pan at a scanning rate of 5 ºC min$^{-1}$ in a nitrogen inert atmosphere.

2.4.4. Thermogravimetric analysis

The thermal stability of PU0 and TiO$_2$-PU0 nanocomposite films was determined by thermogravimetric analysis (TGA) using a TGA/SDTA 851 Mettler Toledo. Between 5 and 10 mg of each sample were exposed to a dynamic run from 25 to 800 ºC, at a heating rate of 10 ºC min$^{-1}$ in nitrogen atmosphere.

2.4.5. Atomic force microscopy

Atomic force microscopy (AFM) captured images of the morphology of PU0 and TiO$_2$-PU0 nanocomposite films at room temperature by applying a resonance of 320 kHz, collecting the height and phase images simultaneously. The obtained AFM images were similar and, for this reason, only phase images are shown. A Nanoscope V scanning probe microscope (Multimode 8 Bruker Digital instruments) with an integrated force generated by cantilever/silicon probes with a tip radius of 5-10 nm and 125 µm long was utilized. Different areas of the films were scanned to ensure that the obtained morphology was representative.

2.4.6. Optical microscopy

In order to ensure that PU0 and TiO$_2$-PU0 nanocomposite films were homogeneous at microscopic level, optical microscopy (OM) was employed. Images were taken with the x10 objective of a Nikon Eclipse E600.
2.4.7. Mechanical testing/self-healing ability

Mechanical properties and self-healing ability of PU0 and TiO$_2$-PU0 nanocomposite films at room temperature were studied by tensile test using an Instron 5967 testing machine provided with a 500 N load cell and pneumatic grips to hold samples. At least 6 specimens (10 mm x 4.5 mm x 0.3 mm) of each composition were tested (original specimens and healed specimens). All investigated films were kept at 60 °C in vacuum before testing carried out at a crosshead speed of 10 mm min$^{-1}$. For the self-healing measurement, specimens were cut and put into contact for 23 h in a desiccator and then kept for 1 h at 60 °C in vacuum before testing. The time between specimen cut and testing after healing was established to be 24 h. Tensile modulus (E), tensile strength ($\sigma_{\text{max}}$), stress at break ($\sigma_b$) and elongation at break ($\varepsilon_b$) were determined from the obtained stress-strain curves.

The ratio of elongation at break, tensile strength, stress at break and modulus of the healed specimen to that of the original specimen were taken to determine the healing efficiency.

\[
\text{Healing efficiency} = \frac{\text{Mechanical Property (healed)}}{\text{Mechanical Property (original)}} \times 100
\]

(1)

2.4.8. Contact angle/Self-healing

The hydrophilic nature of PU0 and TiO$_2$-PU0 nanocomposite films was analyzed by static water contact angle (WCA) using a SEO Phoenix300 equipment at room temperature. At least 10 measurements were performed by sessile drop method for each film. Deionized water drop was deposited in the surface of the film by syringe tip. Young-Dupré equation (Equation 2), where $W_a$ corresponds to the work of adhesion (mN m$^{-1}$), $\gamma$ to the surface energy (mN m$^{-1}$) and $\sigma$ to the contact angle (radians), allowed calculating the surface energy of each film[38], original and self-healed.

\[
W_a = \gamma(1 + \cos \sigma)
\]

(2)
2.4.9. Electrostatic force microscopy

Conductive properties of TiO$_2$-PU0 nanocomposites films were studied by electrostatic force microscopy (EFM). EFM measurements were performed using the Dimension Icon scanning probe operating in lift mode (lift height ~400 nm) equipped with a Pt/Ir coating tip with a resonance frequency around 75 kHz. A voltage was applied to the cantilever tip in order to detect the secondary imaging mode derived from tapping mode that measures the electric field gradient distribution. This technique allows to measure qualitatively conductive properties at the nanometric level of TiO$_2$ nanoparticles embedded in the PU0 matrix.

