

Hydration in a New Semiaromatic Polyamide Observed by Humidity- Controlled Dynamic Viscoelastometry and X-ray Diffraction

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ABSTRACT: Hydration in a new semiaromatic polyamide, named polyamide 9-T (PA9-T), a copolymer of terephthalic acid with *n*- and *iso*-nonanediamine, is studied by dynamic viscoelastic analysis under controlled humidity conditions and wide-angle x-ray diffraction analysis in comparison with common polyamide nylon 6. The storage modulus of PA9-T is retained at up to 60 °C with increasing humidity, then dropping with further increases in temperature past 70 °C. The decrease in mechanical properties at 70 °C due to moisture uptake is found to be substantially improved by annealing to develop molecular packing and/or crystallization. In contrast, the storage modulus of very highly crystallized (50% crystallinity) nylon 6 decreases markedly with humidity at low temperatures such as 20 °C. Thus, PA9-T retains its mechanical properties in humid atmospheres at much higher temperatures than nylon 6. The crystalline x-ray diffraction peaks for nylon 6 corresponding to (002) + (202) of α form shift upon absorption of moisture, speculated to be due to the weakening of hydrogen bonds and the subsequent conformational disordering of the chains. Unlike nylon 6, the crystalline peaks of PA9-T do not shift due to moisture uptake. This is considered to be attributable to that the long aliphatic chain in PA9-T forms the large hydrophobic domain, rendering PA9-T less hygroscopic than nylon 6. Additionally, strong hydrogen bonds formed by terephthalamide residues together with a strong stacking force of phenylene groups may also repel water, preventing moisture bind with the amide groups of PA9-T crystals.

Keywords: humidity; poly(nonamethylene terephthalamide); dynamic viscoelastometry; crystalline polyamide; nylon 6

1. Introduction

Polyamides are generally known for their high water absorption capability. Once absorbed, the water is considered to be present in the free volume, inducing property changes through the connection of molecular chains to form hydrogen bonds and hydrogen bridges.¹ In commercially available and thermoplastic polyamides, moisture has been reported to act as a plasticizer in the polymer matrix, lowering the glass-transition temperature (T_g).² The scission of hydrogen bonds by water is expected to cause undesirable changes or decrease of

mechanical properties. As such, the changes in structure and properties of various polyamides due to moisture absorption have been investigated over a wide range of temperature, including polymeric materials such as nylon 12^{1,3}, nylon 66^{4,5,6}, nylon 1010⁵, nylon 6⁷, nylon 610^{5,8}, nylon 612⁹, recycled nylon 66¹⁰, and semiaromatic polyamide synthesized using aliphatic diamine and metha- or para-oriented phthalic acids¹¹.

Poly(nonamethylene terephthalamide), named as PA9-T, is a new type of a semiaromatic polyamide and an engineering thermoplastic, that has been developed by Kuraray Co. Ltd.¹² and commercialized as GENESTARTM. The concept of PA9-T has been arisen in order to make a new polyamide with higher heat resistance possessing processability by melt-processing. PA9-T was first synthesized incorporating the nonamethylene-group of only normal chain into terephthalamide structure, and has a relatively high melting temperature of ca. 310 °C for melt-processable polyamide. Later on, in order to enhance the melt-processability by lowering of its melting point, another grade was produced by replacing a part of *n*-nonanediamine with *iso*-nonanediamines to copolymerize terephthalic acid, and the resultant melting point was decreased up to around 260-270 °C.

PA9-T has recently received an extensive attention due to a number of outstanding properties. When compared to other heat resistant polyamides excepting wholly aromatic polyamides, PA9-T has several superior features such as low moisture absorbency, high heat resistance, high abrasion resistance, high chemical resistance, and superior dimensional stability. Especially, it has high blister resistance at 260 °C, a higher reflow temperature of lead-free solder, thus, it has been highly valued as a corresponding material in electronics industry. Additionally, due to its high heat-moisture resistance, PA9-T exhibits excellent mechanical properties and dimensional stability in highly humid atmosphere even at high temperature. For example, after heat-moisture treatment at 140 °C for 1500 min under high pressure, the PA9-T fiber retained 85% of its original strength, compared to only 10% in the case of a polyester fiber.¹³ Thus, PA9-T is currently being considered as a replacement for the polyester and common polyamide in aprons and curtains, especially in the medical and food industries, where they are sterilized by vapor-heat treatment. These properties shown above are superior to those of other thermoplastic polyamides including semiaromatic polyamides. For further spreading the industrial applications of PA9-T, understanding of the detailed analyses of structure and properties against moisture has been necessary, because there is a possibility that humidity may influence the properties due to its amide groups.

The effect of humidity on properties of solid polymers with polar groups has been reported to be non-negligible.¹⁴ In this regard, humidity-controlled dynamic viscoelastic analysis (DVA) represents a modern, sophisticated technique for detecting simultaneous changes in

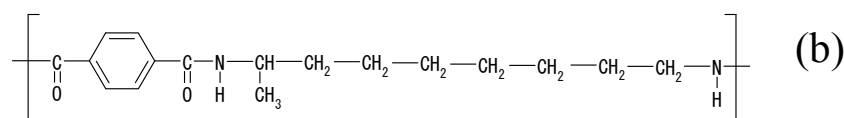
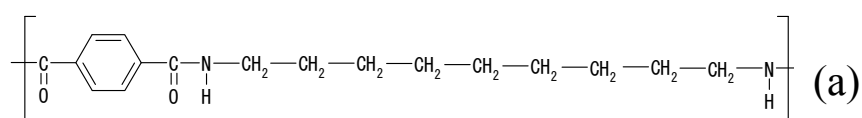
the sample with gradual change of relative humidity (RH), which can be varied linearly or stepwise at prescribed temperature.¹⁵ This technique makes it possible to discuss in detail the role of moisture in the physical and mechanical character of polymers.

