Investigation of the nanomechanical properties of nylon 6 and nylon 6/clay nanocomposites at sub-ambient temperatures

Jian Chen\textsuperscript{a}, Ben D. Beake\textsuperscript{b}, Gerard A. Bell\textsuperscript{b}, Yalan Tait\textsuperscript{c} and Fengge Gao\textsuperscript{c}

\textsuperscript{a}School of Materials Science and Engineering, Jiangsu Key Laboratory of Advanced Metallic Materials, Southeast University, Nanjing, Jiangsu Province, China; \textsuperscript{b}Micro Materials Ltd., Wrexham, UK; \textsuperscript{c}School of Science and Technology, Nottingham Trent University, Nottingham, UK

\textbf{ABSTRACT}

The nanomechanical properties of nylon 6, nylon 6/exfoliated clay and nylon 6/non-exfoliated clay nanocomposites have been investigated from room temperature to $-10$ $^\circ$C in a controlled environment with humidity less than 1% RH. The hardness, elastic modulus and creep resistance of nylon 6 were improved in the nanocomposites across the temperature range. However, the effective reinforcement of the clay depended on the temperature due to the change between the glassy and transition states in the nylon. The exfoliated clay nanocomposite showed the greater improvements than in the non-exfoliated clay nanocomposite at all testing temperatures due to the improved constraint of the polymer chains by the clay platelets in the exfoliated structure. The surface mechanical properties of nylon 6 and the nanocomposites were also found to be highly sensitive to the moisture level during the tests; increasing the humidity in the room temperature tests resulted in a dramatic decrease in hardness and stiffness due to plasticisation by water molecules. The kinetics of the re-humidification process on nylon 6 were studied by monitoring the change in nanoindentation response. Analysis of the indentation creep revealed a significant change in the strain rate sensitivity when the humidity of the near-surface region probed by nanoindentation was in the vicinity of the glass transition.

\section{1. Introduction}

Clay-reinforced nylon nanocomposites have received great interest since 1990s \cite{1,2} due to their excellent mechanical properties and other enhanced properties, e.g. heat distortion temperature, fire retardancy, barrier resistance and ion conductivity \cite{3,4,5} which promote their industrial applications, particularly in the automotive sector.

The strengthening mechanisms for nylon nanocomposites have been investigated and it is understood that the high aspect ratio, interfacial area and stiffness of the clay platelets play important roles, especially when they are well dispersed in the matrix.\cite{3,4,5,6,7} The composition, phase structure and microstructure of the matrix also contribute to the final mechanical properties of the composites.\cite{8} The matrix-related factors may become more important when the composites are required to be used over wide-ranging environmental conditions. For example, the phase structure and the mechanical properties of nylon and its composites are very sensitive to the in-service temperature.\cite{9,10,11,12,13} When the temperature increases above the glass transition temperature ($T_g$), nylon
undergoes a transition from a highly brittle structure (glassy state) to a liquid-like structure (rubbery state), with significant changes in the strength and stiffness. A number of studies have been carried out for bulk materials in the past.[14,15]

Localised mechanical properties of advanced polymers and composites have received great interest due to the popularity of the polymeric micro-electromechanical systems (MEMS) and the development of injection micro-moulded components. Nanomechanical testing (nanoindentation) has become an integral technique in improving our fundamental understanding of the basis of mechanical properties of materials and the importance of the nanoscale on the behaviour at a larger length scale. Nanoindentation has shown its superiority in characterising the surface properties of nanocomposites as only a localised area is indented and a number of properties can be calculated such as hardness ($H$), elastic modulus ($E$) and creep parameters.[4,9,16−21] However, nanomechanical tests are usually performed in ambient laboratory conditions even if the materials being developed will be subject to a different environment in use. To further utilise the potential of the technique, it is important to measure the nanomechanical properties of materials under test conditions that are closer to their operating conditions where the results are more relevant for improved understanding of the links between properties and performance and design advanced materials systems for increasingly demanding applications over a range of temperature or moisture. With suitable environmental control, it is now possible to run in situ nanoindentation at temperatures above or below ambient laboratory temperature. Lu et al. [22] investigated the PMR-15 polyimide up to 200 °C using nanoindentation and found its elastic modulus showed a linear decrease with the increase of the temperature. Gray et al. [16,23] studied the mechanical properties of PET (poly(ethylene terephthalate)) films with different process history and crystallinity from 60 °C to 110 °C using another dual-heating nanoindentation design. They found a strong correlation between the $T_g$ and the mechanical properties and creep parameters determined from nanoindentation curves. In a similar design, Chen et al. [24] investigated the surface mechanical properties of atactic polypropylene ($T_g \sim 18$ °C) at sub-ambient temperature down to $−30$ °C and found the relationships between temperature, hardness and creep parameters.