3. Results and Discussion

3.1. FTIR spectra

Figure 2 displays the FTIR spectra of PU0 and TiO$_2$-PU0 nanocomposite films. As it can be observed, the spectra of PU0 and TiO$_2$-PU0 nanocomposite films did not show significant differences. In all spectra there are broad absorbance peaks in the region of 3500-3000 cm$^{-1}$, which correspond to the stretching vibration of the hydrogen bonded, at higher wavenumber peak[10,15], and non-hydrogen bonded, closer to 3200 cm$^{-1}$[10], N—H groups[6,8,10,15]. The intense bands between 3000 and 2750 cm$^{-1}$ correspond to the asymmetric and symmetric stretching vibrations of C—H groups[8,15], whereas the peaks around 1700 cm$^{-1}$ are due to stretching vibrations of the hydrogen bonded and non-hydrogen bonded carbonyl groups[39] of both urea and urethane[8,10,15]. The peaks at 1100 cm$^{-1}$ correspond to the stretching vibration of C—O—C ether group[8,15] of the employed PEO. The absence of a band at 2270 cm$^{-1}$, related to NCO groups[6,8], meant that the reaction was completed and there were not NCO groups present in the structure of the prepared PU0 and the nanocomposite films.
Figure 2. FTIR spectra of the PU0 and TiO\textsubscript{2}-PU0 nanocomposite films.

Regarding the differences between the spectra of PU0 and nanocomposite films, the most evident one is a peak at 800 cm\textsuperscript{-1} corresponding to Ti—O—Ti, which widens with the increase of TiO\textsubscript{2} nanoparticles content. The association of this peak is according to literature[8,40,41]. This widening with the increase of the TiO\textsubscript{2} nanoparticles content confirms the successful addition of inorganic nanoparticles to the PU0 dispersion.

3.2. Thermal characterization and stability

The thermal characterization of the films was performed by DSC (Figure 3a). The glass transition temperatures (T\textsubscript{g}) of all investigated films were below room temperature (Supplementary Information Table S2). The T\textsubscript{g} of the PU0 matrix decreased with the increase of the TiO\textsubscript{2} nanoparticles content. The T\textsubscript{g} of the PU0 matrix shifted 7 °C to lower temperature for 40TiO\textsubscript{2}-PU0 nanocomposite, indicating interactions between the TiO\textsubscript{2} nanoparticles and the polymer matrix. Thus, the addition of TiO\textsubscript{2} nanoparticles conferred mobility to the polymer chains[7] at the same time as acting as reinforcement[42]. This might be consequence of TiO\textsubscript{2} nanoparticles interacting with the hard segment (MDI-SDBS segment) possibly allowing a higher soft segment (PEO) mobility.
Figure 3. (a) Heating scan and (b) TGA curves of the PU0 and TiO$_2$-PU0 nanocomposite films.

TGA measurements were carried out in order to investigate the thermal stability of the films. Figure 3b shows the TGA curves of all the investigated materials (dTGA curves can be found in Supplementary Information Figure S1). The degradation process consisted of two steps weigh loss. The first step took place from 310 to 323 °C (Supplementary Information Table S3), and corresponded to the hard segment decomposition, whereas the second stage occurred around 393-406 °C (Supplementary Information Table S3), and was related to the soft segment decomposition[16]. Incorporation of TiO$_2$ nanoparticles into the PU0 matrix led to a decrease in the thermal stability, as the starting decomposition temperature of the nanocomposites was lower if compare to the starting decomposition temperature of PU0. This modest decay in the thermal stability might have been the aftermath of possible interactions between TiO$_2$ nanoparticles[43], which is enhanced with the increase on TiO$_2$ nanoparticles content.

