KEEPING WEBS WRINKLE-FREE AND DIMENSIONALLY STABLE AFTER HEATING

By
Dilwyn P Jones*

Abstract

Web dimensions are affected by tension, temperature and humidity. This paper will summarise the understanding of viscoelasticity, thermal and hygroscopic expansion, shrinkage, and their anisotropy, using polyester as an example. Thermomechanical and Dynamic Mechanical Analysis data are particularly useful to understand and predict substrate behaviour.

Many web processes involve heating to cure or dry a coating and subsequent cooling; but problems may arise as a result of the thermal behaviour. Wrinkles may form in long unsupported spans and be set-in as temperature falls. Tension whilst hot can increase the residual shrinkage, hence reducing the dimensional stability during subsequent processing and in the final product.

Predictions of web width changes during heating and cooling, together with the tendency of the web edges to travel straight, shows which phenomena are responsible for generating wrinkles. This analysis can show whether there is scope for optimising the temperature profile or placing a spreading device to reduce wrinkles.

1   Introduction

Heating webs for the purposes of drying or curing a coating or adhesive sometimes results in unwanted problems. Firstly, wrinkles may form and are set-in on cooling, resulting in visual defects and a loss of flatness. The final product, and subsequent processing steps, can be affected. Secondly, a thermal cycle may result in a change of dimension of the web and features on it, and also freeze-in strain, which reappears during subsequent heating. These changing dimensions cause problems when the registration of successive precise process steps is needed, and must be allowed for. The changes are caused by mechanical stress, temperature and changes in ambient moisture. Understanding the origin and magnitude of the effects is important for application in fields such as plastic electronics [1].

The second section of this paper focusses on the fundamental properties that underlie dimensional stability issues. Film manufacturers rarely give more information than Young's modulus and coefficient of thermal expansion in machine and transverse directions (MD and TD), and the amount of shrinkage after exposing the film to a particular temperature (e.g. 150°C for 30 minutes). The measurement and interpretation of more fundamental properties can become very involved: the approach here provides a framework that can be used for both quantitative calculations and qualitative understanding of processes. The third section describes the behavior of film in a long unsupported span in an oven where the web is both heated and cooled. Conditions which lead to unwanted dimension change, trough and wrinkle formation are identified so they can be avoided.

2   Web Properties

The properties of polymers depend not only on the name of the material, but also on the details of composition and manufacturing process. Users need to be aware that changing the supplier, grade and thickness can affect the performance of the substrate. Typical specifications are broad, and may not have been established for specialized applications such as flexible electronics. Mapping out all aspects of dimensional stability would be a very time-consuming and costly exercise. Instead, a streamlined approach, proposed here, leads to a set of properties that can be used for quantitative predictions, including mathematical models, and a more pictorial understanding of web behavior.

* Dr Dilwyn P Jones, Consultant, Emral Ltd
Mailing Address: Emral Ltd, Greenabella, Bentley Wynd, Yarm, Cleveland, TS15 9BS, UK
Tel +44 (0)7970 269575. *e-mail* Dilwyn.Jones@emral.co.uk *website* www.Emral.co.uk

2.1 Viscoelastic Behavior

Polymer films have a time-dependent response to stress, even for the lowest values [2]. Three manifestations are shown in Figure 1. Application of load (stress) leads to a gradually increasing strain (creep). When the load is removed, the strain gradually recovers. Secondly, rapid application of strain generates a stress that falls (relaxes) with time. Returning to zero strain reverses the direction of stress, which then decays towards zero. Thirdly, in an oscillatory test, strain lags behind stress. The in-phase component represents storage of recoverable energy, and the out-of phase component energy loss or dissipation. This combination of elastic and viscous behavior is described by a viscoelastic response.
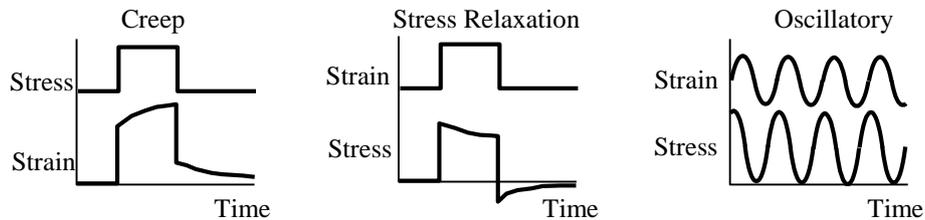

Figure 1 – 3 manifestations of viscoelastic behavior.