As mentioned above, the mechanical properties of nylon depend strongly on the in-service temperature, which could lead to a change in properties, even their failure mechanisms. Therefore, it is important to investigate the influence of temperature on the nanomechanical behaviour of nylon—clay nanocomposites. Such questions are of particular importance since they can promote our scientific understanding in the strengthening mechanism of nanocomposites and their suitability for applications at sub-ambient temperatures at which these composites were in the glassy state. To the knowledge of the authors, as yet there have been only limited reports in this area. Selzter et al. [9] investigated the effects of temperature on nylon and nylon/organoclay nanocomposites indirectly by saturating in water to reduce the glass transition temperature, and subsequently performing nanoindentation and cantilever-bending at room temperature. They found that the creep compliance was reduced in the nanocomposites and concluded that the nano-fillers have constraint effects on the rubbery polymer matrix at the molecular level.

Nylon is strongly moisture-sensitive.[12,13,20,25] Bell et al. reported that the hardness and modulus of nylon decreased by $\sim 50\%$ and $\sim 65\%$, respectively, from their values in normal laboratory conditions when tested fully immersed and equilibrated in water [20] since the absorbed water molecules act as an effective plasticiser, resulting in a dramatic decrease in the $T_g$ and mechanical properties.[9,11,26] Water absorption behaviour is often considered as a diffusion process whose mechanisms can be investigated by measuring the changing mechanical properties during humidification. Nonetheless, it is difficult to monitor the real-time mechanical properties, and more commonly tests were performed off-line with the samples removed from the wet surroundings and dried before testing. In this study, the nanomechanical properties of pure nylon and nylon/clay composites including 5 wt.% non-exfoliated clay and 5 wt.% exfoliated clay were tested from $−10$ °C to $27$ °C by nanoindentation and the effects of temperature on $H$, $E$ and creep parameters were investigated. In addition, the effects of humidity on their nanomechanical properties were also studied by an active purging system to reduce the humidity to under 1% RH, to allow comparison with tests at high moisture level (70% RH).
Furthermore, the use of nanoindentation to study the evolution of the nanomechanical properties during \textit{in situ} re-humidification of a moisture-sensitive polymer has been demonstrated.

2. Experimental

2.1. Materials

Nylon 6–clay nanocomposites were produced by compounding a medium molecular weight nylon 6 (Ultramid B3 purchased from BASF) with 5 wt.% organoclay Cloisite 93A and 15A, respectively, using a Prism Eurolab 16 mm twin-screw with 40/1 L/D ratio. Extruded samples were cooled in a water bath and chopped into pellets using a pelletiser. The feeding rate, screw speed and processing temperature applied were 15%–20%, 400 rpm and 235 °C, respectively. X-ray diffraction analysis and transmission electron microscopy (TEM) of the composites produced showed that clays in composites produced from Cloisite 93A were well exfoliated whilst the composites produced from Cloisite 15A exhibited intercalated structure or non-exfoliated NC. Crystallinity measurements were carried out using differential scanning calorimetry (DSC) analysis. The crystallinity of pure nylon 6, nylon 6/5 wt.% non-exfoliated clay (nylon/C-5) and nylon 6-5 wt.% exfoliated clay (nylon/EC-5) were 21.2, 17.5 and 17.6 wt.% respectively.

2.2. Nanomechanical tests

The mechanical properties were measured using an instrumented nanoindentation (NanoTest Vantage, MicroMaterials Ltd.) with a sub-ambient temperature capacity as described in [24]. Both indenter and sample were actively cooled using a dual-cooling system with separate coolers on the indenter and sample to avoid strong thermal gradients and minimise any thermal drift. The isothermal contact thus achieved is similar to the approach taken in high-temperature tests.[27] The frosting at sub-ambient temperature was overcome by active purging with pure Ar gas.