In the previous paper, the authors clarified the influence of moisture in the several relaxation processes of PA9-T through conventional temperature-controlled DVA.¹⁶ The location of water in the PA9-T polymer matrix was also investigated by temperature-controlled wide-angle x-ray diffraction (WAXD) and temperature-controlled Fourier transform infrared spectroscopy (FT-IR). Both studies strongly indicated that water exists solely in the amorphous regions of the polymer.¹⁶ The present study attempts to better understand the features underlying the role of water in PA9-T through humidity-controlled DVA and WAXD. The results for PA9-T are compared with the results for another common thermoplastic polyamide, nylon 6, which has been investigated extensively regarding the influence of moisture.^{14,17-19}

2. Experimental

2.1 Materials

PA9-T is a random copolymer prepared by condensation polymerization of terephthalic acid with *n*- and *iso*-nonamethylenediamines; namely 1,9-nonanediamine and 2-methyl-1,8-octanediamine. The chemical formulae of the two repeating units are as follows:



The structure of PA9-T used in this study consists of an equimolar ratio (50/50) of (a) and (b).

In the nomenclature of PA9-T, PA is an abbreviated form of polyamide, the numeral '9' indicates the number of C atoms in the diamine and 'T' represents first letter of terephthalic acid.

2.2 Sample Preparation

PA9-T and nylon 6 pellets were obtained from Kuraray Co. Ltd. and Toray Co. Ltd., respectively. Thin films of PA9-T and nylon 6 were prepared using a laboratory hot press. The pellets were compression-molded at 280 °C for PA9-T and 260 °C for nylon 6. The polymer was first melted under contact pressure between the two hot plates, then pressed very slowly to avoid bubble formation in films, and finally held for 3 min. Molten films in the hot press were then quenched in ice water to give films of approximately 50 μm in thickness.

For humidity-controlled DVA measurements, PA9-T film samples of different densities were prepared by annealing in a vacuum oven with a small tension at 180 °C for between 10 min and 1 h. The nylon 6 film was annealed at 180 °C for 1 h.

2.3 Measurements

Density (ρ) of the film samples was determined using small pieces at 25 °C by a floatation method using a reference solution of carbon tetrachloride and *n*-heptane. The volume crystallinity (X_v) of PA9-T was calculated from the densities of the crystalline and amorphous phases, $\rho_c = 1.2236$ and $\rho_a = 1.1261$ g cm⁻³, respectively,²⁰ using the following equation

$$X_v = (\rho - \rho_a) / (\rho_c - \rho_a)$$

The x-ray profile of the annealed nylon 6 exhibited the characteristics of the α -crystalline phase.²¹⁻²³ The crystallinity was calculated to be 50% based on the densities of the amorphous and α -crystalline phases, 1.10 and 1.17 g cm⁻³, respectively.²²

WAXD measurements were performed by transmission mode with a Rigaku Rotorflex RU-200B diffractometer using Ni-filtered CuK α radiation at 40 kV and 150 mA.

The storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) were obtained by DVA measurement using an ITK Co. DVA-225 instrument with stretching mode of 10 Hz and heating rate of 10 °C min⁻¹. In the present work, humidity-controlled DVA was performed at a scanning rate of 1% RH min⁻¹ from 15 to 90% RH at constant temperature. During humidity-controlled DVA, the change in sample length was observed to evaluate the elongation of the sample due to humidity effects. As sample thickness and the humidity scanning rate have been reported to influence the dynamic modulus and sample elongation¹⁴,

the film thickness was set at a constant ca. 50 μm and the scanning rate was maintained constant at 1% RH min^{-1} in all measurements.

3. Results and Discussion

3.1 Characteristics of PA9-T samples

Table 1 lists the density and volume crystallinity of as-prepared (unannealed) and annealed PA9-T films. The density of the as-prepared sample (1.132 g cm^{-3}) increased to 1.147 g cm^{-3} after annealing for 1 h. The corresponding crystallinity of these two samples was 6% and 21%, respectively. Figure 1 shows WAXD profiles for the as-prepared and annealed PA9-T films. For the samples annealed for more than 20 min, crystalline peaks due to a reflection originating from the fiber period of the PA9-T crystal are clearly visible at $2\theta \approx 5^\circ$. In the same samples, the peak at $2\theta \approx 20^\circ$ was much sharper and more intense. The peak position did not shift upon annealing, located in the same position irrespective of whether the samples were amorphous or crystalline. The peak at $2\theta \approx 20^\circ$ is attributable to a reflection of the distance between molecular chains, and demonstrates that this distance does not change upon crystallization.

Figures 2a and 2b show the storage modulus and $\tan\delta$ curves for the as-prepared and annealed PA9-T films. For the as-prepared films, E' initially falls abruptly then rises again at around 140°C , reflecting the transition from glassy to a rubbery state at 120°C and subsequent crystallization at 150°C . That is, the crystallization temperature of this PA9-T film is about 150°C , indicating that the annealing temperature of 180°C is sufficient to crystallize PA9-T. For the sample annealed for 10 min, the fall and rise at around 140°C were much less extreme, which may at first glance be related to the increased crystallinity of the PA9-T film. However, the sample annealed for 10 min did not exhibit any crystal diffraction in the WAXD profile (Fig. 1), suggesting the formation of a partially ordered phase, such as a partially oriented polymer-chain stack held together by hydrogen bonds with some fraction of imperfectly ordered phase (intermediate between amorphous and crystalline) that does not produce crystal diffraction at $2\theta \approx 5^\circ$. It is found that annealing for more than 20 min is required to form the highly ordered phase that produces strong crystalline peaks in the WAXD profiles. This can be considered to be a unique characteristic of PA9-T. Evidence of the existence of an intermediate phase has also been observed previously for laser flow-drawn PA9-T fibers, which exhibited increased density and birefringence in contrast to as-spun