Standard tests for Young's modulus of polymers usually employ a linear increase of strain with time [3]. Viscoelastic behavior leads to curvature of the stress-strain plot even close to the origin, and a dependence on fitted slope with strain rate. The modulus value falls with increasing temperature: this too is a consequence of viscoelastic behavior.
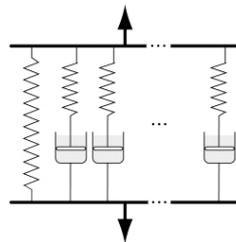

Figure 2 – Spring and dashpot model for viscoelastic solid.

At small strains, creep, stress relaxation and oscillatory tests show a linear relationship between stress and strain, and a superposition principle can be applied for loading sequences. The behavior is described by a model consisting of an arrangement of springs and dashpots. For stress relaxation, the easiest representation is to have a number N_k of Maxwell elements in parallel (figure 2). Strain is applied to all elements equally. The stress σ falls quickly in those with low dashpot viscosity, and slowly with high viscosity. Each element stress decays exponentially with a relaxation time τ_k and contributes an amount E_k to the initial stress, so the response to a strain ε imposed at $t=0$ is given by:

$$\sigma = E(t)\varepsilon = \left(E_0 + \sum_1^{N_k} E_k e^{-t/\tau_k}\right)\varepsilon \qquad \{1\}$$

Polymers are characterized by a very broad spread of relaxation times, covering many orders of magnitude. This reflects the range of sizes and local environments of chain segments in the disordered amorphous phase. In practical tests, there are always some elements that respond elastically and others whose stress decays very quickly. The "instantaneous" or elastic response in a test is not a true property, and depends on how quickly the load is applied. The constant E_0 that includes all elements that do not relax in the experimental timescale.

The results of different tests are related in simple viscoelastic materials. Full and accurate characterization of stress relaxation and creep requires specialized equipment and lengthy experimental programs, as reviewed in [**Error! Bookmark not defined.**]. However, thermal analysis instruments can be used to generate data quickly by testing for short durations at a range of temperatures.

2.2   Time-Temperature Superposition

The tests reported here were carried out using Dynamic Mechanical Analysis (DMA) in stress relaxation mode [4]. A 5 mm wide specimen was clamped at both ends, leaving a 15 mm gauge length. It was mounted in the instrument, surrounded by a furnace. A thermocouple next to the specimen monitors temperature and feeds back to the furnace to control temperature as required. A flow of dry air or nitrogen is used to promote thermal equilibration and prevent moisture absorption. A small preload of 1 mN was applied to keep the specimen taut prior to the application of the test strain. The temperature was ramped up to the each new test temperature then held at the value for 10 minutes. The test strain of 0.2% was applied for 30 minutes, recording load as a function of time. A complete set of data from 10 to 150°C took a day to acquire.

Typical results are shown in figure 3, with the load converted to modulus. Stress decays with time at each temperature. Behaviour close to room temperature is nearly elastic, but there is still some stress relaxation. The strongest time dependence occurs between 60 and 110°C. At higher temperatures, the modulus is small but only decays weakly during the test.
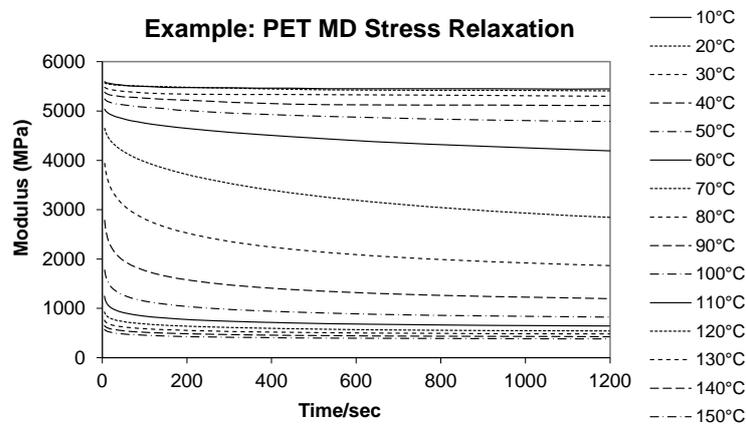

Figure 3 – Typical stress relaxation curves for PET film at different temperatures.

