

Influence of Water on the Nanoindentation Creep Response of Nylon 6

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ABSTRACT: A nanoindentation system fitted with a fluid cell has been used to probe the influence of water on the nanoindentation creep response of commercial Nylon-6 samples. Measurements on samples taken while immersed in deionized water were compared with measurements under usual ambient ($\sim 50\%$ relative humidity) conditions. Water absorption reduces hardness by around 50% and elastic modulus by around 65%. The dimensionless creep parameter, $A/d(0)$, where A is a constant and $d(0)$ is the initial penetration at the start of the creep-hold period, is a

measure of the proportion of time-dependent deformation compared with the total deformation. This parameter decreases significantly in water. We have suggested previously that $A/d(0)$ correlates with $\tan \delta$. The observed reduction in $A/d(0)$ when wet is consistent with a decrease in the $\tan \delta$ peak due to a shift in the glass transition temperature when wet. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 577–582, 2008

Key words: nylon; mechanical properties; indentation

INTRODUCTION

Mechanical properties of biological and polymeric samples may vary considerably when in a fluid environment compared with the usual ambient ($\sim 50\%$ relative humidity, RH) testing conditions. While hydrophobic polymers do not absorb water significantly (so their mechanical properties are unchanged), polar materials in contrast such as biopolymers (for example DNA, elastin, starch, and cutin^{1,2}) absorb water and can swell significantly at saturation. Their mechanical properties are interlinked with their water content. It can be necessary to understand their properties and behavior in fluid media, so it is highly desirable to test under these conditions rather than to attempt to infer from measurements under normal laboratory testing conditions.

Nanoindentation is fast becoming a popular technique but hitherto commercial nanoindentation systems have not operated in fluid conditions. Recently, the testing capability of one commercial nanomechanical testing instrument has been extended by the development of a fluid cell allowing nanoscale test-

ing of samples fully immersed in fluids. The cell works with the instrument's pendulum design and the horizontal loading has certain benefits for testing in fluid [see fluid cell design and nanoindentation conditions Section].

In this article, we have used the fluid cell to investigate the influence of water on the nanomechanical properties of commercial Nylon-6 materials. Nylon was selected as a reliable benchmark test sample as it is already well known from testing by Tabor and others that water adsorption has a significant impact on many of its properties at the macroscale.^{3–9} Nylon 6 can absorb a surprising amount of water either by immersion or simple exposure to high humidity. The effect on the glass transition and mechanical properties is an important consideration in the use and suitability of the material for specific applications. With its polar nature and open microstructure nylon is readily plasticized by water. Plasticization decreases specific interactions such as hydrogen bonds in the amorphous regions of the polymer. Cohen and Tabor,³ and later Amuzu,⁴ have shown that the friction and shear strength of Nylon is a strong function of humidity. Cohen and Tabor showed that friction of Nylon on glass is increased in water because of the increased contact area when wet.³ More recently Stuart and Briscoe⁵ suggested that the observed increase in wet friction with load on Nylon was also due to this increasing contact

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area. Newman et al. have reported that water immersion resulted in a greater reduction in elastic modulus on Nylon 7 than Nylon 11, presumably because of the higher intermolecular interactions of the former.⁶

In addition to changes in the hardness and elastic properties on immersion, we were interested in the influence of absorbed water on the indentation creep behavior of nylon. Approaches to modeling the time-dependent deformation of polymeric systems in nanoindentation can assume constitutive models such as linear viscoelasticity with data fitted to 3-element (Maxwell or Voigt) or 4-element (combined Maxwell-Voigt) models.^{10,11} These are standard elastic equations with time-dependent terms added to represent the fluid-like behavior without necessarily any real physical significance.¹⁰ Although values of fitting parameters can be obtained, it is not at all clear that the fitting is sufficiently robust so that these are really representative. Fits to these equations can be somewhat inexact in practice,¹¹ questioning the reliability of the fitting parameters. In contrast, we have previously concentrated on the exact fitting of the initial phase of nanoindentation creep data to a simple logarithmic equation originally developed for soft metals^{12–14} [Eq. (1)].