The samples were first measured at ambient conditions (27 °C and 70% RH) to compare the properties of the three samples. The load was increased with a constant loading rate of 0.2 mN/s to 10 mN, and then the peak load was hold for 60 s. Finally, the load was decreased with a fixed unloading rate of 0.2 mN/s, with a further hold period at 90% unloading for creep recovery assessment. Each test was repeated 20 times.

Afterwards, the sealed chamber was purged with pure Ar to remove the moisture for 24 h. When the dew point was reduced lower than −30 °C, these samples were cooled down to −10 °C without any frosting observed on the sample surfaces. Thus, the atmosphere is considered moisture-free. The sub-ambient nanoindentation was then performed using the similar loading–hold–unloading protocol except the peak load set to 20 mN. Nanoindentation tests at −5 °C, 5 °C and 27 °C were then conducted sequentially. The tests on nylon samples were repeated 10 times, and the tests for the composites were repeated 20 times. After completion of the tests at 27 °C, the Ar purging was turned off to let the pure nylon be slowly re-humidified. The \textit{in situ} nanoindentation tests were carried out at different times (0, 106, 173, 233, 482, 1362 and 1636 min) during the process.

\( H \) and \( E_r \) were calculated from the unloading curves using standard methods.[28] The reduced indentation modulus \( (E_r) \) is related to the elastic modulus of the material according to Equation (1).

\[
\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_s^2}{E_s},
\]

where \( E_i \) and \( \nu_i \) are the elastic modulus (1160 GPa) and Poisson ratio (0.07) of the diamond indenter, \( E_s \) and \( \nu_s \) are the elastic modulus and the Poisson ratio of the tested sample. As \( H \) and \( E_r \) were determined from the unloading curve, the influence from time dependency was considered and the tests were designed accordingly. In this study, the hold time at the peak was set to 60 s to
allow the creep rate drop significantly before unloading. Using the approach of Ngan et al. [29], the creep rate at initial stage of unloading was carefully checked to avoid errors in the measured properties. The evolution of the indentation depth (the creep depth) during the hold period was analysed using a logarithmic method,[16,30] which can be expressed as

$$\frac{\Delta d}{d_t(=0)} = \frac{A}{d_t(=0)} \ln \left( \frac{t}{\tau_L} + 1 \right),$$

where $\Delta d$ and $t$ are the creep depth and creep time during the hold period, $A$ and $\tau_L$ are termed as the extent parameter and the time constant, respectively. $d_t(=0)$ is the initial depth at the beginning of the hold period. Thus, $\Delta d/d_t(=0)$ can be termed as the creep strain. $A/d_t(=0)$ is the dimensionless fractional increase in depth during creep and termed as creep strain rate sensitivity.

3. Results

3.1. Nanoindentation results at room temperature with a high moisture level

Figure 1(a)–(c) shows all 20 nanoindentation load–displacement curves for pure nylon, nylon/C-5 and nylon/EC-5 samples when tested at room temperature 27 °C with a high moisture level of 70% RH. The curves for pure nylon (Figure 1(a)) showed the high repeatability expected from a mechanically homogenous sample. In contrast, the behaviour for nylon/EC-5 (Figure 1(b)) and nylon/C-5 (Figure 1(c)) was more variable due to the greater inhomogeneity. The analysed $H$ and $E_r$ shown in Figure 1(d) confirm that the surface mechanical properties were greatly improved in the nanocomposites. The exfoliated clay showed slightly higher improvements which $H$ and $E_r$ were improved $\sim$120% and $\sim$400%, respectively.

![Figure 1. Nanoindentation load–displacement curves of (a) pure nylon 6, (b) nylon 6/exfoliated clay and (c) nylon 6/non-exfoliated clay and (d) their hardness and reduced elastic modulus measured in 70% RH.](image-url)
3.2. Nanoindentation results at sub-ambient temperature with a low moisture level

Typical nanoindentation load–displacement curves of pure nylon 6, nylon 6/EC-5 and nylon 6/C-5 at temperature from $-10^\circ C$ to $27^\circ C$ in a moisture-free atmosphere are shown in Figure 2. The relative performance of the dry samples at $27^\circ C$ is the same as for the results measured in humid environment shown in Figure 1, although the absolute values are much higher, as shown in Figure 2(d). By comparison with (as yet unpublished) data on similar nylon polymers at different humidity, we estimate the humidity for the purge surroundings to be less than 1% RH.

