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ANNEALING EFFECT ON SEMI-CRYSTALLINE MATERIALS IN CREEP BEHAVIOR

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Abstract

Three glass reinforced polymers of Nylon 66, PET and HT-Nylon with glass transitions of 58, 72, and 132°C are selected for checking the necessity of high temperature annealing and degree of its impact on creep strains. The improvement after annealing depends on the polymer type of whether it is fast or slow crystallizing at molding process and whether it has hydrogen bonded sheets. The physical property changes observed of these materials before and after annealing support the explanation of crystal reorganization through crystallization, free volume reduction through densification and crystal perfection through better chain packing. The prediction of long-term creep strains up to 10 years using time-temperature superposition technique has been the practice for last 13 years in our laboratory. The accuracy of the prediction are shown in confidence level of about 90%.

Keywords: annealing effect, creep, HTN 51, Nylon 66, PET, time-temperature superposition

Introduction

Characterization of time-dependent behavior of polymer composites for structural stability is essential to predict long-term continuous usage under stress. The industrial processes of injection molding, co-extrusion and blow molding to produce large and small dimensionally stable parts have the utilization in automobiles' under-the-hood parts [1], gas pipelines, computer housing and hand-held communication devices, complicated modern electronic switches, and even soda bottles. A large material selection covers the temperature range of utility from ambient to over 200°C. The time-dependent deformation or strain of thermoplastic polymers from sustaining applied stress is expected as a result of their relatively weak interchain forces acting between its constituents. Unlike decades ago, the resources of actual long-term testing of material properties have been reduced near zero and rely on the accelerated tests for the predictions. The accelerated test methods are based on time-temperature superposition [2] and variations of this technique, i.e., time-aging time and time-strain superposition [3–4], in which a series of isothermal short-term compliance curves can be shifted on logarithmic time scale to build a master curve in decades of time.

The creep behavior are referred frequently and has been related to microhardness [5], bond interchange of polyester [6], aging effect [7], induced secondary crystallinity

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[8], actual design of cartridges [9], effect of mold temperatures [10] in extensional, bending, compressional modes. In this paper, we will show the prediction of long-term creep results in relatively short experimental time in our laboratory and how they are in good agreement with the actual creep data. Whether the annealing of glass reinforced PET, Nylon 66 and high-temperature nylon above their glass transition temperatures affects the physical properties and the long-term creep strains.

Experimental

Materials

Three materials are selected for illustrating the annealing effect – all of these molded tensile bars are in 10×4 mm (width×thickness) of the ISO standard. A low-crystalline PET black grade Rynite® RE5265 with 15% added glass reinforcement and density of 1.445 g cm^{-3}, crystallinity at 22%. A Nylon 66 in natural color grade, Zytel® 70G33 NC with 33% added glass reinforcement and density of 1.396 g cm^{-3}. A high-temperature nylon (HTN) with composition of 6T/DT 50/50 in natural color grade, Zytel® HTN51G35 NC with 35% added glass reinforcement and density of 1.472 g cm^{-3}. T is the terephthalate, while D is 2-methylpentamethylenediamine. The specimens were sealed in moisture barrier bag till testing. Annealing was carried out at 170–180°C oven in nitrogen purge for 2 h.

Accelerated creep

The accelerated creep was carried out in TA Instruments 983 DMA in creep mode under nitrogen purge of 20 mL min^{-1}. The molded bar with effective volume of 40×10×4 mm was clamped in jaws of DMA and performed the length correction before starting. The test was then set up a 1500–2500 min experiment consisting of a series of isothermal steps of 30 min temperature equilibration, 15 min loading, and 60 min recovery without load. The method allowed the isothermal steps to continue in 5°C increments from 25 to 85 (for PET), to 140°C (for Nylon 66 and for HTN 51). The short-term compliance *vs.* time curves using 25°C as the reference temperature were shifted horizontally in the logarithmic time scale till the curves were overlapped smoothly. A master curve was then created for both the unannealed and the annealed bars. Separate experiments of acceleration from 170 to 220°C were carried out for prediction creep strains of glass reinforced Nylon 66 and HTN 51 at 170°C.

Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis was carried out in TA Instruments 2980 DMA in dual cantilever mode of 35 mm large clamp. The specimen was heated at 1°C min^{-1} from –140 to 200°C at oscillation amplitude of 10 μm and 6 frequencies (0.1, 1, 3, 5, 10, 20 Hz). The loss modulus and tan delta peak shifts with frequency are used to calculate the activation energies of alpha and beta relaxation. Both the unannealed and the annealed bars were scanned the same way for monitoring the changes.

DSC and density

Both the unannealed and the annealed bars were scanned in TA Instruments 2920 DSC at 10°C min^{-1} rate from 0 to 300°C for PET and Nylon 66 and to 350°C for HTN 51. The densities from a helium pycnometer, AccuPyc 1330, were tested at ambient temperature.