Time-temperature superposition (TTS) allows the viscoelastic performance to be predicted outside the range of experimentally measured times [2]. The procedure was carried out manually using Microsoft Excel®. The curves in figure 3 were replotted on a logarithmic time scale, then a horizontal shift applied to each curve in turn to coincide with the "master curve" as it builds up. A reference temperature of 50°C was chosen: this curve is not shifted. The resulting superposed curves are shown in figure 4, extending over 18 orders of magnitude in time.
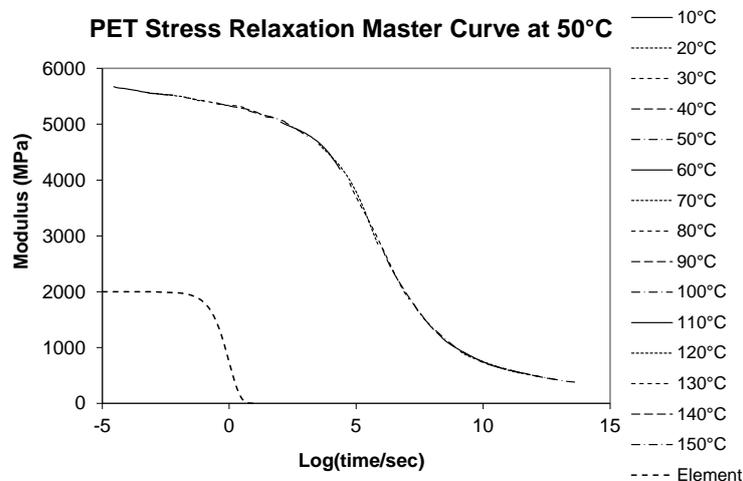

Figure 4 – PET stress relaxation curves at different temperatures superposed by a horizontal shift to produce a master curve. The dashed line shows the response of a single spring-dashpot element.

This "master curve" is fitted (using Excel® Solver) to the sum of terms in equation 1, for relaxation times of 0.001, 0.01,…10^{17} sec. Figure 4 also shows the response of an element with relaxation time 1 sec, showing it is very much narrower than the broad response of the material. Modern DMA instruments offer automated TTS analysis.

The shift factor relates "reduced time" t_r at reference temperature T_r to time t at actual temperature T.

$$t_r = a(T)t \qquad \{2\}$$

A plot of log(shift factor) versus temperature is shown in figure 5. The dependence is linear below 110°C, and is represented by:

$$\log_{10}(a(T)) = s(T - T_r) \qquad \{3\}$$

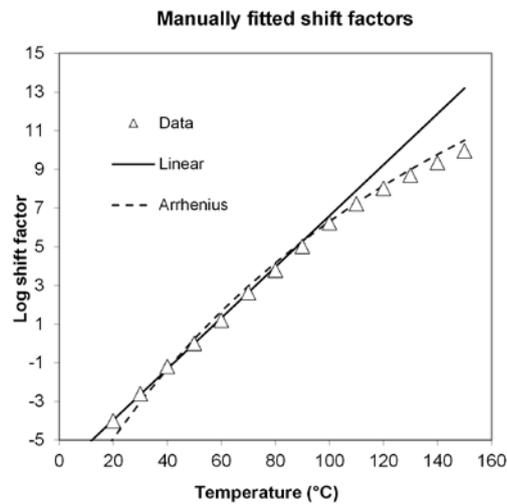The slope s is 0.128 K^{-1}, so a 10-fold increase in time is equivalent to a temperature drop of 8°C.

Figure 5 – Shift factors as a function of temperature for the curves in figure 4, showing data and fits to a straight line and Arrhenius dependence.

2.3   Using viscoelastic data

For simple estimates, the MD creep curve can be used to predict the extension produced by the web tension, and the width contraction estimated using a constant Poisson's ratio, typically 0.3. More advanced modelling is often useful, for example in modeling curl development [5] and behaviour of stacks of film on rigid formers [1], but is beyond the scope of this paper.
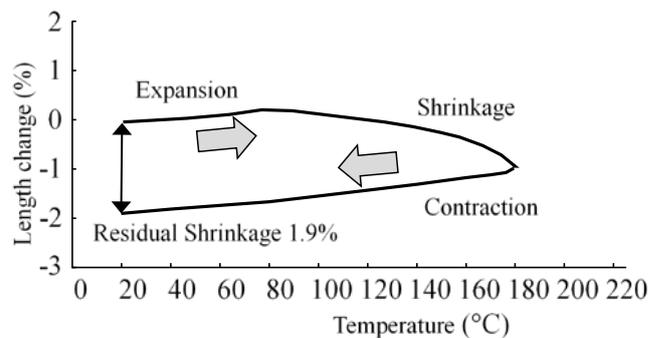
2.4   Dimension Changes from Temperature

Figure 6 – Length changes in PET film during cycling to 180°C, measured by TMA.

Manufactures normally quote MD and TD values of the coefficient of linear thermal expansion at room temperature, and of shrinkage developed after holding a specimen unrestrained for 5 minutes at an elevated temperature, often 120 or 150°C.

The behavior of film as temperature changes can be understood by using Thermomechanical Analysis (TMA). The specimen environment is similar to the DMA, and its length is measured as temperature is programmed through a succession of ramps and hold times [6]. Figure 6 shows the TMA used to replicate a 180°C shrinkage test on normal PET, with a heating rate of 5 deg/min. The film expands up to 80°C, but then shrinks on further heating. It is around 1% shorter at 180°C than its original length. On cooling, there is further contraction, giving a net length reduction of 1.9% on return to room temperature.