The calculated $E_r$ and $H$ results at different temperatures are shown in Figure 3. Data on pure nylon showed a high repeatability (SD < 3%) throughout the testing range, confirming the reliability of the sub-ambient temperature nanomechanical tests. As with the tests at high moisture level, the mechanical inhomogeneity of both nanocomposites resulted in more variability in their nanomechanical response, but this was not any worse at low temperature than at $27^\circ C$. $E_r$ (Figure 3(a)) and $H$ (Figure 3(b)) were clearly improved in the nanocomposites, with the enhancements in the exfoliated clay being more significant at lower temperatures. When the temperature was decreased from $27^\circ C$ to $-10^\circ C$, $E_r$ and $H$ of pure nylon increased almost linearly. For the nanocomposites, a similarly rapid increase in $H$ and $E_r$ was found between $27^\circ C$ and $5^\circ C$, but the improvements became less marked with further reduction in temperature. For nylon 6/C-5, these mechanical parameters showed decreasing trends from $27^\circ C$ down to $5^\circ C$, and with further reduction in temperature, $H$ and $E_r$ showed no clear changes. For nylon 6/EC-5, $H$ and $E_r$ exhibited the maximum values at $-5^\circ C$.

Figure 4(a)–(c) shows typical creep strain curves collected during the hold period in sub-ambient temperature tests. The total creep depth (Figure 3(d) and Table 1) decreased with decreasing temperature from $27^\circ C$ to $-5^\circ C$ significantly. With further reduction in temperature to $-10^\circ C$, only...
nylon/EC-5 exhibited decreased creep depth, and the creep depth began to increase again for the other samples. Similar results were also found for the initial creep depth $d(t=0)$ as shown in Table 1.

By fitting the creep data with the logarithmic equation (Equation (2)), the fit parameters, $A$, $B$ and $A/d(t=0)$ are plotted in Figure 5. The creep extent, $A$, and the creep strain rate ($A/d(t=0)$) reduced as the temperature was lowered from 27 °C to $-5$ °C for all three samples. When the temperature was further reduced to $-10$ °C, these parameters continued to decrease for nylon/EC-5 but began to rise again for nylon 6 and nylon/C-5.

![Figure 3](image.png)

**Figure 3.** (a) Reduced elastic modulus and (b) hardness measured at different temperatures.

![Figure 4](image.png)

**Figure 4.** Typical creep curves for (a) pure nylon, (b) nylon/exfoliated clay and (c) nylon/non-exfoliated clay at different temperatures, (d) the creep depth.
4. Discussion

4.1. Comparison of nanoindentation and dynamic mechanical analysis

The results of both dynamic mechanical analysis (DMA) from [31] and nanoindentation for pure nylon are shown in Figure 6. The glass transition temperature $T_g$ of nylon is $\approx 45 \, ^\circ C$. As the $T_g$ does not vary much for its nanocomposites,[9] it can be assumed that nylon and its nanocomposites undergo two states from $-10 \, ^\circ C$ to $27 \, ^\circ C$, the glassy state and the transition zone. As shown in Figure 6(a), the $E_r$ results showed a comparable temperature dependence to that shown by the storage modulus. Similarly, the creep strain rate, which elsewhere has been shown to correlate with $\tan \delta$,[23] also follows a similar temperature dependence. The good agreement with traditional DMA bulk testing provides validation for the sub-ambient nanoindentation measurements.