Results and discussion

Time-temperature superposition

The simplest creep experiment measures the strain as a function of time responding to the applied step stress to a viscoelastic material is shown in Fig. 1. The creep compliance, $S(\sigma, t)=\varepsilon(\sigma, t)/\sigma$, is the strain $\varepsilon(\sigma, t)$ resulting from the stress σ applied and held constant for time t. The responding strain is the sum of three parts ($\varepsilon_1+\varepsilon_2+\varepsilon_3$): the immediate elastic strain, the delayed strain (creep) and non-recoverable strain lost to the flow. The elastic strain (ε_1) is recovered at the moment of releasing the stress, while

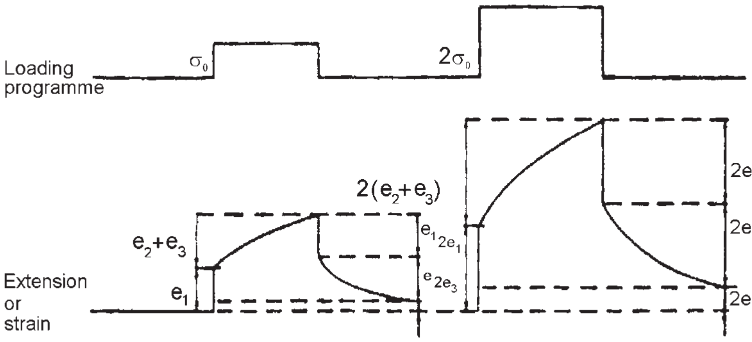

Fig. 1 Deformation of a linear viscoelastic solid: σ is the imposed stress, ε_1, ε_2 and ε_3 are the responding elastic strain, creep strain and viscous flow

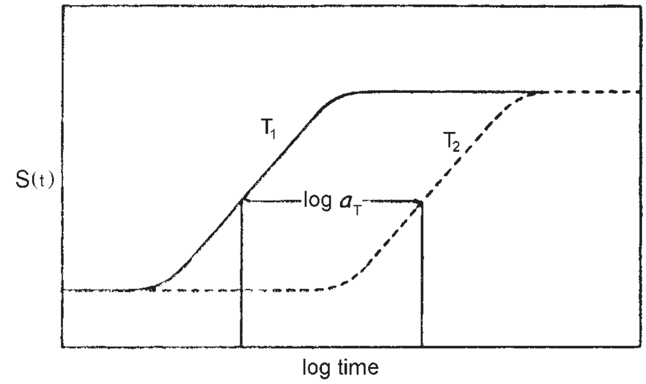

Fig. 2 Schematic illustration of the simplest form of time-temperature equivalence for the flexural compliance $S(t)$

the delayed strain (ε_2) is also recoverable at sufficient time. The strain due to viscous flow is $\varepsilon_3(\sigma,t)=\sigma t/\eta$, where η is the viscosity. In testing temperature range we use, the non-recoverable part of the strain (ε_2) can be neglected, because the viscosity is high at the testing temperature. The recovery is generally 95% or better under the testing condition. Most polymeric solids are tested at relatively low stresses to obey linear viscoelasticity theory with the strains produced. At single constant stress, the resulting creep strain is then simplified to $\varepsilon(t)=\sigma S(t)$.

A simple form of time-temperature equivalence is shown in Fig. 2. It shows that the compliance of an idealized polymer at T_1 and T_2 can be superimposed by a horizontal displacement. The viscoelastic behavior at one temperature can be related to that at another temperature by a change in time scale only. Some application suggested an additional small vertical shift [6]. In practice, vertical corrections are very small as compared to the large changes in the viscoelastic behavior. Therefore, it is adequate to apply horizontal shifts on the time scale only.

Isochrones

Isochronous plots are useful to engineer designing purposes, which provide information of the % strain (deformation) at required material service time under the applied stress. They are generated by cross plotting the total strains obtained from master curves against stress levels for specific times. For each service temperature, i.e. the reference temperature of the experiment, a set of new isochrones can be generated for the prediction of the utilities.

Accuracy of prediction on accelerated creep

We show two sets of actual long-term data published in DuPont Design Handbook [11] of glass reinforcement Nylon 66 (Zytel® 70G33L nc10) and POM polyoxymethylene (Delrin® 500 nc10) and the good agreements [12] they have been compared to the data generated using the accelerated creep method described in this paper. For fair comparison, the size (31×13×3.2 mm), polymer composition of the test bars were carefully matched as well as humidity control before testing. The Nylon 66 test bars were conditioned in a humidity controlled laboratory (RH at 50±5%) for a week before being tested in a load range of 0–30 MPa. It should be noted that the accelerated creep method would dry up the previously conditioned specimen as the test proceeded to higher than ambient temperatures. In Fig. 3, we show two sets of isochrones: (A) the ASTM creep test result at 23°C taken from an actual 5000 hours experiment that has been published in Design Handbook for DuPont Engineering Polymer, Module II, (B) the 3000-minute accelerated creep test result from 25°C to 140°C in 5°C isothermal steps. The agreement is excellent. In Fig. 4, another sets of isochrones are compared using POM: (A) the ASTM creep test result at 23°C in air taken from an actual 10000 hours experiment and in Design Handbook for DuPont Engineering Polymer, Module III, (B) the 2500-minute accelerated creep test result from 25°C to 120°C. The agreement is in near 90% confidence.