(amorphous) fibers that do not display any clear sign of crystal formation in WAXD photographs.²⁰

For the annealed samples, β_2 and β_1 relaxations appear in the $\tan \delta$ curve, and have been previously identified as so-called ‘water peaks’ based on the complete disappearance of these peaks with the evaporation of moisture and high intensity in water-soaked samples.¹⁶ The value of $\tan \delta$ curve decrease with increase of annealing time, implying the gain of restriction of thermally molecular motion. (Exceptionally, the $\tan \delta$ curve is little bit higher for 1h annealed sample. This is considered to be caused by moisture absorption during sample setting for DVA measurement.) From the fall and rise in the E' curve and the height of the α -relaxation peaks corresponding to T_g in the $\tan \delta$ curve, it is evident that the as-prepared sample is quite amorphous. With increasing annealing time, E' improves remarkably and T_g shifts towards higher temperatures due to an increase in crystallinity.

3.2 Humidity-controlled DVA measurement

Figure 3 illustrates the humidity dependence of the viscoelastic properties of the as-prepared PA9-T film at temperatures of 50, 60 and 70 °C. In the author’s previous report on PA9-T,¹⁶ it was found that after the sample had been dried in a vacuum oven at high temperature (~200 °C), environmental moisture reentered into the specimen while the sample was being loaded into the DVA instrument for measurement. This can be resolved by both drying the sample (at T_g) and performing measurement in the closed environment of the DVA apparatus. In the present study, all samples were initially dried by heating up to the T_g temperature of 130 °C (below the crystallization temperature)²⁴ in the DVA instrument prior to humidity scanning. The nonoccurrence of crystallization was confirmed during heat-drying by WAXD. As seen in figure 3a, the E' values for 50 and 60 °C remained relatively constant over the whole range of RH, whereas the E' value decreased gradually at 70 °C from 60% RH. The E'' curve displays the same trend.

The samples became softer with increasing RH and were elongated by the light tensile force applied by the DVA apparatus to prevent slackening of the sample¹⁴. The samples exhibited up to 7% elongation in case of the scanning at 70 °C, as shown in figure 3c. The present result of decreasing E' with moisture uptake at 70 °C may be reasonably related to the disappearance of the water peak (β_1 relaxation) at around 70 °C in the $\tan \delta$ curve. These results imply that the mechanical properties of amorphous PA9-T are almost insensitive to

moisture at up to 60 °C, but become appreciably affected by moisture at 70 °C, particularly above 60% RH.

Humidity-controlled DVA was also performed at 70 °C for annealed PA9-T samples with various densities in order to observe the dependence of the mechanical properties on both crystallinity and humidity. Figure 4 shows the variation in E' , E'' and elongation with at 70 °C. Similar to the as-prepared sample, E' dropped with increasing RH for samples annealed for up to 20 min. However, this drop in E' was considerably suppressed for samples annealed for 30 min and 1 h. E'' and elongation increased with RH for all samples, but the degree of increase tended to become smaller with increasing annealing time, that is, with increasing crystallinity. For example, the as-prepared sample (6% crystallinity) became elongated by up to 7%, whereas the sample annealed for 1 h (21% crystallinity) exhibited less than 1% elongation. The high elongation of the as-prepared sample may be due to its low crystallinity. The sample annealed for 10 min exhibited very similar behavior to the other annealed samples in terms of E' and E'' , yet its elongation was more similar to that of the as-prepared sample. This may reflect the characteristics of its structure as an intermediate phase between the amorphous and crystalline states, being sensitive to moisture like the perfectly amorphous phase. The PA9-T films annealed for longer periods, with crystallinity of 17% and 21%, exhibited almost no change (or only a very slight change) at 70 °C in terms of mechanical properties regardless of the RH.

Figure 5 illustrates the dependence of the viscoelastic properties of nylon 6 annealed at 180 °C for 1 h on humidity. All nylon 6 film samples were dried by heating to 100 °C in the DVA instrument prior to humidity-controlled DVA scanning. As shown in the figure, the E' of nylon 6 decreased gradually with increasing RH at all measurement temperatures (20–50 °C), with the rate of decrease becoming more rapid with increasing temperature, particularly near T_g (i.e., 50 °C). E'' curves exhibit peaks, and the peak position shifts to lower humidity with increase of measurement temperature. This means dissipation of mechanical energy due to molecular slippage of nylon 6 by water occurs more easily at higher temperature. Elongation also increased with temperature. However, at all measurement temperatures, the nylon 6 film exhibited high sensitivity to moisture, despite its high crystallinity of 50%.

It should be noted from these results that under same annealing conditions (180 °C for 1 h), PA9-T reached a crystallinity of around 21% and nylon 6 reached 50%, yet PA9-T retains its mechanical properties at much higher temperatures than does nylon 6. Moreover, there is an

indication that the PA9-T crystals have a much higher resistance to moisture in comparison to that of nylon 6 crystals. Although most of the water is considered to penetrate into the amorphous regions, there have been some suggestions that water can also affect the ordering of crystalline regions^{17,19,25,26}. To examine this, the structural changes in the crystalline regions of PA9-T and nylon 6 accompanying hydration were investigated further.