$$\text{Increase in depth} = A \ln(Bt + 1) \quad (1)$$

The quality of fit to the creep deformation during this initial phase is excellent in practice. The approach has been recently adapted (normalizing by the initial penetration depth) and the sensitivity of a dimensionless creep parameter, $A/d(0)$, has been investigated recently as a measure of time-dependent deformation during indentation at constant force at room temperature,^{15,16} and also at elevated temperature¹⁷ as shown in Eq. (2).

$$d/d(0) = [A/d(0)] \ln(Bt + 1) \quad (2)$$

where A and B are constants, $d(0)$ is the initial deformation at the beginning of the hold period at peak load in an indentation test, and d is the increase in depth during the hold period so that $d/d(0)$ is the fractional increase in depth which occurs during this hold period. Values of $A/d(0)$ for a range of polymer systems appear to correlate with $\tan \delta$ and also with

the distance from the test temperature to the glass transition temperature.¹⁶ It has been shown by DMA measurements that water absorption alters both the magnitude of the $\tan \delta$ peak and the glass transition temperature.⁹ The tensile strength of dry Nylon 6 at 20°C is typically 76–97 MPa. The properties are highly dependent on water content. Water will behave as a plasticizer, i.e., the glass transition process moves to a lower temperature upon exposure to moisture. The effect of plasticization is easily shown with polyamides by immersing of dry material in water. Within a very short time scale, this material can absorb between 6 and 9% by weight of water and this will lower the glass transition to about 20°C affecting both modulus and $\tan \delta$. Once a polymer is at or above its glass transition temperature, it will tend to creep when any applied load occurs. It is of interest to investigate whether the nanoindentation creep analysis could show a similar effect at a more highly localized scale.

EXPERIMENTAL

Materials

Two commercial Nylon 6 materials were tested. Tarnamid T30 (hereafter designated "T30") was obtained from Zakłady Azotowe (Tarnow, Poland), and a comparative sample (hereafter designated "N6") was obtained from Polysciences Inc. (Warrington, PA). Specimens were prepared by injection moulding under comparable processing conditions. Physical characteristics of the samples studied are given in Table I.

Fluid cell design and nanoindentation conditions

A NanoTest system (Micro Materials) fitted with a fluid cell was used for the nanoindentation testing. The fluid cell design is shown schematically in Figure 1. Horizontal loading has some benefit for testing in fluid including (i) the use of an indenter adapter allowing the indenter to be fully immersed in cell, (ii) all electronics are well away from the cell, so it can be heated to body temperature and above without risk of steaming of the capacitive displacement sensor, (iii) possibility of fluid exchange during experiment (iv) no significant buoyancy problems, (v) no large change in meniscus position during

TABLE I
Physical Characteristics of the Materials Studied

Material	Symbol	M_w^a (g/mol)	X_c (wt %)	Density (g/cm ³)	T_m (°C)	η_{rel}^a
Tarnamid T30	T30	31,000	35.2	1.105	224	3.8
Polysciences M_w 35,000	N6	35,000	32.1	1.100	222	4.1

^a According to the producer: M_w , molecular weight; X_c , degree of crystallinity (DSC; 10°/min); T_m , melting temperature (DSC; 10°/min); η_{rel} , relative viscosity (H₂SO₄/25°C).