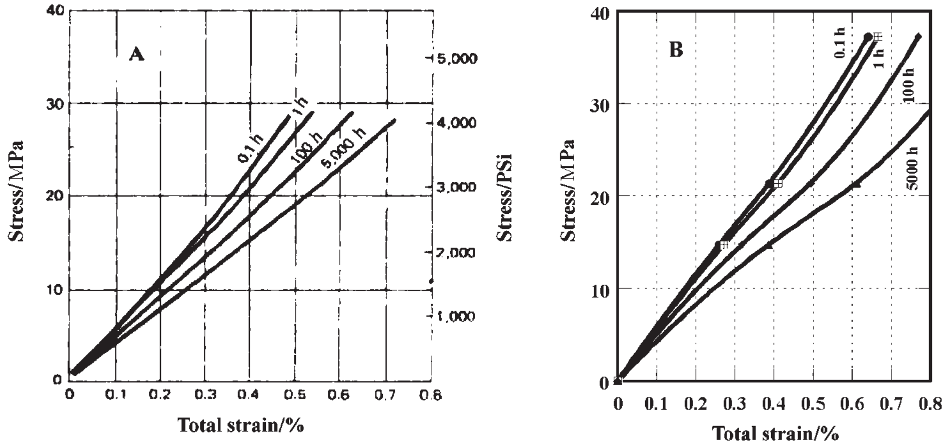

Fig. 3 Good agreement of long-term creep strains for Zytel®70G33L nc10: A – actual long-term test result, B – accelerated test result

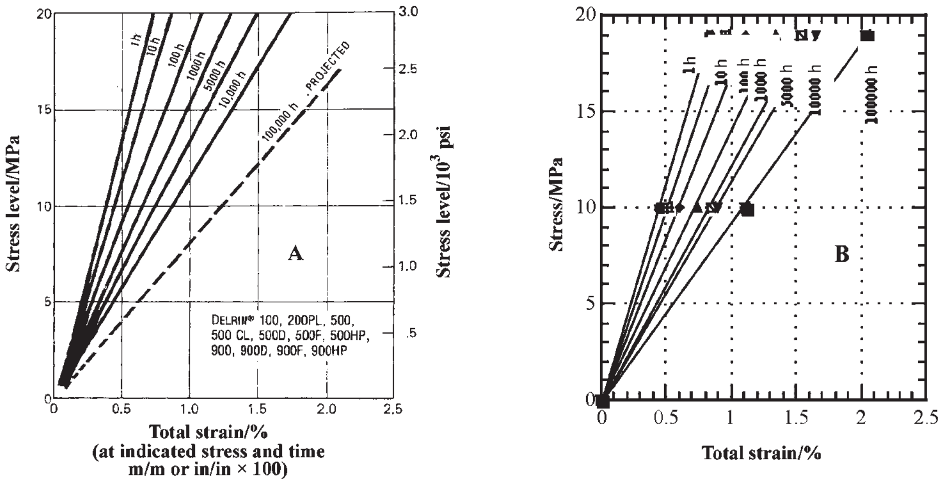

Fig. 4 Good agreement of long-term creep strains for Delrin®500 nc10: A – actual long-term test result, B – accelerated test result

Annealing effect on the creep data

The three selected glass reinforced structural polymers for this paper have very different T_g's taken at the α relaxation in DMA at 1 Hz: the Nylon 66 at 58°C, the PET at 72°C, high-temperature nylon (HTN) at 132°C. The accelerated creep compliance prediction for long-term utility based on time-temperature superposition method uses the series of short-term isothermal creep compliance from 25°C to temperatures

Table 1 The predicted total strains at 25°C at the time indicated using accelerated creep master curves