3.3 Water in crystalline regions

In order to observe the affect of water in the crystalline regions of PA9-T and nylon 6, highly crystalline films were prepared by annealing as-prepared films at 230 and 190 °C, respectively, for 1 h in a vacuum oven under slight tension. Both samples were then soaked in water and boiled for 30 min to allow sufficient water to infiltrate into the films. WAXD profiles of both soaked films were then taken immediately. Other soaked films were dried in a vacuum oven at 180 °C for 1 h to remove water, after which WAXD measurements were taken. In this case, to prevent the re-absorbance of atmospheric moisture into the dried films, a closed system was used during WAXD measurement, and a constant dry N₂ gas flow was maintained around the film samples. To avoid instrumentation error, silicon powder was also applied to the samples for calibration against known values (111) of silicon at around $2\theta \approx 28.4^\circ$.

Figure 6 shows the WAXD profiles of dried and wet nylon 6 films. The position of the intense (200) peak of α -nylon 6 at low 2θ values, representing the distance between hydrogen-bonded chains, occurred in the same location for the wet and dry samples. In contrast, the second peak at $2\theta \approx 24^\circ$, representing the (002) + (202) peak of α -nylon 6 and corresponding to the distance between hydrogen-bonded sheets, was shifted noticeably in the wet sample. The corresponding lattice spacing d (measured from Bragg's equation^{27,28}) decreased from 3.697 to 3.667 Å upon becoming wet, implying that the changes in the lattice spacing of nylon 6 are not due to direct diffusion of water into the crystal lattice. However, this outcome is in agreement with the previous investigation by Murthy et al.¹⁷, according to whom the lattice spacing change may occur due to swelling of the non-crystalline regions, ultimately causing some lateral rearrangement of hydrogen-bonded sheets in the crystalline regions. In humidity-controlled FT-IR measurements, Zhou et al.¹⁴ found that moisture induced disordering in the crystalline region of moistened nylon 6 film. Softening of the hydrogen bonds and conformational disordering of the chains were speculated to occur as effects of water absorption. Thus, considering the humidity-controlled DVA results obtained

in this study, the nylon 6 crystals appear to be affected by moisture, with a resultant degradation of mechanical properties.

Figure 7 shows the WAXD profiles of dried and wet PA9-T films. The sharp crystalline peak observed at $2\theta \approx 20^\circ$ did not change upon becoming wet, implying that the lattice spacing of the PA9-T crystal is not changed by the absorption of moisture. However, on closer inspection, the WAXD profiles in figure 7 appear to consist of several peaks that cannot be individually resolved in either the wet or dry samples. It is presumed that the PA9-T is difficult to crystallize as only one major peak is observed in the equatorial plane at $2\theta \approx 20^\circ$ for even samples annealed for a long time at 230°C . This temperature is high enough to cause crystallization, being very close to the onset of crystalline melting point of PA9-T crystals i.e., 260°C as determined by DSC.²⁰ However, it is considered that a sample of much higher crystallinity is necessary to obtain more perspicuous data regarding the effect of water in PA9-T crystals. To obtain such data, it will be necessary to elucidate appropriate conditions for resolving the individual crystal peaks.

In another attempt to resolve the XRD peaks, PA9-T film was annealed at much higher temperatures, such as near T_m , using a hot press. After testing a range of temperatures and durations, an optimal condition for separating the XRD peaks was obtained: annealing at 255°C for 5 min, which is within the temperature range of crystal melting of PA9-T. Figure 8 shows the WAXD profiles of dried and wet PA9-T films annealed under these conditions. No significant change in the positions of the two diffraction peaks was observed after the infiltration of water, indicating that the PA9-T crystals are not affected by water. This outcome supports our previous findings based on temperature-controlled WAXD that water does not affect the crystalline regions of PA9-T.¹⁶ This resistance to water absorption can be attributed to that the longer 9- or 8-methylene sequences in the repeating unit of PA9-T may form larger hydrophobic domains by aggregating of the sequences, and the stronger hydrogen bonding by terephthalamide residues compared to nylon 6 may prevent water from binding with amide groups. These may be the prime factors for the lower hygroscopicity of PA9-T (ca. 0.17%)¹². It is then likely that the resistance of PA9-T crystal to moisture affects greatly contributes to the retention of its mechanical properties at high humidities, particularly in highly crystalline samples.

4. Conclusions

As-prepared PA9-T film was found to retain its mechanical properties in highly humid atmospheres at up to 60 °C, but to begin to decrease at 70 °C. The retention of mechanical properties with increasing humidity at 70 °C could be greatly improved by increasing the crystallinity of the films through annealing. Conversely, the mechanical properties of very highly crystalline (50%) nylon 6 begin to decrease with increasing humidity even at 20 °C. The resistance of PA9-T to moisture can be attributed to the lower hygroscopicity of crystalline regions owing to long methylene groups and strong hydrogen bonds formed by terephthalamide residues compared to that of nylon 6.

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Figure and Table Captions

Table 1 Density and volume crystallinity of as-prepared and annealed (180 °C) PA9-T films.

Figure 1 WAXD profiles of as-prepared and annealed PA9-T films.

Figure 2 (a) Storage modulus (E') and (b) loss tangent ($\tan\delta$) curves for as-prepared and annealed PA9-T films.

Figure 3 Variation in (a) storage modulus (E'), (b) loss modulus (E'') and (c) elongation of as-prepared PA9-T samples with humidity at various temperatures.

Figure 4 Variation in (a) storage modulus (E'), (b) loss modulus (E'') and (c) elongation of as-prepared and annealed PA9-T samples with humidity at 70 °C.

Figure 5 Variation in (a) storage modulus (E'), (b) loss modulus (E'') and (c) elongation of annealed nylon 6 samples with humidity at various temperatures.

Figure 6 WAXD curves for annealed wet and dry nylon 6 films.

Figure 7 WAXD curves for wet and dry PA9-T films annealed at 230 °C.

Figure 8 WAXD curves for wet and dry PA9-T films annealed at 255 °C.