For applications where dimensional stability is required, manufacturers supply "heat-stabilized" film with reduced shrinkage in the TD alone or both directions. Figure 7 shows the TMA trace of stabilized film under the same conditions with an expanded vertical scale, displaying expansion on heating and contraction on cooling. Shrinkage on heating does not occur. The net dimension change is an increase of 0.1%.
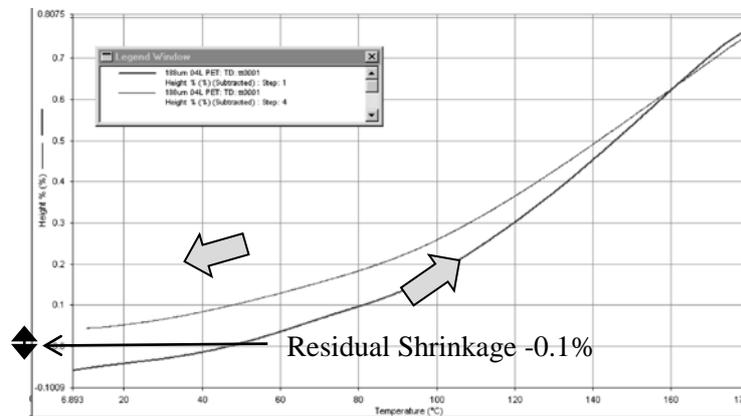
Figure 7 – TMA trace of length changes in stabilized PET film during cycling to 180°C.

Further insight can be gained from a repeated cycling experiment, shown in figure 8. In the initial ramp up to 140°C, shrinkage develops above 80°C as before, and the specimen contracts on cooling. During the next ramp to 160°C, the length retraces the previous cooling curve up to 140°C, apart from a small shift attributed to thermal lag. Shrinkage only develops once the previous maximum temperature is exceeded. Similar behavior occurs on subsequent cooling and heating to 180 and 200°C. A single heating ramp follows the outer envelope of the steps.
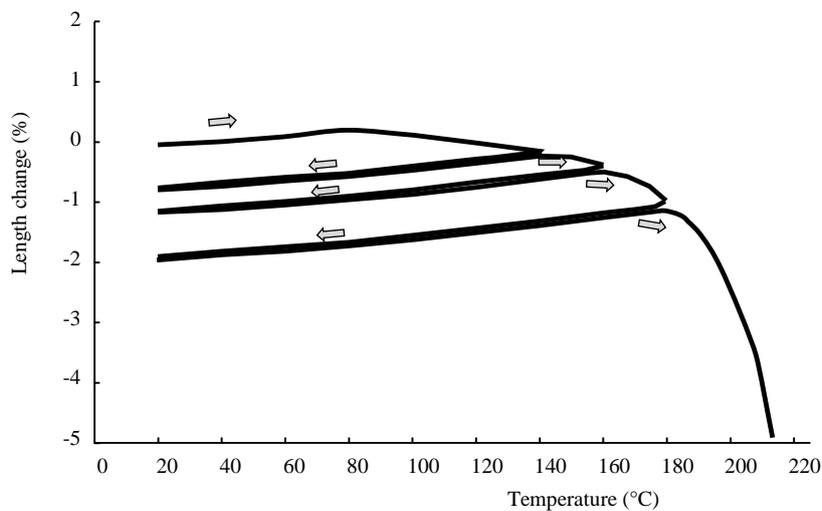
Shrinkage appears only on the first pass through a given temperature. Once it has developed, heating and cooling below that temperature follow the same curve. The cooling and reheating curves from different temperature are all parallel, attributed to an underlying, reversible, thermal expansion.

Heating under low tension allows shrinkage to develop, and is said to relax or heat-stabilize the film because that shrinkage does not appear on subsequent reheating. It does not affect the reversible thermal expansion contribution, nor shrinkage developed above the stabilization temperature.

2.5   Viscoelastic Description of Shrinkage

As-manufactured polyester films shrink when they are heated above their glass transition temperature. If a specimen is held at fixed temperature in the TMA, shrinkage develops during the heating and also slowly during the hold time. Experiments on film that has been extended at high temperature show similar shrinkage behavior to as-made film [7]. This evidence suggests that shrinkage is a viscoelastic recovery phenomenon, with the initial strain provided during manufacture or deformation.