Strain at time	Stress MPa	PET unannealed/ %	PET annealed/ %	Nylon 66 unannealed/ %	Nylon 66 annealed/ %	HTN 51 unannealed/ %	HTN 51 annealed/ %
Initial	10	0.232	0.183	0.124	0.158	0.093	0.100
	25	0.580	0.460	0.310	0.392	0.240	0.250
1 h	10	0.238	0.187	0.131	0.177	0.096	0.106
	25	0.600	0.470	0.330	0.435	0.242	0.260
10 h	10	0.240	0.192	0.138	0.195	0.102	0.116
	25	0.620	0.480	0.346	0.475	0.252	0.290
10^2 h	10	0.242	0.201	0.150	0.216	0.113	0.130
	25	0.650	0.500	0.375	0.525	0.280	0.330
10^3 h	10	0.260	0.220	0.168	0.242	0.140	0.150
	25	0.660	0.550	0.423	0.588	0.343	0.370
10^4 h	10	0.298	0.248	0.190	0.265	0.180	0.170
	25	0.740	0.620	0.475	0.655	0.440	0.430
10^5 h	10	0.388	0.288	0.214	0.288	0.230	0.200
	25	0.960	0.720	0.538	0.710	0.560	0.500

Table 2 The elastic and delayed (creep) strains at 25°C

Strain	PET unannealed/ %	PET annealed/ %	Nylon 66 unannealed/ %	Nylon 66 annealed/ %	HTN 51 unannealed/ %	HTN 51 annealed/ %
Elastic strain, 10 MPa	0.232	0.183	0.124	0.158	0.093	0.10
Creep strain, 10^5 h 10 MPa	0.388–0.232= 0.156	0.288–0.183= 0.105	0.214–0.124= 0.09	0.288–0.158= 0.13	0.230–0.093= 0.137	0.20–0.10= 0.10
Elastic strain, 25 MPa	0.58	0.46	0.31	0.392	0.235	0.25
Creep strain 25 MPa	0.96–0.58= 0.38	0.72–0.46= 0.26	0.538–0.31= 0.228	0.710–0.392= 0.318	0.56–0.235= 0.325	0.50–0.25= 0.25

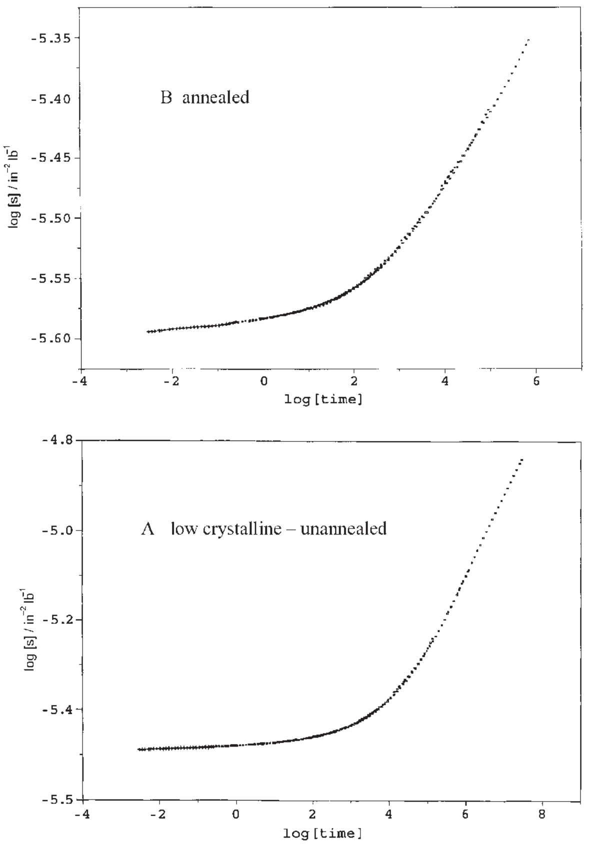

Fig. 5 Master compliance curves created after shifting, reference temperature at 25°C: A – low-crystalline PET/15% glass unannealed, B – annealed at 170–180°C

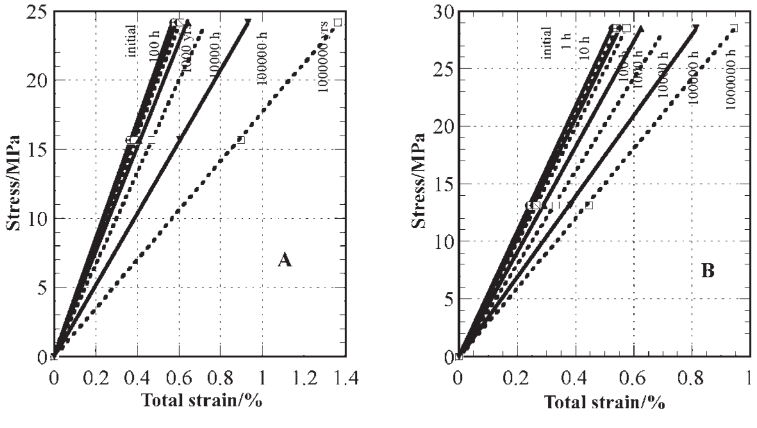

Fig. 6 Isochronous stress-strain curves predicted from accelerated method for PET/15% glass A – unannealed, B – annealed