Table 1: Density and volume crsyntallinity of as-prepared and annealed (180° C) PA9-T films

Sample	Density (g cm ⁻³)	Crystallinity (%)
Original	1.1319	5.9
Annealed 10 min	1.1354	8.9
Annealed 20 min	1.1373	11.5
Annealed 30 min	1.1424	16.7
Annealed 1 h	1.1466	21.1

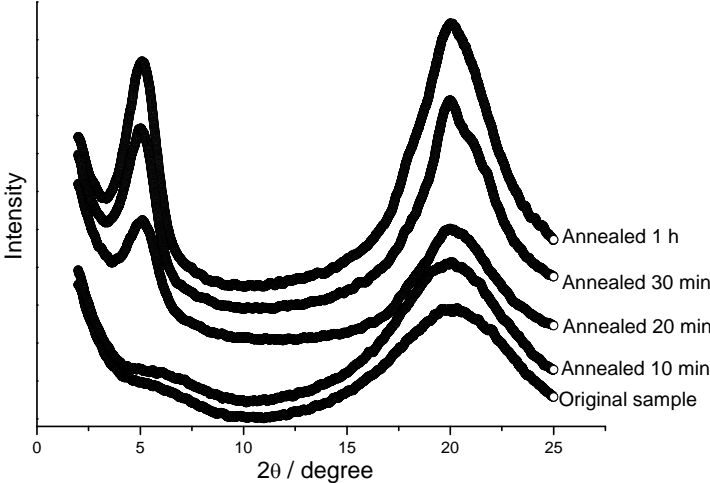


Figure 1. WAXD profiles of as-prepared and annealed PA9-T films

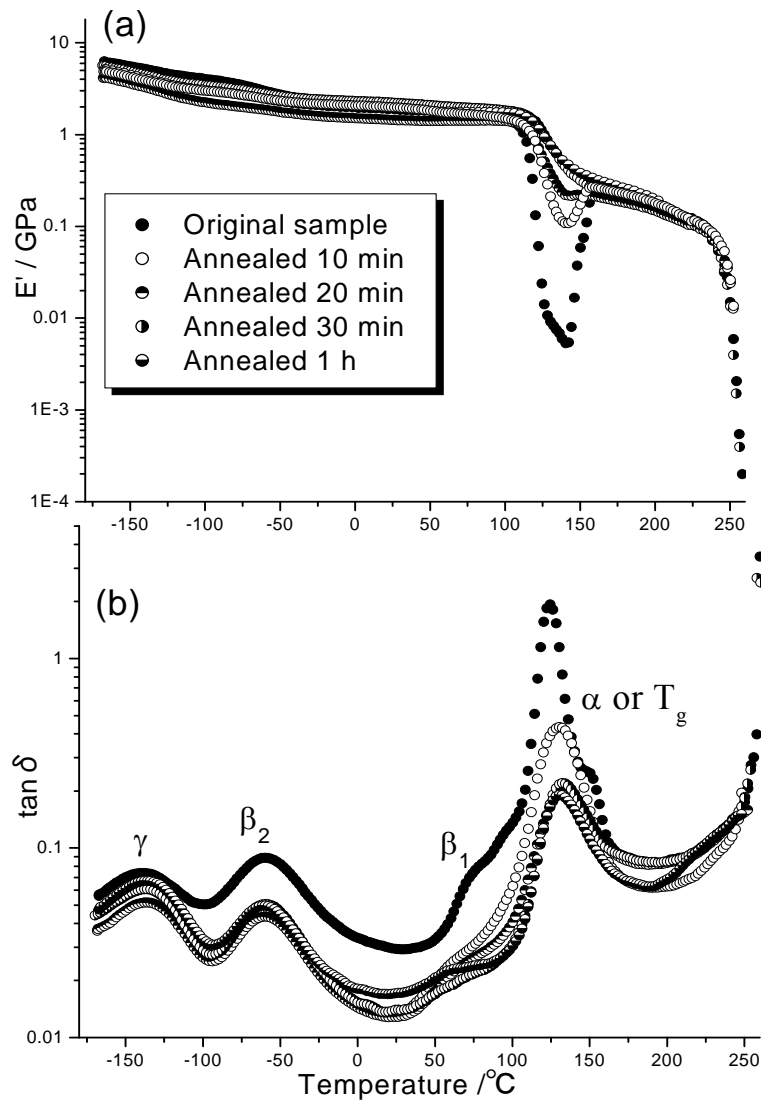


Figure 2. (a) Storage modulus (E') and (b) loss tangent ($\tan \delta$) curves for as-prepared and annealed PA9-T films