4.2. Mechanical properties at sub-ambient temperatures

The nanomechanical properties of pure nylon 6 and its nanocomposites clearly depend on the testing temperature (Figure 3). At room temperature ($27 \, ^\circ C$), $E_r$ for nylon/EC-5 was improved by

| Temperature (°C) | $d_0 = 0$ (nm) | $\Delta d$ (nm) |
|-----------------|----------------|-----------------|
|                | Nylon | Nylon/EC-5 | Nylon/C-5 | Nylon | Nylon/EC-5 | Nylon/C-5 |
| $-10$          | 1837 ± 10 | 1704 ± 85 | 1795 ± 77 | 149 ± 11 | 115 ± 15 | 142 ± 20 |
| $-5$           | 1889 ± 27 | 1713 ± 178 | 1773 ± 46 | 133 ± 9  | 125 ± 24 | 124 ± 10 |
| $5$            | 1953 ± 32 | 1762 ± 121 | 1799 ± 178 | 140 ± 9  | 130 ± 21 | 129 ± 17 |
| $27$           | 2149 ± 15 | 1958 ± 97  | 1984 ± 154 | 183 ± 7  | 160 ± 16 | 172 ± 29 |

Figure 5. Fitted creep parameters (a) $A$, and (b) $A/d_0 = 0$. 

Table 1. Typical creep data including initial creep depth $d_0 = 0$ and the total creep depth $\Delta d$. 

Figure 6. Fitted creep parameters (a) $A$, and (b) $A/d_0 = 0$. 

JOURNAL OF EXPERIMENTAL NANOSCIENCE
around 29% over pure nylon. The dispersion of clay in the polymer matrix usually results in three general types of composites,[5,9,32] (1) separated polymer/clay composite, (2) polymer/intercalated clay composite and (3) polymer/exfoliated clay nanocomposite, with the latter often exhibiting the best mechanical properties due to the large aspect ratios of the filler, huge interfacial areas between the filler and the matrix, resulting in a more effective molecular-level constraint.[5,11] The improved properties found for the exfoliated-clay nanocomposite are consistent with this.

To further identify the effectiveness of the different nanocomposite processing routes at lower temperatures, Figure 7 shows the temperature dependence of normalised $H$ and $E_r$, i.e. dimensionless parameters obtained by dividing the values of pure nylon at the same temperature. Presenting the data in this way more clearly shows that the improvements by exfoliated clay were less influenced by the temperature than those by the non-exfoliated clay. For example, the improvement of $E_r$ and $H$ for nylon/C-5 at the lowest temperature ($-10^\circ C$) was $\sim 15\%$ and $\sim 3\%$, respectively, while the improvements for nylon/EC-5 were as high as $\sim 33\%$ and $\sim 15\%$. These results are consistent with the molecular-level constraints introduced by the nano-clay still effectively enhancing the mechanical properties at low temperatures, although to a lesser extent than at room temperature.

As mentioned above, nylon and nanocomposites move from a glassy state to a transition state from $-10^\circ C$ and $27^\circ C$. In turn, the ductile—brittle transition (DBT) should be considered as it can be strongly affected by temperature.[33] For polymers, both yield strength ($\sigma_y$) and fracture strength ($\sigma_b$) change with the temperature following different trends.[34] The intersection is considered as the DBT temperature. Thus, when temperature is decreased to the DBT temperature, $\sigma_y$ usually increases linearly.[35] With a further decrease of temperature, the polymer starts to fail at $\sigma_b$.

For pure nylon, $H$ in Figure 3(b) is almost linearly increased with the decrease of temperature. It suggested that the ductile deformation played a dominant role. For the composites, $H$ was
significantly improved by the addition of fillers and influenced by temperature. \( H \) showed a turning point at \(-5^\circ C\) and \(5^\circ C\) for nylon/EC-5 and nylon/C-5, respectively. Below this point, no clear increase in \( H \) can be found. For a glassy polymer, crazing and shear banding are the most important deformation mechanisms.\[36\] Kim et al. carried out in situ deformation experiments on nylon/exfoliated clay samples under a high-voltage electron microscope. The main deformation mechanism was microvoid formation in the vicinity of fillers in the plastic-deformed matrix.\[37\] As reported in \[38\], filler morphology and filler–matrix adhesion affect the locations of the DBT, which is essential to failure of crazes. For the nylon/exfoliated clay composites,\[37\] it was found that the microvoid formation took place more uniformly and homogeneously throughout the deformed specimen, and thus a well-improved stiffness/strength/toughness balance was achieved.\[37\] Our results are consistent with this view. The elastic modulus of semi-crystalline polymers increases with a reduction in temperature below \( T_g \) since less molecular segments are movable. However, with further reduction in temperature down to \(-10^\circ C\), the molecular segments are almost immobile in these glassy polymers and a more gradual increase in modulus with decreasing temperature is expected.