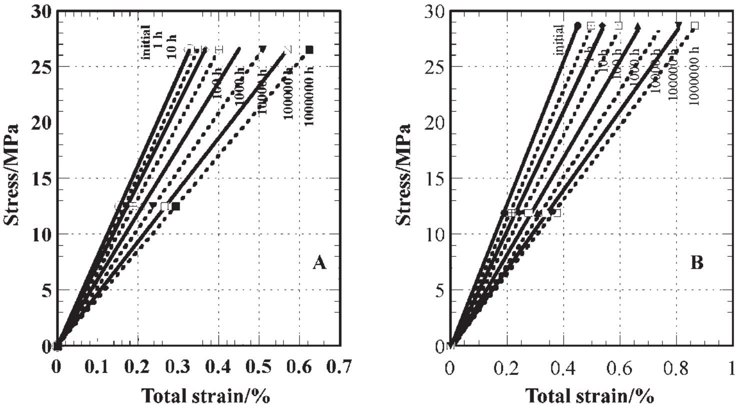

Fig. 7 Isochronous stress-strain curves predicted from accelerated method for Nylon 66/33% glass A – unannealed, B – annealed

above T_g (to 85°C for PET and to 140°C for the two nylons). The master compliance curves after superposition of a pair unannealed and annealed glass reinforced PET is illustrated in Fig. 5. The annealed PET has lower compliance, therefore lower % strain at the constant applied stress. The predicted % total strains at 25°C in decades of time of PET along with the other pairs of glass reinforced polymers are given in Table 1. The % total strains at stress level in the range between 0–25 MPa can be interpolated from these isochronous curves. The strain at zero time (initial) is the elastic strain ε_1. The lower stress of 10 MPa produces lower strain than the 25 MPa stress does. Since the stress has been kept constant throughout the experiment, the recoverable elastic strain changes only due to the temperature step. The creep strain portion is used for prediction of long-term property. In Table 2, we single out the 10^5 h strains to compare the three pairs of the unannealed *vs.* the annealed.

For PET with added 15% glass, the annealing at 170–180°C has reduced both the elastic and creep strains by 21 and 32% at the same stress levels. The two sets of isochronous stress-strain curves of the same PET unannealed and annealed pair is shown in Fig. 6. We believe that the polymer chain mobility at a temperature depends on the free volume at that temperature. The fractional free volume of PET filament has been suggested to be 0.060 at ambient condition by Yamaguchi, Saeki and Yamanaka [15]. Annealing at temperature between T_g and T_m of PET induced secondary crystallization on the surface of the primary crystals. The chain mobility of the region adjacent to the crystal surface was thus reduced which led to density increase and free volume reduction. The secondary crystallization at annealing temperature producing a group inferior crystals in the bulk and between lamellar stacks is commonly known for PET [8]. In fact, the creep experiment progresses beyond 80°C can not be applied the time-temperature superposition technique because of the crystallization in progress. There is a wider applicable range of PET than very thin PET films found by Spinu and McKenna [7]. There are changes in basic properties of PET after annealing; the fact will be provided in next section to support this explanation.

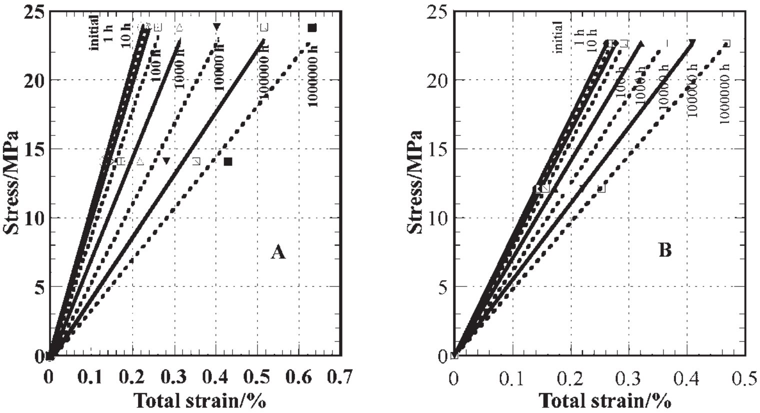

Fig. 8 Isochronous stress-strain curves predicted from accelerated method for HTN 51/35% glass A – unannealed, B – annealed