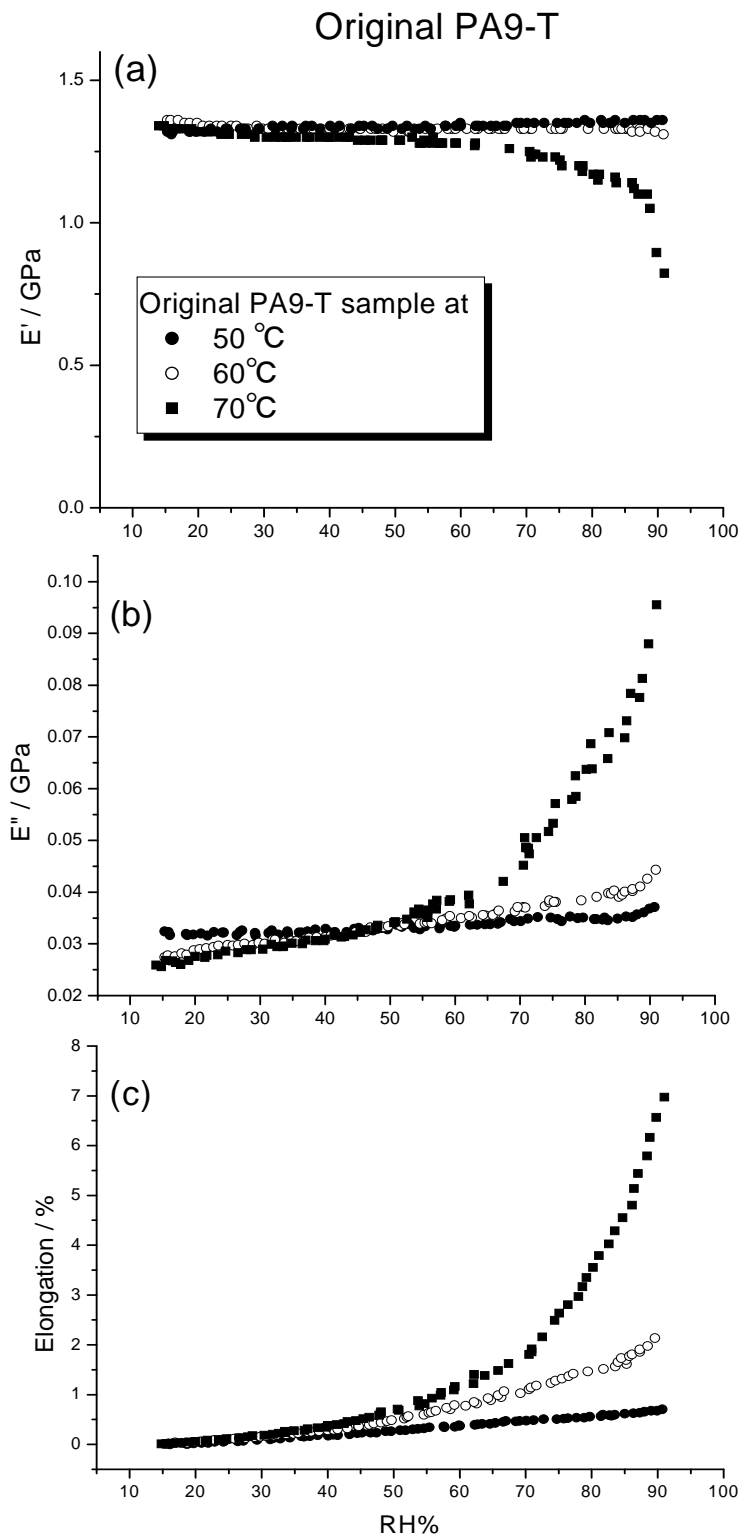


Figure 3. Variation in (a) storage modulus (E'), (b) loss modulus (E'') and (c) elongation of as-prepared PA9-T samples with humidity at various temperatures