The biaxial orientation process heat-sets the film in ovens above 210°C. whilst held in clips, preventing contraction. This causes structural and conformation change in the polymer, with crystals growing and the amorphous orientation relaxing. Rather than returning to the unstretched dimensions of 25-30% of the stretched film, the film only seeks to contract by around 4% after heat-setting. Cooling under restraint freezes in most of this strain, and the contraction on release is only around 0.2%. The remaining 3.8% can be gradually recovered as shrinkage on heating.
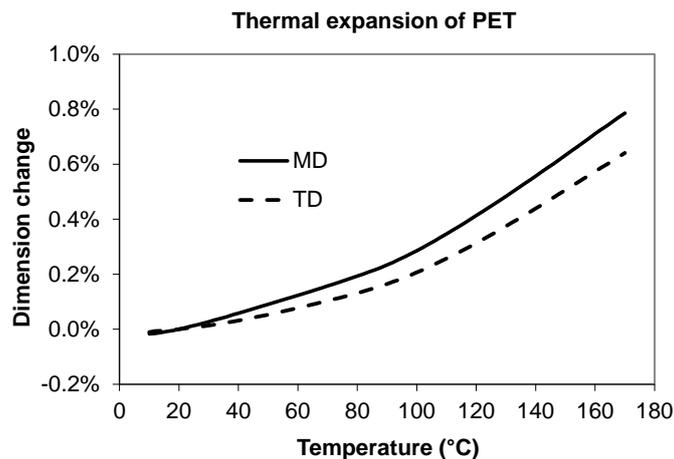

Figure 9 – Length changes in PET film due to thermal expansion, measured during a reheat temperature ramp using TMA.

The reversible thermal expansion and shrinkage curve can be measured on the TMA with an initial ramp, cooling, and then a reheat. The reheat gives the thermal expansion contribution, with the coefficient normally increasing with temperature (figure 9). Subtracting this from the initial heating trace gives the shrinkage as a function of temperature (figure 10). To convert this to reduced time (also in figure 10) at a heating rate of r K/s, the incremental version of equation 2 is integrated to give:

$$t_r = \frac{10^{s(T-T_r)}}{rs\ln10} \qquad\qquad \{4\}$$

The example shows an expansion in the TD, and shrinkage at high temperature in the MD. There is quite a marked expansion in the MD around 100°C. The origin of this is not clear, as it would require MD compression to generate.
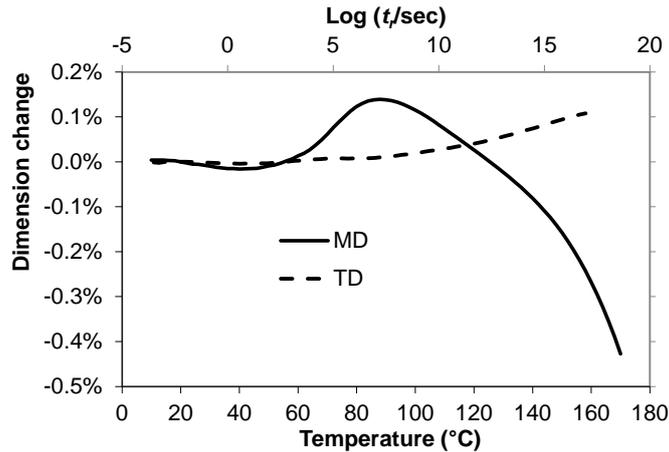
Figure 10 – Thermal shrinkage as a function of temperature (lower axis) and reduced time (upper axis), obtained by subtraction of reheat from initial heating trace on the TMA.

2.6   Moisture Effects

Polymers with polar groups such as polyesters and especially polyamides absorb moisture from their environment, whereas polyolefins such as PP and PE are little affected. Although water permeability is commonly measured, it is also important to know the solubility and diffusion coefficient. PET absorbs water in proportion to the relative humidity of the surroundings: 0.4 % by weight is absorbed at 80 % RH [8]. The solubility is independent of temperature up to 150°C.

The rate at which equilibrium is attained depends on the film thickness and diffusion coefficient, itself dependent on temperature. Data on PEN are similar to PET [**Error! Bookmark not defined.**].

Moisture absorption causes expansion in all directions, greater in directions of lower molecular orientation. The in-plane coefficient of hygroscopic expansion of polyester is around 7 ppm for a change of 1% RH [9].

The absorbed moisture affects the mobility of polymer segments, and acts as a plasticizer to reduce viscoelastic relaxation times during creep. The limited data available [10] have been interpreted by applying a moisture shift factor, analogous to TTS. There is a factor of 10 reduction in relaxation time for a 20 to 40% increase in RH. The moisture shift factor varies with temperature, according to the data.

These effects are less important than temperature changes, but nevertheless should be considered for critical applications such as plastic electronics. Passing a polyester web through an oven will remove moisture because the RH will be low. This will cause contraction, which will reverse as the web slowly reabsorbs moisture at room temperature. There will be a difference between web from the inside and outside of a wound roll, because of the time it takes moisture to diffuse away from the surface.