For Nylon 66/33% glass, the actual % total strains is about half of that in PET- it is a better choice of material for more stringent dimensional stability under stress. The increased amount of glass reinforcement contributes the low creep strains. In computed percentage-wise it appears to be large – the annealing increased the elastic strain by 26% and creep strain by 39% at the same stress levels. The isochrones of this pair are given in Fig. 7. Nylon 66 is a fast recrystallizing polymer; it normally has small fraction of amorphous phase from molding process. We will show that annealing did not improve the crystallinity, although the density and T_g did increase slightly. The fractional free volume of nylon filament has been suggested to be 0.029 at ambient condition, about half of that of PET filament [15]. The increased strain by annealing, though small in actual strain and appeared to be large in computed percentage, is the observed fact. Nylon family behaves more complicated than other flexible chain thermoplastics – the crystal structure is in hydrogen-bonded sheets. The annealing has small effect to the spacing fixed by hydrogen bond sheet, but large effect to the spacing between the sheets, which results in specific volume increase of crystalline phase through increase of crystallized chain sequences and change of packing density of chain molecules inside the crystallites. Derks *et al.* in their study of Nylon 46 showed heat treatment at temperature above T_g and below melting peak removes the molding imperfection by better packing of the hydrogen bonded sheets and produces large melting enthalpy increase [13]. Hinrichsen showed that the perfection of the crystal structure in general does not accompany a significant melting enthalpy increase [14]. Our experience confirmed what Derks *et al.* has reported [13] that the crystallinity of Nylon 46 can not be determined by simple DSC scans. The creep data predicted for Nylon 66 at 170°C (another reference temperature) show that the annealed and the unannealed are similar. This is compared in Table 3.

HTN 51 is an aromatic diacid copolymer of 6T/DT in 50/50 composition. It is a slow recrystallizing polymer. The molding produces large fraction of amorphous phase. The annealing at 180°C under nitrogen for 2 h has reduced but did not mini-

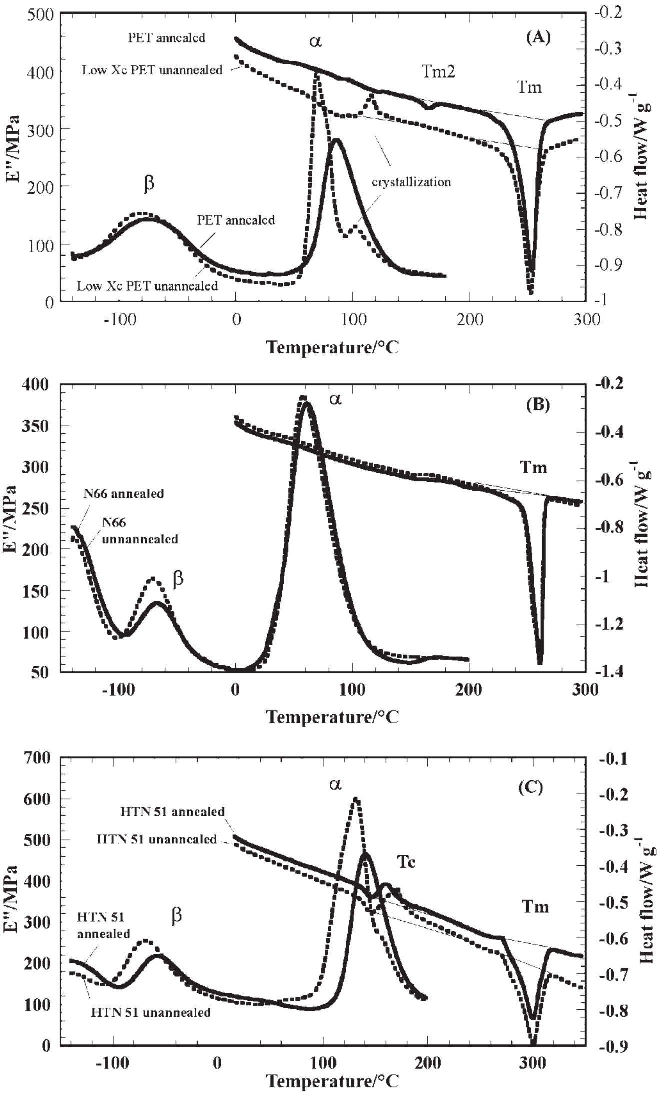

Fig. 9 DMA loss spectra and DSC heat flows for the unannealed *vs.* annealed: A – PET/15% glass, B – Nylon 66/33% glass, C – HTN 51/35% glass

mize the amorphous phase. The predicted 25°C long-term creep data do not show significant improvement by annealing. This is the best of the three structural polymers compared – the 10^5 h (>10 years) creep strain is only 0.10 not including the 0.10% of elastic strain which is recoverable at the release of stress. The amount of glass reinforcement is the highest of the three. It would be one of the choices of the most stringent dimensional requirement. The numerical data is in Tables 1 and 2. The isochronous stress-strain curve of the annealed HTN 51 at 25°C is given in Fig. 8.

Similar to PET, the annealing at temperature higher than HTN 51's glass transition has induced crystallization, then reduced the molecular mobility and free volume. This treatment has shown reduced creep strains at 170°C, even though not at 25°C – a temperature the chain mobility has been frozen in place. The predicted % strains of the pair HTN 51 at 170°C are compared in Table 3.