The TiO$_2$ nanoparticles content introduced into the PU0 matrix in each nanocomposite was determined taking into account the difference between the residue of pristine TiO$_2$ nanoparticles and the residue of each nanocomposite.
3.3. Morphology

The morphology of PU0 and nanocomposite films was studied by AFM. OM micrographs of each of the investigated films were also added to Figure 4. As proved by OM results, investigated NC did not show any agglomeration of the TiO$_2$ nanoparticles at the microscopic scale. As expected from our previous studies[36,44], PU0 film did not show any phase separation (see Figure 4) between soft (PEO) and hard segment (MDI-SDBS). As consequence, TiO$_2$ nanoparticles were not located in any particular domain, since for investigated nanocomposites PU0 acted as homopolymer (Figure 4b-d). The TiO$_2$ nanoparticles dispersed in the matrix formed spherical nanoclusters[45] given the tendency they have to interact with each other[17]. Some of the nanoclusters were interconnected[45], what could provide conductivity at a macroscopic level if it creates a percolation path[46]. Nevertheless, neither OM nor AFM did show any agglomeration of the TiO$_2$ nanoparticles in the polymer matrix. The amount of TiO$_2$ clusters increased with the increase of TiO$_2$ nanoparticles content in TiO$_2$-PU0 nanocomposites, as shown in Figure 4b-d.
Figure 4. AFM phase images (3µm x 3 µm) of (a) PU0, (b) 10TiO₂-PU0, (c) 20TiO₂-PU0 and (d) 40TiO₂-PU0. The inset in each AFM image corresponds to OM micrographs.

3.5. Mechanical properties

The mechanical properties of PU0 and TiO₂-PU0 nanocomposite films obtained from the strain-stress curves are shown in Table 1. An increase of the TiO₂ nanoparticles content resulted in films with higher modulus, tensile strength, stress at break. The enhancement of the mechanical properties with increase of TiO₂ nanoparticles is especially visible comparing their Young´s modulus. The Young`s modulus value of PU0 matrix increased 575% when 40 wt% TiO₂ nanoparticles was added, being 6.2 MPa for PU0 and 41.9 MPa for 40TiO₂-PU0.
nanocomposite. However, incorporation of the TiO$_2$ nanoparticles led to smaller deformation at break. The deformation at break was reduced more than by half, decreasing from 490.4% for PU0 to 200.5% for 40TiO$_2$-PU0. This was an expected result as the TiO$_2$ nanoparticles can act as reinforcement of the polymer matrix[9] making TiO$_2$-PU0 nanocomposite films more rigid than PU0 film.

Table 1. Young’s modulus, tensile strength, stress at break, deformation at break and toughness of PU0 and TiO$_2$-PU0 nanocomposite films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E$ (MPa)</th>
<th>$\sigma_{\text{max}}$ (MPa)</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU0</td>
<td>6.2 $\pm$ 1.7</td>
<td>1.5 $\pm$ 0.2</td>
<td>0.7 $\pm$ 0.1</td>
<td>490.4 $\pm$ 90.2</td>
</tr>
<tr>
<td>10TiO$_2$-PU0</td>
<td>12.6 $\pm$ 2.2</td>
<td>1.6 $\pm$ 0.3</td>
<td>1.0 $\pm$ 0.2</td>
<td>288.9 $\pm$ 20.3</td>
</tr>
<tr>
<td>20TiO$_2$-PU0</td>
<td>25.0 $\pm$ 10.4</td>
<td>2.2 $\pm$ 0.3</td>
<td>1.3 $\pm$ 0.3</td>
<td>298.2 $\pm$ 49.8</td>
</tr>
<tr>
<td>40TiO$_2$-PU0</td>
<td>41.9 $\pm$ 9.1</td>
<td>2.6 $\pm$ 0.4</td>
<td>2.0 $\pm$ 0.6</td>
<td>200.5 $\pm$ 73.0</td>
</tr>
</tbody>
</table>

3.6. Self-healing

The self-healing ability of the prepared PU0 and TiO$_2$-PU0 nanocomposite films was studied by means of their mechanical properties and contact angle. 40TiO$_2$-PU0 was not analyzed since it required more than 24 h to recover to show the self-healing ability. For this measurement, films were cut and left healing during three repetitive cycles. Firstly, the films were cut in half and then left healing, whereas for the second cut films were cut from the upper left to the lower right across the trace of the first cut and then left healing. Finally, the third cut went from the upper right to the lower left across the trace of the first two cuts and then left healing for the last time. The cutting/recovery cycles of each investigated film are shown in Figure 5. The prepared materials exhibited intrinsic self-healing ability thanks to the presence of hydrogen bonds between urethane and urea groups[24,26] with the ether oxygen of PEO[47] and also hydrogen bonding of TiO$_2$ nanoparticles[3] with the poly(urethane-urea) matrix. The flexible
network together with high urethane and urea linkages enabled a high initial plastic deformation. Additionally, taken into account that the $T_g$ of investigated materials was below room temperature, this conferred the investigated PU0 and TiO$_2$-PU0 nanocomposite films enough flow to ensure the recovery of the damaged area thanks to the reversible hydrogen bonding[24].