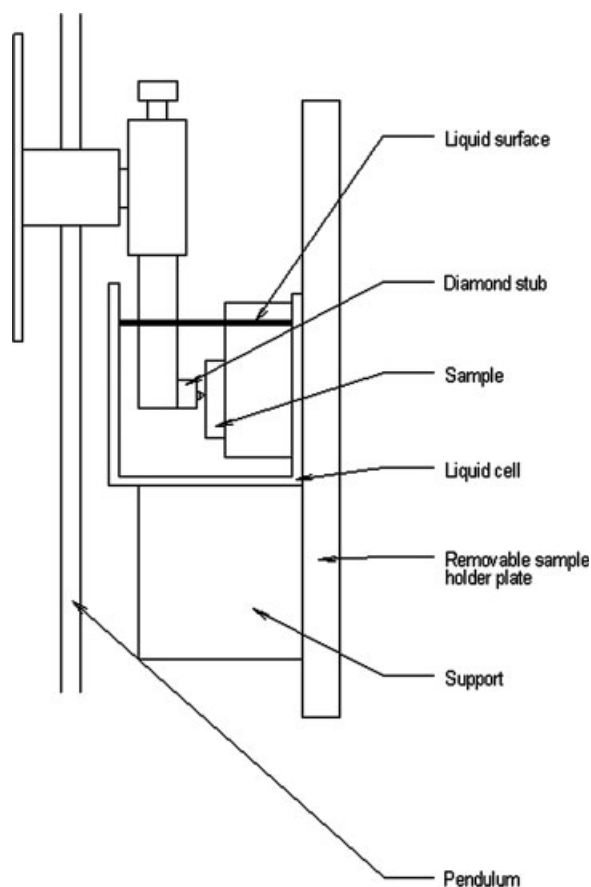


Figure 1 Schematic of NanoTest fluid cell.

indentation. During the design and commissioning of the fluid cell, nanoindentation tests were performed on samples that did not significantly alter their mechanical properties on exposure to water (polypropylene, fused silica) to confirm its correct operation.

The indentation test temperature was 25°C. In what follows “dry” is taken to mean testing in ambient laboratory conditions (~ 50% RH). On immersion in deionized water, the samples were left for > 24 h to equilibrate (saturate). Repeat indentations were performed to 0.5, 5, and 10 mN. Indentations (5–20) were performed on each sample at each force dry and a similar number were performed wet. Loading conditions for the 0.5 mN indentations were 0.05 mN/s loading rate, 50 s hold at peak load and unloading was at 0.05 mN/s to 90% unloading where an additional hold of 120 s allowed measurement of the rate of creep recovery. A linear fit was performed through the last 70 s of the creep recovery data to determine the apparent (close to) linear creep recovery rate. This creep recovery data was not used to correct the indentation data for thermal drift, which itself is in smaller orders of magnitude. For the 5 and 10 mN indentations, the conditions were the same except the loading and unloading rates were set to 0.2 mN/s, producing the load

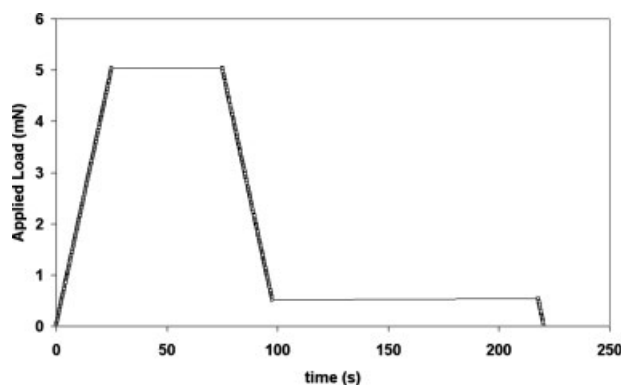


Figure 2 Loading history for indentation to 5 mN.