Table 3 The predicted total strains at 170°C at the time indicated using accelerated creep master curves

Strain at time	Stress MPa	Nylon 66 unannealed/ %	Nylon 66 annealed/ %	HTN 51 unannealed/ %	HTN 51 annealed/ %
Initial	10	0.265	0.260	0.234	0.213
	25	0.680	0.640	0.580	0.525
1 h	10	0.297	0.288	0.282	0.257
	25	0.770	0.720	0.700	0.635
10 h	10	0.322	0.310	0.313	0.281
	25	0.825	0.770	0.780	0.690
10^2 h	10	0.350	0.332	0.350	0.305
	25	0.900	0.830	0.870	0.760
10^3 h	10	0.383	0.366	0.400	0.340
	25	0.990	0.910	0.990	0.830
10^4 h	10	0.435	0.425	0.460	0.380
	25	1.125	1.020	1.140	0.925
10^5 h	10	0.480		0.540	0.434
	25	1.250		1.340	1.050

Annealing effect on the basic properties of three reinforced polymers

The three glass reinforced polymers have very different T_g's taken at the α relaxation in DMA, 1 Hz: the Nylon 66 at 58°C, the PET at 72°C, HTN, at 132°C. After annealing at 170–180°C in dry nitrogen for 2 h, the glass transitions increase to 62, 86, and 140°C for Nylon 66, PET and HTN, respectively. It should be noted that the glass transition temperatures taken at DSC heat capacity discontinuous region are lower than DMA loss peak positions. This is because DMA measurement is frequency dependent, while DSC is not. For crystalline polymers, the intensities of the transition by DSC are generally small and less reliable. In glass transition region, polymer chains undergo cooperative configurational rearrangement motion, known as α relaxation in these polymers, at which thermal expansion, heat capacity, modulus show discontinuity. Annealing at temperature between T_g and T_m induces crystallization of the amorphous phase, results in thickening the lamellae, restricting the chain mobility in the rigid amorphous phase between lamellar stacks [8], and reducing free volume in general. These are accompanying with increase in modulus, T_g, density, crystallinity and secondary crystallization. The following facts will support the changes in basic properties.

The PET/15% glass is seen not only an increase of T_g by ΔT=15°C by the heat treatment, but also shows an increase in density from 1.445 to 1.456 g cm^{-3}, in melting peak from 254.2 to 253.4°C, in normalized enthalpy from 36 to 47 J g^{-1}. In addition, the following properties are shown to increase: modulus at 25°C from 4.07 to 4.40 GPa; the modulus at 150°C (a temperature above its T_g) from 1.06 to 1.19 GPa; the activation energy of the α relaxation (T_g) from 420.5 to 425.5 kJ mol^{-1}; the activation energy of the β relaxation from 42.6 to 61.0 kJ mol^{-1}. (Note: The change of the activation energy of the α relaxation before and after annealing is not large.) These add up to fact that annealing at 170–180°C has induced the crystallization in amorphous phase allowing the low-crystalline PET to become high-crystalline PET. The heat-induced crystallization can be found in dynamic scans of DMA and DSC in Fig. 9A, where a loss modulus peak and a crystallization peak are seen at 105–110°C range. The annealing left a secondary crystal melting peak at 170–180°C range in the annealed DSC curve. The activation energies of both α and β relaxations are calculated from the slope of log*f* *vs.* 1/*T* in the multifrequency scans of DMA loss spectrum (0.1, 1, 3, 5, 10, 20 Hz). It is shown in Fig. 10. Dubner and Schultz [6] showed activation energy from slope of lna_T *vs.* 1/*T* of its α relaxation to be 606.1 kJ mol^{-1} after being annealed at 90°C for 1440 min; their activation energy for β relaxation was also high. The summarized physical properties before and after annealing are given in Table 4.

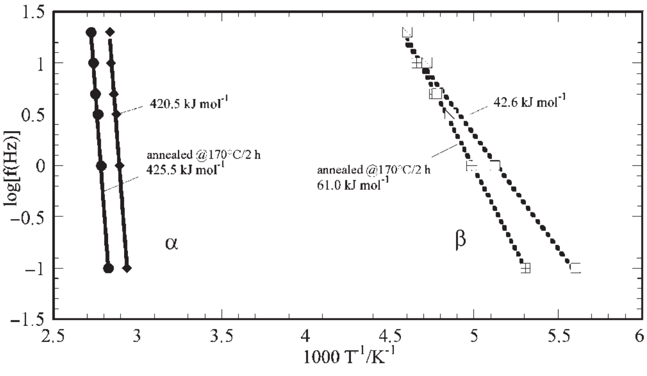

Fig. 10 Activation energies of alpha and beta relaxations of PET /15% glass (Rynite®5265BK)