The total creep depth generally decreased with the decrease of temperature with the exception of the total creep depth for nylon and nylon/C-5 at \(-10^\circ C\) which was higher than at \(-5^\circ C\). Creep in polymeric materials is usually related to the free volume available for molecular motions.\[17,39\] Decreasing the temperature below \( T_g \) reduces the free volume. In principle, brittleness and crack propagation at lower temperature could result in enhanced time-dependent deformation,\[39,40\] but we consider it more likely that the slight increase in creep depth at \(-10^\circ C\) on nylon 6 and non-exfoliated nanocomposite is a consequence of being on the shoulder of the \( \beta \) relaxation peak of nylon 6. Low-temperature DMA data on other nylon 6–clay nanocomposites reported in \[9\] show that it is centred around \(-50^\circ C\) and that \( \tan \delta \) begins to rise again when the temperature decreases below \(-15^\circ C\). For nylon/EC-5, the creep depth was reduced over the range of \(27^\circ C\) to \(-10^\circ C\), which may imply that the shoulder of the \( \beta \) relaxation peak does not extend quite as far as \(-10^\circ C\) in the near-surface region of the exfoliated nanocomposite, which could be explained by the improved molecular-level constraints due to the small size and high surface area of the clay platelets, together with the short inter-particle distance which prevents free rotation of the matrix molecular chains.\[41\] Vlasveld et al. \[32\] also found that clay can impose constraints on the polymer molecules.

### 4.3. Real-time evolution of \( H \) and \( E_r \) during in situ humidification of nylon 6

Figure 4(d) shows that the mechanical properties of nylon and its composites strongly depend on the moisture level in the surrounding environment, with \( H \) and \( E_r \) severely reduced by moisture absorption. Absorption and transportation of water in the polymer are kinetic processes \[13\] which, depending on their time-scale, could be followed by the changing mechanical properties of the surface layers probed by nanoindentation. To confirm the idea and further investigate the evolution of the real-time nanomechanical properties, multiple nanoindentation tests were conducted during in situ humidification for pure nylon 6 and the change in \( H \), \( E_r \) and creep depth with time are shown in Figure 8. It clearly shows that the mechanical properties strongly depend on the moisture absorption time with a relatively rapid drop over the first \(~200\) min followed by a much slower rate of decrease. The decrease is ascribed to the plasticisation effect of water,\[9,12,42\] as it increases polymer flexibility or mobility. The absorption of water results in a decrease of the \( T_g \) of the polymer,\[9\] with a \(~50^\circ C\) reduction in glass transition temperature when saturating dry nylon 6 in water. The variation in creep depth is consistent with the movement of the glass transition of the surface region as the sample humidifies. When dry the glass transition temperature is higher than the test temperature and the creep is low. As the sample humidifies, plasticisation causes this glass transition temperature to decrease, until it is below the test temperature.
5. Conclusions

The nanomechanical properties of nylon 6, nylon 6/exfoliated clay and nylon 6/non-exfoliated clay nanocomposites have been investigated at different sub-ambient temperatures and moisture levels using nanoindentation. Several conclusions are drawn:

1. The hardness, elastic modulus and creep resistance of the nanocomposites are better than that of nylon 6 from $-10^\circ C$ to $27^\circ C$ when tested in a controlled environment with humidity less than 1% RH. However, the enhancement of the different nanocomposites was temperature-dependent, being more pronounced at higher temperatures.

2. The exfoliated clay showed a greater improvement than the non-exfoliated clay at all testing temperatures due to the improved constraint of the polymer chains by the clay platelets in the exfoliated structure.

3. The surface mechanical properties of nylon 6 and the nanocomposites were also found to be highly sensitive to the moisture level during the tests; increasing the humidity in the room temperature tests from <1% RH to ~70% RH resulted in a dramatic decrease in hardness and stiffness due to plasticisation by water molecules.