![Figure 5. Visual self-healing process of (a) PU0, (b) 10TiO$_2$-PU0 and (c) 20TiO$_2$-PU0.](image)
The hydrophilic nature of prepared PU0 and TiO$_2$-PU0 nanocomposite films after the successive cutting/recovery cycles was studied by static contact angle measurements. As showed in Table 2, PU0 as well as the TiO$_2$-PU0 nanocomposite films showed a hydrophilic character. As expected, taking hydrophilic nature of TiO$_2$ nanoparticles into account, the incorporation of TiO$_2$ nanoparticles into the PU0 matrix did not change hydrophilic character of the matrix [20]. The hydrophilic character of the PU0 and TiO$_2$-PU0 nanocomposite films decreased slightly after consecutive cutting/recovery cycles. The surface energy of both PU0 and TiO$_2$-PU0 nanocomposite films (Supplementary Information Table S4), calculated from the Young-Dupré equation using the contact angle measurement, was almost unaltered after the successive recovery cycles. The obtained value for each film and healing cycle agreed with the surface energy that can be found in literature for polyurethane films[48].

**Table 2.** Contact angle of the original PU0 and TiO$_2$-PU0 nanocomposite films and of the healed films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Original (º)</th>
<th>1st healing (º)</th>
<th>2nd healing (º)</th>
<th>3rd healing (º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU0</td>
<td>62.4 ± 6.9</td>
<td>61.2 ± 8.3</td>
<td>53.7 ± 2.5</td>
<td>57.1 ± 9.5</td>
</tr>
<tr>
<td>10TiO$_2$-PU0</td>
<td>65.6 ± 9.0</td>
<td>50.1 ± 5.5</td>
<td>54.9 ± 3.5</td>
<td>56.6 ± 4.9</td>
</tr>
<tr>
<td>20TiO$_2$-PU0</td>
<td>65.7 ± 6.6</td>
<td>57.6 ± 2.9</td>
<td>57.7 ± 2.3</td>
<td>59.4 ± 2.9</td>
</tr>
</tbody>
</table>

The healing efficiency of self-healing ability of PU0 and TiO$_2$-PU0 nanocomposite films by means of their mechanical properties in Figure 6. 10TiO$_2$-PU0 showed the highest healing efficiency for tensile strength and stress at break. This tendency was quite similar also for 20TiO$_2$-PU0, which showed the greatest healing efficiency for modulus. Nonetheless, PU0 exhibited a high healing efficiency for deformation at break. Healing efficiency for deformation at break of 10TiO$_2$-PU0 was also high in contrast with the poor healing efficiency of 20TiO$_2$-PU0 for this mechanical property. Therefore, nanocomposite showed, in general, a greater
healing efficiency than the matrix. Inasmuch as a decrease in mechanical properties after the incorporation of nanofillers is linked to inferior healing efficiency[33,49], observed increase in mechanical properties after incorporation of TiO$_2$ nanoparticles to PU0 would have been the cause for the increase in healing efficiency that took place for nanocomposites. This idea was supported by the fact that healing efficiency of nanocomposites was inferior to the one of PU0 for elongation at break, the mechanical property reduced by incorporation of TiO$_2$ nanoparticles. Nevertheless, this can be overcome by the disrupting effect over hydrogen bonding and sulphonate group interactions of PU0 matrix that TiO$_2$ nanoparticles displayed[26], resulting in a decrease of healing efficiency and leading to longer times for reparation with the increase of TiO$_2$ nanoparticles content in nanocomposites. This would explain the decrease in healing efficiency from 10TiO$_2$-PU0 to 20TiO$_2$-PU0, as well as the long time required for 40TiO$_2$-PU0 nanocomposite to self-heal.