history shown in Figure 2 for the 5 mN indentation. A diamond indenter with the tip radius function $A_c = 6000 h + 22 h^2$ (essentially a Berkovich with a rounded spherical end cap) was used. Hardness and elastic modulus were determined using the procedure of Oliver and Pharr¹⁸ from an original analysis by Sneddon. To obtain the elastic modulus, the unloading slope is analyzed according to

$$S = 2\beta E_r A^{0.5} / \pi^{0.5} \tag{3}$$

where S is the contact stiffness and E_r is the reduced modulus defined by

$$1/E_r = (1 - \nu_s^2)/E_s + (1 - \nu_i^2)/E_i \tag{4}$$

where ν_s is the Poisson’s ratio for the sample, ν_i is the Poisson’s ratio for the diamond indenter (0.07), E_s is the Young’s modulus for the sample, E_i is the Young’s modulus for the indenter (1141 GPa), β is the correction factor (taken as 1.034). In Table II the reduced modulus E_r (also called the “effective elastic modulus”¹⁸) is quoted. This can be converted to the Elastic (Young’s) modulus using Eq. (4).

TABLE II
Hardness and Reduced Modulus

	H (GPa)	E_r (GPa)
T30 dry 0.5 mN	0.123 ± 0.016	1.70 ± 0.18
T30 wet 0.5 mN	0.046 ± 0.007	0.39 ± 0.04
T30 dry 5 mN	0.117 ± 0.009	1.87 ± 0.04
T30 wet 5 mN	0.052 ± 0.006	0.58 ± 0.06
T30 dry 10 mN	0.111 ± 0.002	1.67 ± 0.07
T30 wet 10 mN	0.055 ± 0.002	0.60 ± 0.05
N6 dry 0.5 mN	0.122 ± 0.016	1.79 ± 0.15
N6 wet 0.5 mN	0.089 ± 0.017	0.70 ± 0.10
N6 dry 5 mN	0.113 ± 0.014	1.72 ± 0.13
N6 wet 5 mN	0.070 ± 0.030	0.70 ± 0.03
N6 dry 10 mN	0.113 ± 0.012	1.60 ± 0.13
N6 wet 10 mN	0.065 ± 0.006	0.67 ± 0.04

Hardness and elastic modulus determined from analysis of unloading segments of indentation curves.

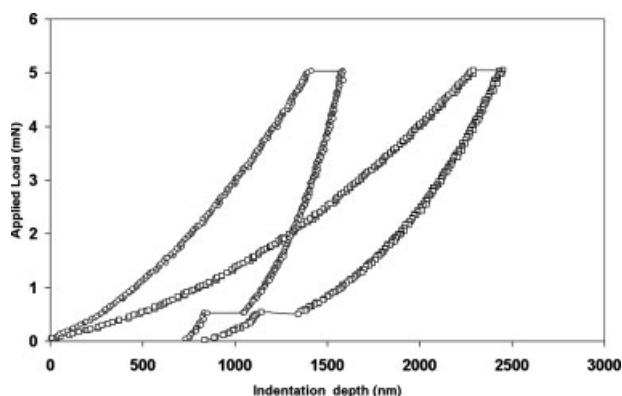


Figure 3 Typical dry (circles) and wet (squares) indentation curves for T30. Berkovich indenter loading at 0.2 mN/s to a peak load of 5 mN. Fifty seconds hold at maximum load for creep. One hundred twenty seconds hold at 90% unloading for creep recovery.

RESULTS AND DISCUSSION

Illustrative indentation curves for T30 dry and wet are shown in Figure 3. Similar curves (not shown) were obtained on N6. Significant indentation creep (Fig. 3 and Table III) and creep recovery (Table III) effects are observed during the hold periods on N6 and T30 both wet and dry. The appreciable creep recovery indicates that the behavior is viscoelastic/viscoplastic. Figure 4 shows the increase in depth during the 50 s hold at peak load for the two indentations in Figure 3.

Hardness and elastic modulus were determined from unloading curves using the procedure of Oliver and Pharr.¹⁸ Although the reliability of absolute values has been questioned due to the accuracy in determining the contact depth (and hence area) on viscoelastic materials, the unloading slope approach should be sufficient to determine the relative changes we are concerned with here. Table II shows how the hardness and reduced modulus vary with

applied force and test medium. Dry data show only minimal difference in mechanical properties between the two Nylon 6 samples. Hardness and elastic modulus determined from the Oliver and Pharr procedure are almost invariant with load, increasing by $\sim 10\%$ for the lowest indentation load compared with the largest. Although the loading rate was reduced, the loading time for the smaller indentations was lower and this may have contributed to the slight effect rather than any particular existing gradient in mechanical properties.