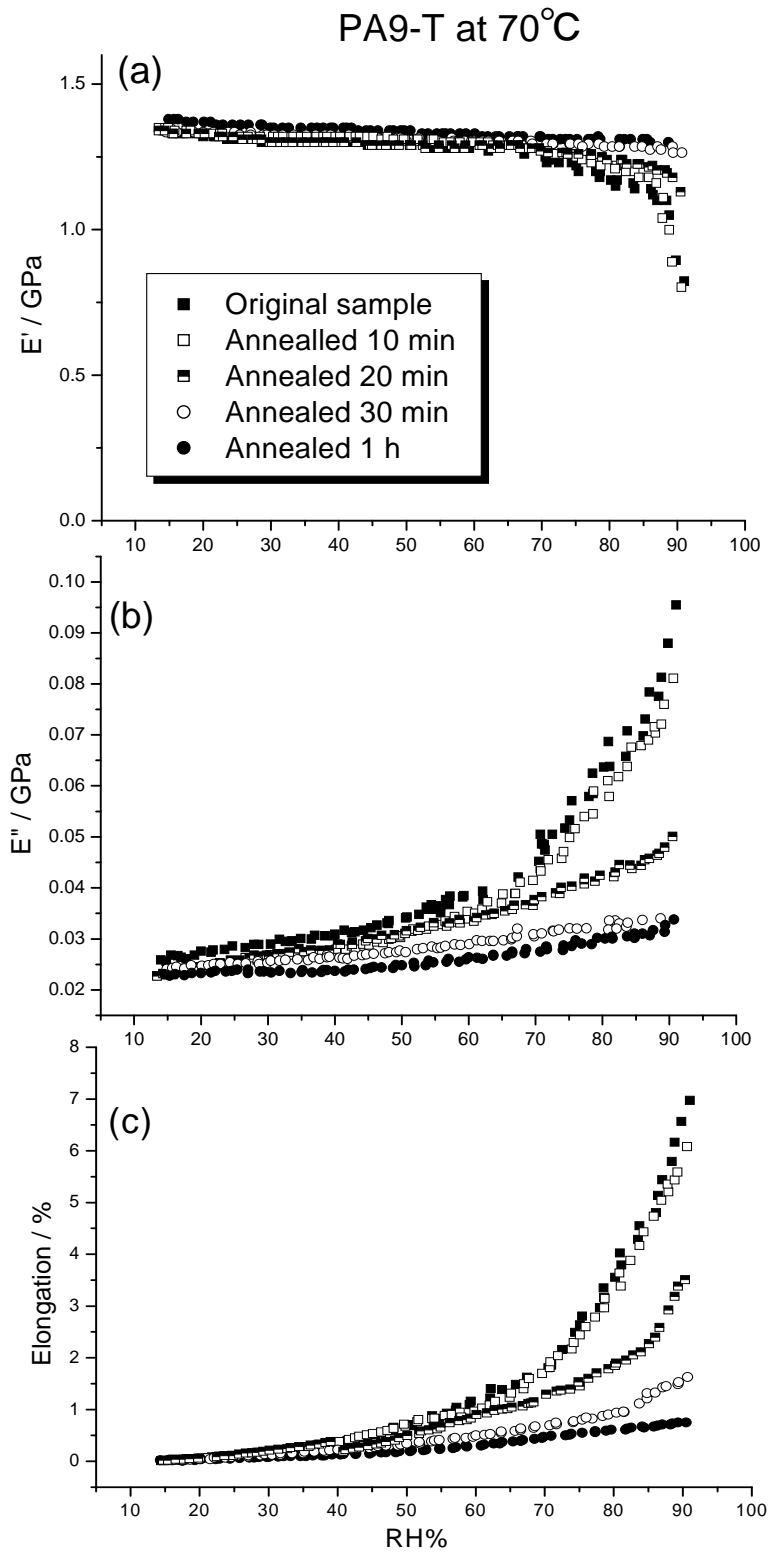


Figure 4. Variation in (a) storage modulus (E'), (b) loss modulus (E'') and (c) elongation of as-prepared and annealed PA9-T samples with humidity at 70 °C

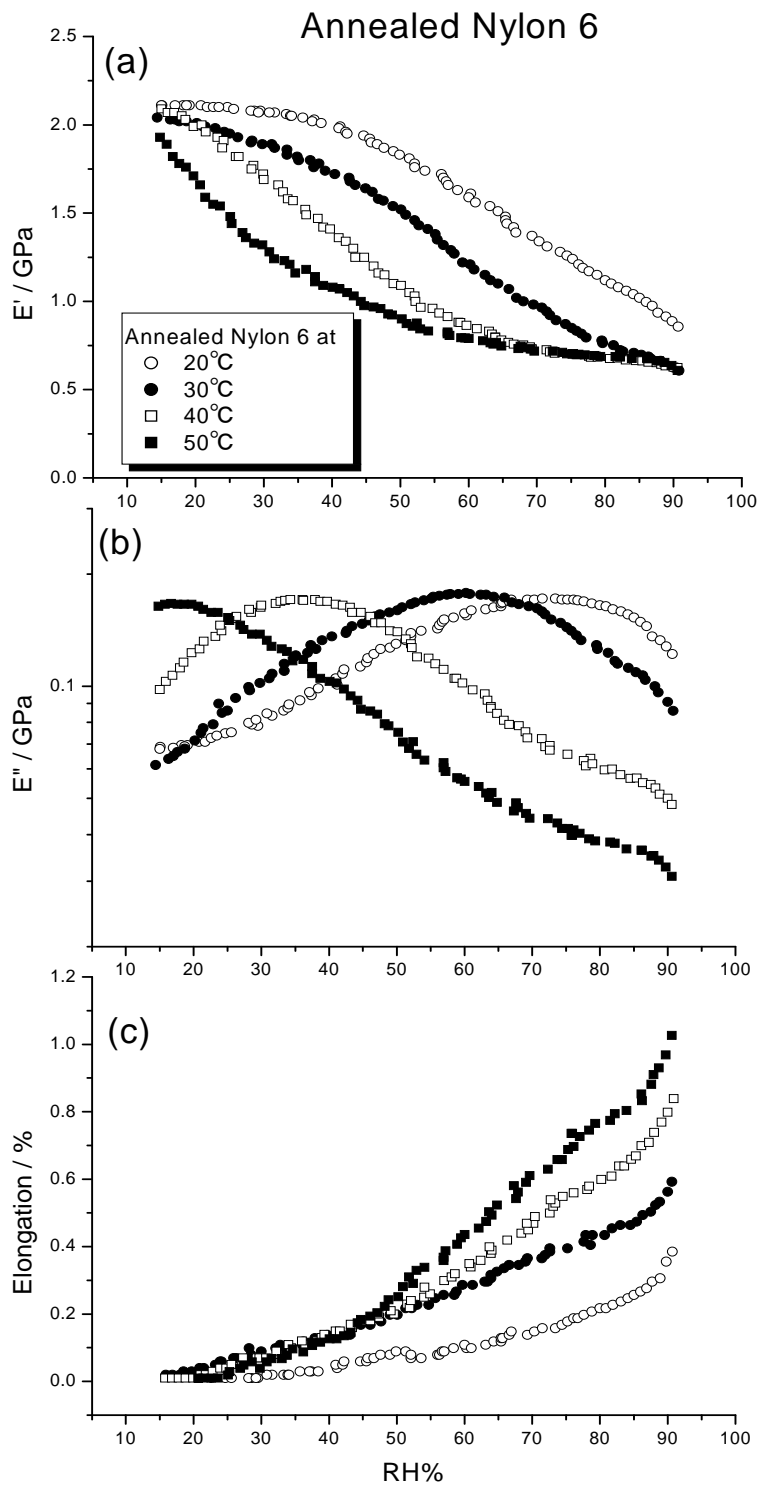


Figure 5. Variation in (a) storage modulus (E'), (b) loss modulus (E'') and (c) elongation of annealed nylon 6 samples with humidity at various temperatures