4. The kinetics of the re-humidification process on nylon 6 were studied by monitoring the change in nanoindentation response. Analysis of the indentation creep revealed a significant change in the strain rate sensitivity when the humidity of the near-surface region probed by nanoindentation was in the vicinity of the glass transition.

Disclosure statement

No potential conflict of interest was reported by the authors.
Funding

This work was supported by the National Natural Science Foundation of China [grant number 11472080]; the Natural Science Foundation of Jiangsu Province of China [grant number BK20141336]; and Jiangsu Key Laboratory for Advanced Metallic Materials [grant number BM2007204].

References

[1] Kojima Y, Usuki A, Kawasumi M, et al. Mechanical properties of nylon 6-clay hybrid. J Mater Res. 1993;8:1185–1189.
[2] Usuki A, Kojima Y, Kawasumi M, et al. Synthesis of nylon 6-clay hybrid. J Mater Res. 1993;8:1179–1184.
[3] Gao F. Clay/polymer composites: the story. Mater. Today. 2004;7:50–55.
[4] Shen L, Phang IY, Chen L, et al. Nanoindentation and morphological studies on nylon 66 nanocomposites. I. Effect of clay loading. Polymer. 2004;45:3341–3349.
[5] Sinha SK, Song T, Wan X, et al. Scratch and normal hardness characteristics of polyamide 6/nano-clay composite. Wear. 2009;266:814–821.
[6] Aravind D, Yu Z. Orientation and the extent of exfoliation of clay on scratch damage in polyamide 6 nanocomposites. Nanotechnology. 2008;19:055708.
[7] Liu TX, Liu ZH, Ma KX, et al. Morphology, thermal and mechanical behavior of polyamide 6/layered-silicate nanocomposites. Compos. Sci. Technol. 2003;63:331–337.
[8] Chen J, Gao Y, Liu W, et al. The influence of dehydration on the interfacial bonding, microstructure and mechanical properties of poly(vinyl alcohol)/graphene oxide nanocomposites. Carbon. 2015;94:845–855.
[9] Seltzer R, Mai Y, Frontini PM. Creep behaviour of injection moulded polyamide 6/organoclay nanocomposites by nanoindentation and cantilever-bending. Compos. Part B Eng. 2012;43:83–89.
[10] Rajeev KR, Gnanamoorthy R, Velmurugan R. Effect of humidity on the indentation hardness and flexural fatigue behavior of polyamide 6 nanocomposite. Mater. Sci. Eng. A. 2010;527:2826–2830.
[11] Vlasveld D, Groenewold J, Bersee H, et al. Analysis of the modulus of polyamide-6 silicate nanocomposites using moisture controlled variation of the matrix properties. Polymer. 2005;46:6102–6113.
[12] Vlasveld D, Groenewold J, Bersee H, et al. Moisture absorption in polyamide-6 silicate nanocomposites and its influence on the mechanical properties. Polymer. 2005;46:12567–12576.
[13] Abacha N, Kubouchi M, Sakai T. Diffusion behavior of water in polyamide 6 organoclay nanocomposites. Express Polym. Lett. 2009;3:245–255.
[14] Kiziltas A, Gardner DJ, Han Y, et al. Dynamic mechanical behavior and thermal properties of microcrystalline cellulose (MCC)-filled nylon 6 composites. Thermochim Acta. 2011;519:38–43.
[15] Shelley JS, Mather PT, DeVries KL. Reinforcement and environmental degradation of nylon-6/clay nanocomposites. Polymer. 2001;42:5849–5858.
[16] Gray A, Orecchia D, Beake BD. Nanoindentation of advanced polymers under non-ambient conditions: creep modelling and tan delta. J Nanosci Nanotechnol. 2009;9:4514–4519.
[17] Beake BD, Bell GA, Brostow W, et al. Nanoindentation creep and glass transition temperatures in polymers. Polym Int. 2007;56:773–778.
[18] Shen L, Phang IY, Liu TX, et al. Nanoindentation and morphological studies on nylon 66/organoclay nanocomposites. II. Effect of strain rate. Polymer. 2004;45:8221–8229.
[19] Shen L, Tjiu WC, Liu T. Nanoindentation and morphological studies on injection-molded nylon-6 nanocomposites. Polymer. 2005;46:11969–11979.
[20] Bell GA, Bielinski DM, Beake BD. Influence of water on the nanoindentation creep response of Nylon 6. J Appl Polym Sci. 2008;107:577–582.
[21] Tranchida S, Piccarolo S, Loos J, et al. Accurately evaluating Young’s modulus of polymers through nanoindentations: a phenomenological correction factor to the Oliver and Pharr procedure. Appl Phys Lett. 2006;89:171905.
[22] Lu YC, Tandon GP, Putthanarat, et al. Nanoindentation strain rate sensitivity of thermo-oxidized PMR-15 polyimide. J Mater Sci. 2009;44:2119–2127.
[23] Gray A, Beake BD. Elevated temperature nanoindentation and viscoelastic behaviour of thin poly(ethylene terephthalate) films. J Nanosci Nanotechnol. 2007;7:2530–2533.
[24] Chen J, Bell GA, Dong HS, et al. A study of low temperature mechanical properties and creep behaviour of polypropylene using a new sub-ambient temperature nanoindentation test platform. J Phys D Appl Phys. 2010;43:425404.
[25] Gargalaka J Jr, Couto RAA, Constantino VRL, et al. Influence of the relative amounts of crystalline and amorphous phases on the mechanical properties of polyamide-6 nanocomposites. J Appl Polym Sci. 2012;125:3239–3249.
[26] Blasi P, D-Souza SS, Selmin F, et al. Plasticizing effect of water on poly(lactide-co-glycolide). J Control Release. 2005;108:1–9.