2.7   Anisotropy and Orientation

Polyester films are described as "balanced" but are produced by a sequential draw process, where the orientation produced by the second (TD) draw is greater than the first (MD). A stable process with equal orientation proved impossible to achieve in early development. The principal directions of orientation are rotated from the MD and TD towards the web edges by the restraint conditions [**Error! Bookmark not defined.**]. Figure 11 shows how lines drawn across the film after the first draw form curves after the second, because the edges are held in clips while the center retracts under MD stress developed in the draw. The film elements towards the edge are subject to a combination of TD stretching and shear.

The principal directions of properties such as refractive index, modulus, thermal and moisture expansion vary from the MD and TD at the web center, to an orientation angle of around 40 degrees at the edges [9]. The orientation angle can be found easily by rotating the film between two polarizing sheets at right angles and finding the angle where no light is transmitted (extinction angle). The properties arise from the orientation distribution of crystals, whose c-axis has a higher stiffness than the others and negative

coefficient of thermal expansion. One crystal population is close the machine direction, and a second forms at an angle. It is possible to relate properties to the crystal orientation distribution derived from wide-angle X-ray diffraction measurements [11].
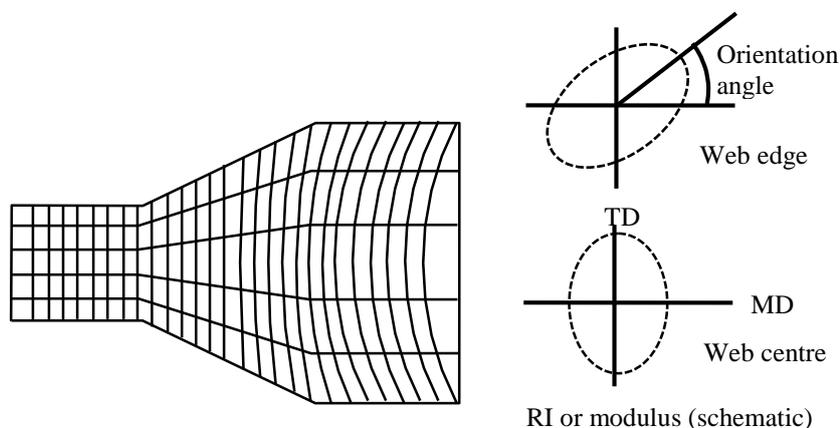
Figure 11 – Schematic diagram of sideways stretching during PET film manufacture, showing distortion of a printed grid. The ellipses at the right sketch the variation of properties such as refractive index and Young's modulus with test direction, at the edge (upper) and center (lower).

At any point, the angular dependence of several properties follows that of the appropriate tensor, with just 3 or 4 parameters needed to describe it [12]. Most properties have their maxima and minima at 90° intervals along the orientation axes. The exception is shrinkage, whose cause is the strain during cooling and any subsequent processing. Its principal axes may shift as the temperature increases, and they do not lie along the orientation axes. Off-axis shrinkage has received very little attention.

2.8   Summary

Temperature and moisture both generate a reversible component of dimension change. 0.05% length increase can be caused by either 20°C or 70% RH increase.

The viscoelastic response to web handling tensions causes significant dimension change once temperature is increased. Linear viscoelastic theory and TTS allow modelling and qualitative understanding of processes. However, there is a shortage of data and validation tests.

Shrinkage is the gradual recovery of strain frozen-in during cooling. Its release is triggered by increased temperature or time-temperature.

Properties are anisotropic with the principal angle changing across the full manufactured width (4 to 9 m). There does not seem to be much pressure to reduce property anisotropy. Partial widths from the center may perform better, but suppliers may be unable or reluctant to be selective about supplying them.

3   Dimension Changes during Web Processing

When the web moves through a line and experiences changes in tension and temperature, its dimensions change as a result of viscoelastic deformation, thermal expansion and contraction, and the development of shrinkage. To a first approximation, these are additive.

It is useful to sketch out the width changes assuming zero TD stress, and then consider whether the web edges will follow that path or not. An imaginary tape element at the web edge prefers to travel straight to minimize its stretch relative to the web centre. The web will achieve close to its predicted width on the roller at the oven exit. Friction can allow a small TD stress to develop [13], but the effect on width is small compared with other changes. Troughs coming onto the roller will normally spread out; but if the web is thin and there is good traction, narrow wrinkles may pass over the roller.