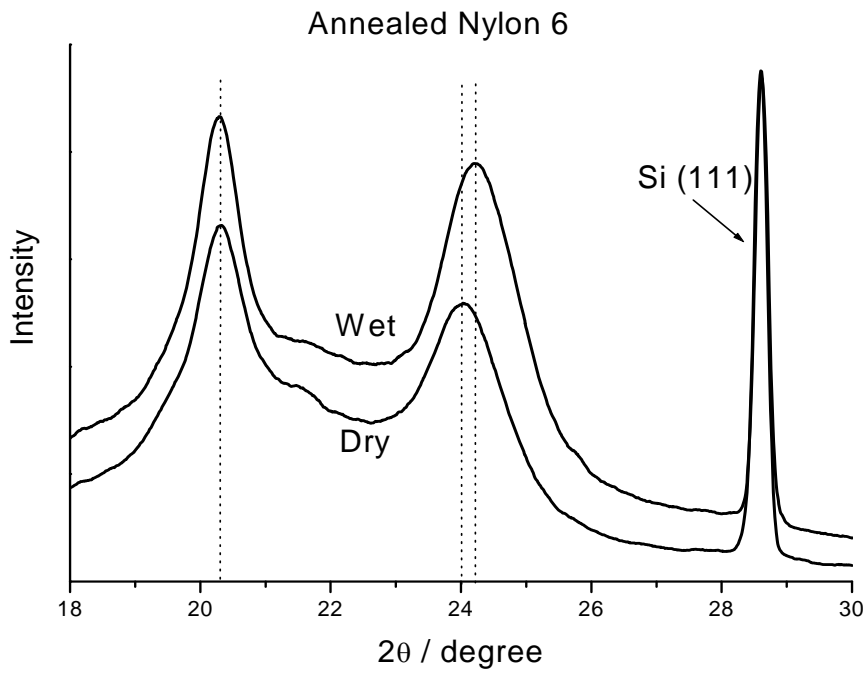


Figure 6. WAXD curves for annealed wet and dry nylon 6 films

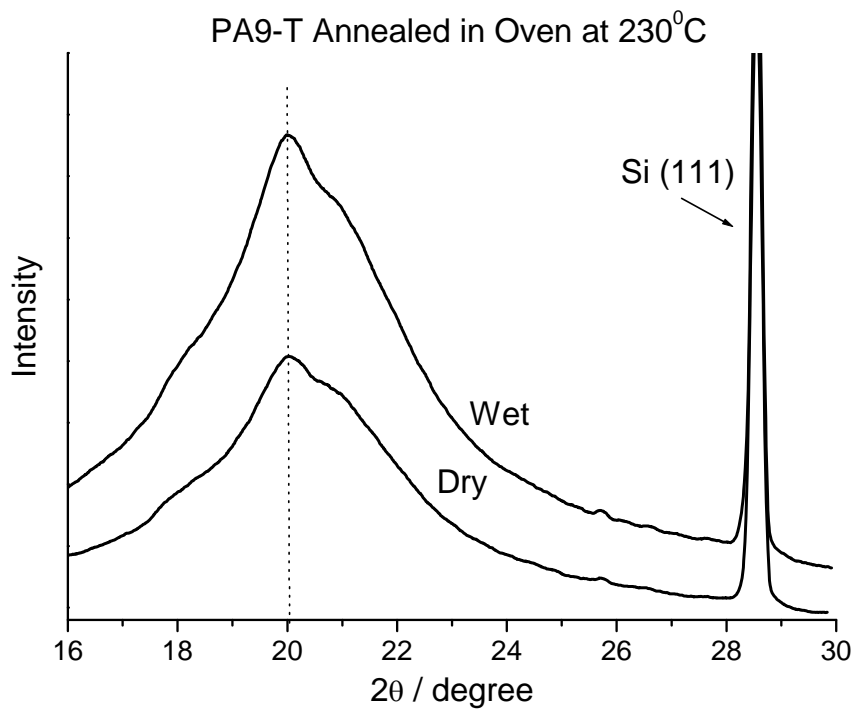


Figure 7. WAXD curves for wet and dry PA9-T films annealed at 230 °C

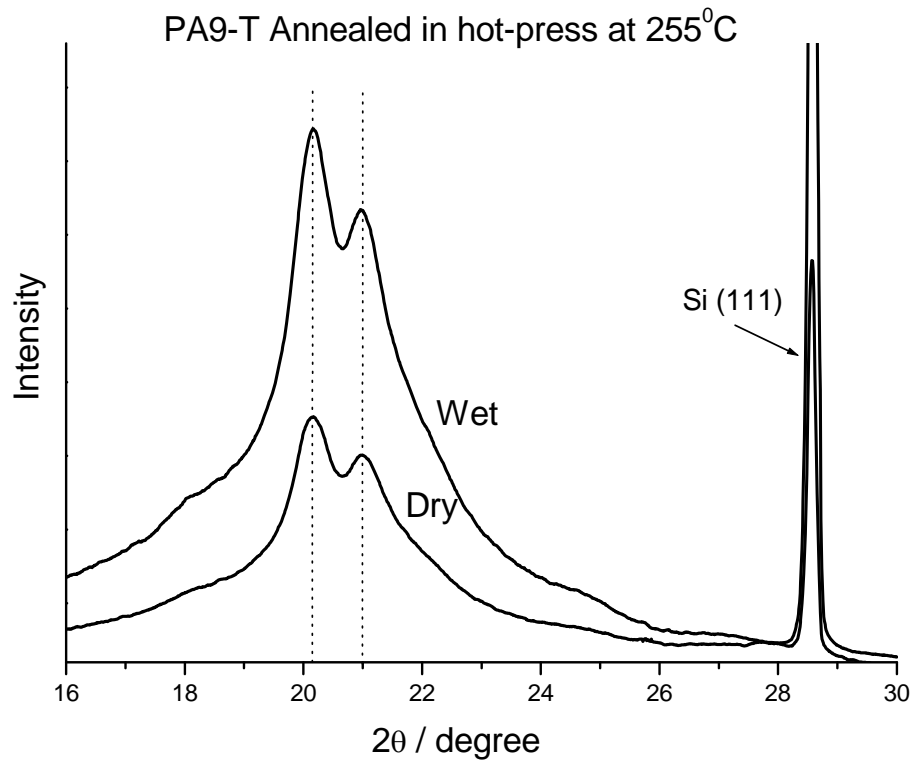


Figure 8. WAXD curves for wet and dry PA9-T films annealed at 255 °C