[27] Smith JF, Vishnyakov VM, Davies MI, et al. Nanoscale friction measurements up to 750°C. Tribol Lett. 2013;49:455–463.

[28] Oliver WC, Pharr GM. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. J Mater Res. 1992;7:1564–1583.

[29] Ngan AHW, Tang B. Viscoelastic effects during unloading in depth-sensing indentation. J Mater Res. 2002;17:2604–2610.

[30] Beake B. Modelling indentation creep of polymers: a phenomenological approach. J Phys D Appl Phys. 2006;39:4478–4485.

[31] Li Y. The development of sub-micro filler enhanced polymer composites. Nottingham: Nottingham Trent University; 2007.

[32] Vlasveld D, de Jong M, Bersee H, et al. The relation between rheological and mechanical properties of PA6 nano- and micro-composites. Polymer. 2005;46:10279–10289.

[33] Jang BZ, Uulmann DR, Vandersande JB. Ductile brittle transition in polymers. J Appl Polym Sci. 1984;29:3409–3420.

[34] Williams ML, Landel RF, Ferry JD. Mechanical properties of substances of high molecular weight. 19. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. J Am Chem Soc. 1995;77:3701–3707.

[35] Ward IM, Pinnock PR. The mechanical properties of solid polymers. Br J Appl Phys. 1966;17:3–32.

[36] Pate RH. Deformation and fracture toughness in high-performance polymers. In: Riew CK, Kinloch AJ; editors. Toughened polymers I. Washington (DC): American Chemical Society; 1993. p. 105–141.

[37] Kim GM, Goerlitz S, Michler GH. Deformation mechanism of nylon 6/layered silicate nanocomposites: role of the layered silicate. J Appl Polym Sci. 2007;105:38–48.

[38] Bucknall CB, Paul DR. Notched impact behaviour of polymer blends. Part 2. Dependence of critical particle size on rubber particle volume fraction. Polymer. 2013;54:320–329.

[39] Brostow W, Hagg Lobland HE. Brittleness of materials: implications for composites and a relation to impact strength. J Mater Sci. 2010;45:242–250.

[40] Brostow W, Deshpande S, Pietkiewicz, et al. Accuracy in locating glass transitions: aging and gamma sterilization of vulcanized thermoplastic elastomers. e-Polymers. 2009;109:1–10.

[41] Lee YH, Bur AJ, Roth SC, et al. Monitoring the relaxation behavior of nylon/clay nanocomposites in the melt with an online dielectric sensor. Polym Adv Technol. 2005;16(2–351):249–256.

[42] Seltzer R, de la Escalera FM, Segurado J. Effect of water conditioning on the fracture behavior of PA12 composites processed by selective laser sintering. Mater Sci Eng A. 2011;528:6927–6933.