Testing wet shows some difference between the two materials with greater decreases in hardness and modulus for T30 than N6, particularly, for the smaller load indentations (see also Fig. 5). The data imply that T30 is more effectively plasticized than N6 and water is more effective at plasticizing the surface layers on T30 which may be due to the slightly lower molecular weight of T30.

There were no observable changes in indentation behavior in leaving the samples immersed in fluid for longer periods. It is reasonable to assume that 24 h immersion is more than adequate for saturation of the surface layers of the polymers, consistent with Tabor's original microindentation data.³

Including hold periods in the load history (see Fig. 2) allows investigation of creep and creep recovery processes. As mentioned earlier, we have recently investigated eqs. (1) and (2) and the use of $A/d(0)$,^{9,10} as a measure of time-dependent deformation occurring during the hold segment at peak load in an indentation test. The fit is good and both samples show similar $A/d(0)$ values dry. Figure 4 shows that there is a small increase in indentation creep in water. Despite this, the proportion of time-dependent deformation compared with the total deformation ($A/d(0)$), decreases significantly in water on N6 and more notably on T30.

On the basis of evidence from nanoindentation data at ambient and elevated temperature, we have

TABLE III
Creep Parameters

	A (nm)	B (s^{-1})	$d(0)$ (nm)	$A/d(0)$	Creep recovery rate (nm/s)
T30 dry 0.5 mN	23.1 \pm 2.8	0.45 \pm 0.15	346 \pm 35	0.067 \pm 0.006	0.07 \pm 0.01
T30 wet 0.5 mN	26.4 \pm 3.5	1.07 \pm 0.38	764 \pm 58	0.034 \pm 0.007	0.12 \pm 0.02
T30 dry 5 mN	61.7 \pm 4.9	0.31 \pm 0.08	1339 \pm 33	0.046 \pm 0.003	0.28 \pm 0.02
T30 wet 5 mN	48.1 \pm 7.9	0.49 \pm 0.11	2403 \pm 156	0.020 \pm 0.003	0.67 \pm 0.11
T30 dry 10 mN	82.8 \pm 3.3	0.18 \pm 0.02	2116 \pm 30	0.039 \pm 0.002	0.50 \pm 0.02
T30 wet 10 mN	68.2 \pm 6.8	0.27 \pm 0.05	3539 \pm 122	0.019 \pm 0.001	0.85 \pm 0.05
N6 dry 0.5 mN	20.8 \pm 1.9	0.58 \pm 0.13	343 \pm 28	0.061 \pm 0.006	0.09 \pm 0.02
N6 wet 0.5 mN	8.7 \pm 1.0	3.3 \pm 0.8	567 \pm 29	0.015 \pm 0.001	0.35 \pm 0.04
N6 dry 5 mN	57.6 \pm 2.3	0.30 \pm 0.07	1422 \pm 42	0.041 \pm 0.002	0.39 \pm 0.02
N6 wet 5 mN	38.7 \pm 3.1	0.56 \pm 0.13	2093 \pm 40	0.018 \pm 0.002	0.51 \pm 0.07
N6 dry 10 mN	83.7 \pm 7.9	0.18 \pm 0.03	2129 \pm 86	0.039 \pm 0.003	0.60 \pm 0.06
N6 wet 10 mN	51.7 \pm 2.2	0.29 \pm 0.05	3181 \pm 110	0.016 \pm 0.001	0.75 \pm 0.07

Creep parameters from eq. (1) using the data during the 50 s hold at peak load.