As can be clearly observed in Figure 6, the healing efficiency decreased with the number of cuts. This could be due to the softness of the samples which made it difficult to keep cut specimens in contact during the healing process[25]. Nevertheless, the loss in the healing efficiency with successive healing cycles for intrinsic self-healing materials is a common effect[50].
**Figure 6.** Healing efficiency of PU0, 10TiO$_2$-PU0 and 20TiO$_2$-PU0 for (a) modulus, (b) tensile strength, (c) stress at break, (d) deformation at break.

### 3.7. Electrostatic Force Microscopy

EFM is a useful technique to study the electric field gradient distribution above the investigated materials. This is a qualitative method which allows identifying the conductive areas of the investigated materials by applying different positive and negative voltages (±V)[51,52].

Firstly, in order to ensure that there was not influence of the topography of the surface of the investigated materials on the EFM measurement a bias of 0 V was applied. As shown in Figure 7 any charged domains were detected confirming that the EFM measurement conditions were adequately chosen[52,53].
Figure 7. EFM phase images (3µm x 3 µm) of (a) 10TiO₂-PU0, (c) 20TiO₂-PU0, (e) 40TiO₂-PU0 and their simultaneously obtained AFM phase images (3µm x 3 µm).

As expected, the locally charged TiO₂ nanoparticles were visualized in corresponding EFM images applying bias of 6 and 9 V. Here it should be mention that in investigated TiO₂-PU0
nanocomposites, the only conductive component were TiO$_2$ nanoparticles[3]. An increase in the positive and negative voltage led to higher contrast between charged and uncharged areas of the investigated nanocomposite surfaces. Consequently, TiO$_2$ nanoparticles responded in the whole range of the applied voltage, regardless of the sign of the applied V. This all indicates that the nanocomposite films acquired conductive behavior after incorporation of TiO$_2$ nanoparticles, as the TiO$_2$ nanoparticles preserved their conductive nature. Taking into account that TiO$_2$ nanoparticles weight content in prepared TiO$_2$-PU0 nanocomposites was lower that the weight content corresponding to the non-conductive poly(urethane-urea), these results make TiO$_2$-PU0 nanocomposite materials potential candidates for semiconductor applications[46].

4. Conclusions

Successful incorporation of TiO$_2$ nanoparticles into synthesized waterborne poly(urethane-urea) with PEO as the soft segment was achieved by \textit{ex situ} physical mixing. This successful incorporation of the titanium dioxide nanoparticles into the poly(urethane-urea) matrix was confirmed by FTIR, TGA, AFM and EFM. Increase of TiO$_2$ nanoparticles content decreased the $T_g$ of PU0 matrix and reduced the thermal stability. The inorganic nanoparticles formed clusters and there are well-dispersed in the poly(urethane-urea) matrix as proved by AFM. Hydrophilic nature of the PU0 did not vary significantly with the incorporation of TiO$_2$ nanoparticles. As sought with the incorporation of TiO$_2$ nanoparticles, modulus and stress at break of nanocomposite films increased as the TiO$_2$ nanoparticles content increased. All investigated films exhibited self-healing ability, however 40TiO$_2$-PU0 required a longer period of time to heal. Healing efficiency of PU0 was the greatest for deformation at break whereas 10TiO$_2$-PU0 and 20TiO$_2$-PU0 showed a greater healing ability for modulus, tensile strength and stress at break, nonetheless the surface energy calculated using contact angle measurement.
was unaffected by the healing process. EFM corroborated that the TiO$_2$ nanoparticles maintained their conductive properties after incorporation into the waterborne poly(urethane-urea). Prepared materials are interesting as a simple method for dispersing TiO$_2$ nanoparticles was employed leading to self-healable nanocomposite films with improved mechanical properties and in which TiO$_2$ nanoparticles kept their conductive properties. These conductive nanomaterials have potential use in a broad field of applications determined by the electrical conductivity of the nanocomposites, while their self-healing ability makes them even more attractive as their lifespan is extended.

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