The Nylon 66/33% glass is seen a ΔT= 4°C increase of T_g after the heat treatment. The as-molded Nylon 66 was sealed in a moisture barrier bag and opened just before test; while the annealed Nylon 66 was also tested as soon as it has cooled from removing from oven. We believe the increase is not due to the reducing in water plastization, but a real densifying. The following properties go up: the density from 1.396 to 1.399 g cm^{-3}; the modulus at 25°C from 6.66 to 6.71 GPa; the modulus at 150°C from 2.62 to 2.74 GPa; the activation energy of β relaxation from 64.8 to

Table 4 Properties of three reinforced polymers before and after annealing

Properties	PET Unannealed/ %	PET Annealed/ %	Nylon 66 unannealed/ %	Nylon 66 Annealed/ %	HTN 51 unannealed/ %	HTN 51 Annealed/ %
Glass/%	15	15	33	33	35	35
Density/g cm^{-3}	1.445	1.456	1.396	1.399	1.472	1.476
$T\alpha$/°C*DMA	71.5	86.2	58.1	62.1	131.8	139.8
T_m/°C	253.4	254.2	260.9	261.3	300.2	299.9
ΔH/ J g^{-1} ** DSC	36	47	75	72	19	30
E'/GPa DMA/25°C	4.07	4.40	6.66	6.71	8.30	8.57
E'/GPa DMA/150°C	1.06	1.19	2.62	2.74	2.97	4.62
$E_{act}\alpha^{***}$ relaxation, kJ mol^{-1}	420	426	429	339	591	543
$E_{act}\beta^{***}$ relaxation, kJ mol^{-1}	42.6	61.0	64.8	74.4	59.8	67.3

[*] Taken at DMA loss peak E'' at 1 Hz

[**] The heats of fusion have been normalized to 100% polymers

[***] Calculated from DMA loss peaks at 0.1, 1, 3, 5, 10, 20 Hz

77.4 kJ mol^{-1}. The β relaxation is localized chain motion. Similar to PET's β relaxation, the increase of the activation energy implies an increase of rigidity of the polymer local motion by a reduction of free volume and imposes a restriction of the motion. Although the DSC melting peak increases slightly from 260.9 to 261.3°C (near the detection limit), the normalized enthalpy actually decreases from 75 to 72 J g^{-1}. The activation energy for α relaxation is also reduced from 429.3 to 339.4 kJ mol^{-1}. It appears that the cooperative chain motion becomes easier by lowering of the activation energy after annealing. The hydrogen bonded sheets should perfect according to Derks *et al.* [13], the packing between the sheets may not which needs additional support of X-ray data. Nevertheless, the changes before and after annealing are small as illustrated in Fig. 9B.

The HTN 51/35% glass shows a ΔT=8°C increase in T_g in accompanying with enthalpy increase of 11.3 J g^{-1} (having been normalized to 100% polymer). The annealing at 180°C for 2 h did not induce its crystallization to maximum, only partially as shown in Fig. 9C. The annealing time was not long enough. The annealing has densified the polymer composite as seen also in following improvements: the density from 1.472 to 1.476 g cm^{-3}; the modulus at 25°C from 8.30 to 8.57 GPa; the modulus at 150°C from 2.97 to 4.62 GPa; the activation energy of the β relaxation from 59.8 to 67.3 kJ mol^{-1}. The increase of activation of β relaxation while decrease in α relaxation (from 591.5 to 543.4 kJ mol^{-1}) is explained the same way as for the nylon 66 after annealing at 170–180°C: the reduction of free volume restricts the local chain motion, the perfection of nylon hydrogen bonded sheets while not the packing between the sheets makes the interchain cooperative motion easier. All the data are summarized in Table 4.

Conclusions

Three glass reinforced structural polymers are compared in their long-term creep properties at 25 and some in 170°C. The slow crystallizing polymers, i.e., PET and HTN 51, are generally molded with large amorphous fractions, while fast crystallizing polymer, i.e., Nylon 66 molds in high crystallinity. Without annealing at high enough temperature the materials will crystallize during the utility and cause a serious dimensional change. This is not a problem for the fast crystallizing polymer, i.e., Nylon 66. The properties before and after annealing process can be monitored using DMA storage and loss spectra, DSC heat flow signals, and bulk density. The degree of creep improvement of these polymers is believed to be reduction of free volume, densification through heat induced crystallization, and configurational rearrangement. For the two nylon test specimens, the decrease the activation of α relaxation allowing the cooperative chain motion easier is explained as the perfection of hydrogen bonded sheets, but is speculated not the packing density between the sheets.

The prediction long-term creep strain using time-temperature superposition technique up to 10 years have shown high confidence by comparing the actual long-term creep data with accelerated data by matching the test specimens.

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