suggested elsewhere that $A/d(0)$ correlates with $\tan \delta$.^{15–17} The decrease in $A/d(0)$ when wet would then be explained by a decrease $\tan \delta$ at the testing temperature due to a decrease in magnitude of the $\tan \delta$ peak and a shift in the glass transition temperature region. Absorption of 1% water has been shown to reduce the α -peak (T_g) by 30°C in Nylon 6,12.⁹ A pronounced reduction in glass transition temperature on water absorption has similarly been reported by Grunina et al. for a range of biopolymers, such as DNA and elastin, using differential scanning calorimetric methods.¹ It has been suggested that addition of water influences the molecular packing in amorphous polymers such as Nylon.⁹ Bonded water molecules lower the amount of interchain H-bonds enabling closer interchain packing density. Decreased cohesive forces resulting from breaking the H-bonds could be responsible for the shift in T_g . The free-volume concept of the glass transition breaks down, as it might otherwise be assumed that the peak would shift to higher temperatures with increasing density.⁹

The reduction in the creep parameter $A/d(0)$ when wet has an influence on hardness and modulus determined from unloading slope analysis after the hold at peak load. It is known that the altering the extent of creep by changing the hold time influences hardness and to a lesser extent elastic modulus on polymeric materials. Altering the creep by changing the test medium should have a related effect. From the data in Table II it is possible to determine the relative change in hardness and modulus on immersion and saturation in water. The ratios of hardness and modulus when wet compared to when dry [H (wet/dry) and E (wet/dry)] are shown for each indentation force in Figure 5. Although there is a decrease in elastic modulus of about 60–70% on immersion the corresponding decrease in hardness is only $\sim 50\%$. The influence of creep on hardness is

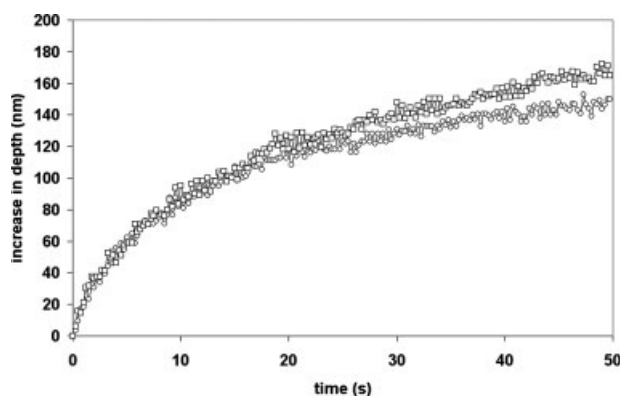


Figure 4 Nanoindentation creep during 50 s hold at 5 mN on T30 after loading at 0.2 mN/s with a Berkovich indenter; wet, \square ; dry, \circ .

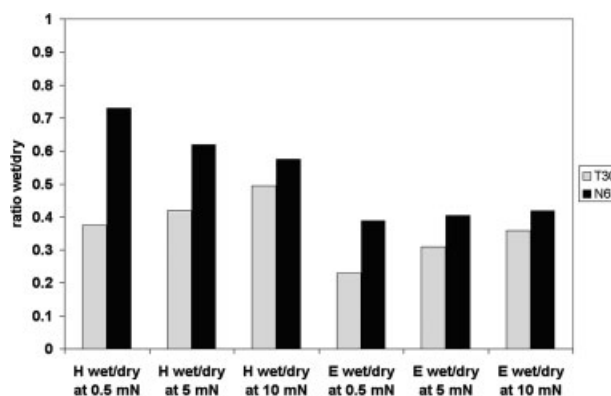


Figure 5 Ratios of hardness (wet/dry) and modulus (wet/dry).

lesser when testing Nylon in water, which is consistent with the lower relative creep when wet. Figure 5 also emphasizes the differences in mechanical behavior between the samples when wet because of the more effective plasticization of T30.