In the span, the edges will move inwards to follow a width contraction, as the free web cannot sustain significant TD tension. By contrast, a web expansion can be accommodated by forming troughs in the MD with the edges travelling straight. Broadly speaking, the edges can follow a concave path prediction;

but they will straighten out a convex path, and troughs will form. If these troughs are present when the web cools, their shape will be "frozen-in". Troughs are less likely in an air flotation oven, where the sinusoidal web path provides shape-stiffening and a true width increase may occur.

3.1 Examples

The deformation mechanisms normally act together, but it is instructive to separate them in order to understand their effects. In all cases, there is a long web span where the web heats and cools without touching any rollers before the exit back at ambient temperature. The sketches show the width variation before the edges have been "straightened out".

Thermal expansion at low tension (Figure 12). The MD mechanical strain is low at all times. Thermal strain during heating causes expansion in both MD and TD, but that is recovered during cooling. There is no change in the unstressed dimensions. However, the web width increase when hot tends to generate troughs.
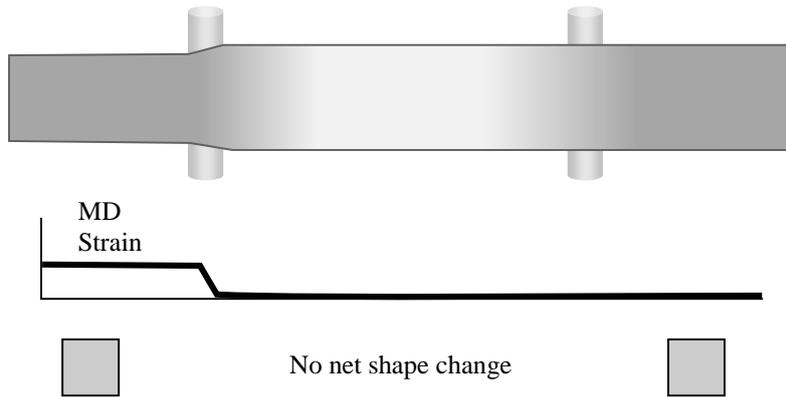

MD Strain

No net shape change
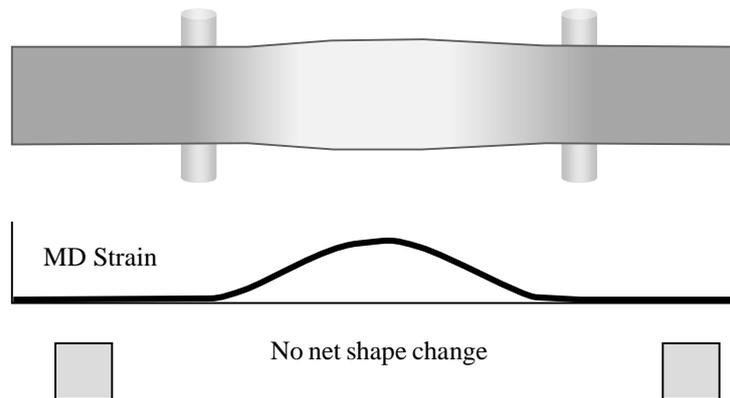
Figure 12 – Web width and MD strain changes from thermal expansion alone, during heating and cooling in an oven.

High tension (Figure 13). The MD mechanical strain increases considerably because of viscoelastic creep at high temperature. The stress is still present during cooling so there is no recovery. Later, removing the tension causes a fall in MD strain, but only the same amount as the tension caused originally when cold. There is therefore an increase in MD length from the high tension and temperature. The width falls in proportion to the extra strain from creep, smaller by a factor of Poisson's ratio. This TD contraction is not recovered so a TD contraction accompanies the MD expansion.

MD Strain

MD elongation and TD contraction frozen
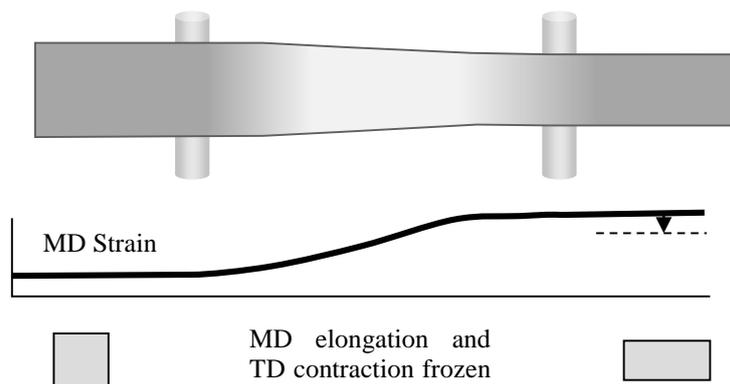
Figure 13 – Width and MD strain changes from high tension during heating and cooling.

Low tension (Figure 14). If the tension is reduced from a high level by driving the oven entry roller, the web width will expand as it leaves the roller. This may cause troughs early in the oven. However there is no effect on the unstrained web dimensions, as long as the tension is low enough.

MD
Strain

No net shape change

Figure 14 – Width and MD strain changes from a reduction in tension over the entry roller followed by heating and cooling, with likely occurrence of troughs or wrinkles.

Shrinkage in both MD and TD (Figure 15). When the web becomes hot, it contracts in both MD and TD. The web dimensions are reduced. The web width starts to fall some distance into the oven, and this pulls the web edges inwards up to that point. As a result, troughs may be generated in the heating region.

MD
Strain

Shrinkage in both directions
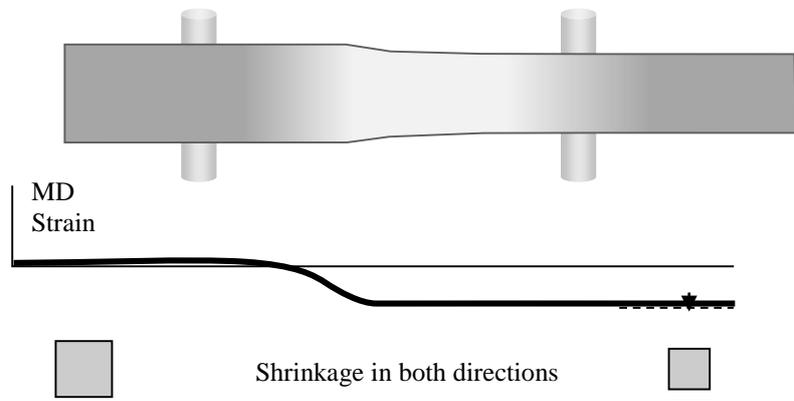
Figure 15 – Width and MD strain changes from MD & TD shrinkage, during heating & cooling.

MD shrinkage and negative TD shrinkage (Figure 16). The web may have these properties as a result of heating and cooling under high tension (Figure 13). After passing through the oven, the web is shorter in the MD but wider in the TD. In the oven, the tendency to increase width stops once the maximum temperature is reached. The edges tend to move in a straight line from the narrower inlet width to the final exit width, and so there is a tendency to form troughs once expansion starts.

MD
Strain

Shrinkage in MD,
expansion in TD
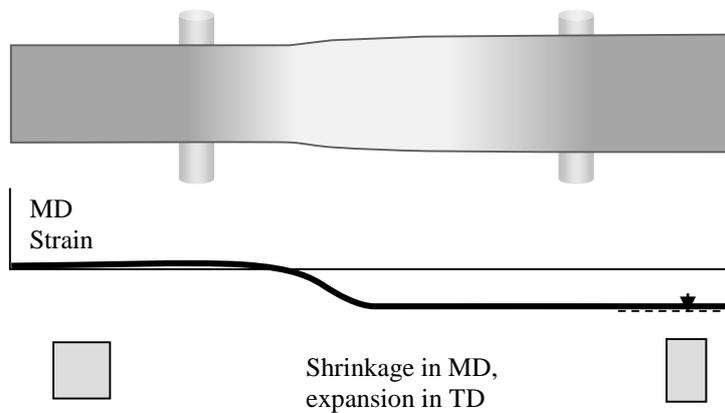
Figure 16 – Web width and MD strain changes from positive MD and negative TD shrinkage, during heating and cooling.

3.2 Discussion

This method can be made more quantitative by estimating the magnitudes of dimension changes using the viscoelastic, thermal expansion and shrinkage data. Shrinkage should be measured on the particular material being used: it may develop gradually as temperature increases, or remain small up to the temperature where the material was earlier heat-stabilized and develop strongly thereafter.

It is important to know the web temperature through the oven. Convective air heating, radiant infrared elements or heated platens are used. The web temperature can be measured with a pyrometer, or predicted using heat transfer theory (with drying if there is a wet coating on the surface). Considering the width variation can guide the selection of set temperatures, particularly in intermediate cooling zones.

Troughing in the oven is common. Making the exit roller a spreader could give a benefit by increasing the width in the last part of the free span. However, it will have limited benefit if the wrinkles originate near the entry. Spreading devices such as edge nips and D-bars could be placed in the oven: consideration of the width changes enables them to be placed at the optimum location.

4 Conclusions

- MD tension causes creep at elevated temperatures, accompanied by TD width reduction.
- Both these dimension changes are frozen-in on cooling
- Thermal expansion gives reversible dimension change, but that from shrinkage is irreversible.
- The web edge can follow a straight or concave path to follow width variations.
- The edge runs straight rather than follow a convex width, but the web forms troughs rather than moving into TD compression.
- Troughs may cause problems: they are set in by cooling, and troughs in thin webs may run over the exit roller as wrinkles.

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