The elastic recovery parameter is defined as the (maximum depth – contact depth)/contact depth. It has been shown elsewhere¹⁷ that this parameter exhibits a minimum near to the glass transition temperature, where the $\tan \delta$ peak is greatest. The shift in T_g and decrease in $\tan \delta$ on plasticization would therefore be expected to have a similar influence on the elastic recovery parameter. The increase in elastic recovery parameter when wet compared with dry is by about 40%, which is consistent with this.

CONCLUSIONS

1. Results with a fluid cell fitted to a commercial nanoindenter are presented in this publication. Measurements on Nylon 6 samples immersed in water for >24 h were compared with tests under usual ambient ($\sim 50\%$ RH) conditions. As expected, water absorption caused clear differences in the mechanical properties of the polymers.
2. The creep parameter $A/d(0)$ —a measure of the proportion of time-dependent deformation compared with the total deformation—decreases significantly in water. We have suggested elsewhere that $A/d(0)$ correlates with $\tan \delta$. The observed reduction in $A/d(0)$ when wet is consistent with a decrease in the $\tan \delta$ peak due to a shift in the glass transition temperature when wet.
3. Changes to the indentation creep response when wet influence the hardness and modulus determined from analysis of the unloading curve; with hardness decreasing by around 50% and elastic modulus by around 65% on immersion. The difference may be related to the role

of creep. The smaller effect of creep on hardness is consistent with the lower relative creep when wet.

4. The use of a fluid cell in conjunction with a humidity control chamber (also possible in commercial nanoindentation systems) would extend the range of nanomechanical testing to cover virtually the entire range of possible moisture content (~ 5 – 100% RH) and is expected to have applications in testing biological samples and polymeric materials at highly localized scale inaccessible to other testing techniques.

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References

1. Grunina, N. A.; Belopolskaya, T. V.; Tsereteli, G. I. *J Phys Conference Series* 2006, 105, 40.
2. Round, A. N.; Yan, B.; Estephan, R.; Stark, R. E.; Batteas, J. D. *Biophys J* 2000, 79, 2000, 2761.
3. Cohen, S. C.; Tabor, D. *Proc Royal Soc London Ser A* 1966, 291, 186.
4. Amuzu, J. K. A. *J Mater Sci Lett* 1984, 3, 291.
5. Stuart, B.; Briscoe, B. *Poly Int* 1995, 38, 95.
6. Newman, B. A.; Kim, K. G.; Scheinbeim, J. I. *J Mater Sci* 1990, 25, 1779.
7. Hahn, M. T.; Hertberg R. W.; Manson, J. A. *J Mater Sci* 1986, 21, 31.
8. Ashida, M.; Noguchi, T.; Mashimo, S. *J Appl Polym Sci* 1984, 29, 4107.
9. McCrum, N. G.; Read, B. E.; Williams, G., Eds. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover Publications: NY, 1991; pp 478–497.
10. Fischer-Cripps, A. C. *Mater Sci Eng A* 2004, 385, 74.
11. Cheng, L.; Xia, X.; Scriven, L. E.; Gerberich, W. W. *Mech Mater* 2005, 37, 213.
12. Beake, B. D.; Chen S.; Hull, J. B.; Gao, F. *J Nanosci Nanotechnol* 2002, 2, 73.
13. Beake, B. D.; Zheng S.; Alexander, M. R. *J Mater Sci* 2002, 37, 3821.
14. Beake, B. D.; Goodes, S. R.; Smith J. F.; Gao, F. *J Mater Res* 2004, 19, 237.
15. Beake, B. D.; *J Phys D: Appl Phys* 2006, 39, 4478.
16. Beake, B. D.; Bell, G. A.; Brostow, W.; Chonkaew, W. *Polym Int* 2007, 56, 773.
17. Gray, A.; Beake, B. D. *J Nanosci Nanotechnol* 2007, 7, 253.
18. Oliver, W. C.; Pharr, G. M. *J Mater Res* 1992, 7, 1564.