# The use of DMTA for predicting standard mechanical properties of developmental polyolefins

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**Abstract** The correlation of linear data from dynamic-mechanical testing (DMTA) to nonlinear data from standard mechanical testing was attempted for a number of quite different polypropylene-based compositions. For limited composition ranges, correlations between storage modulus and stiffness as well as between loss angle integrals and impact strength could be achieved. Challenges in trying to correlate DMTA tests to standard mechanics clearly result from morphology effects at different scales, both in crystallinity and flow-induced superstructures (orientation) and in multiphase impact copolymers or composites. While a relative scaling turned out to be easy, absolute prediction is difficult.

**Keywords** Dynamic-mechanical analysis ·
Polypropylene · Impact strength · Nanocomposite ·
Glass transition · Aging

## Introduction

The increasing development speed already imminent for several years in other areas of chemistry like pharmaceutical and plant-care components, which has allowed a number of breakthrough developments there has also reached the area of polymers. High-throughput experimentation (HTE) has already been applied successfully for polyolefins [1, 2], for example, in the development of polyethylene copolymers with a multiblock structure based on single-sit catalysts with a chain-shuttling agent [3].

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Even more than standard laboratory-based material development, HTE creates the need to test (a) a high number of polymer samples with (b) a very limited amount of material in (c) a short time period.

One of the key targets of such work must be to predict standard mechanics or so-called "datasheet values", which are typically most relevant for industrial development, from small to very small sample quantities. It is quite clear that a number of limitations exist, restricting the actual predictability of material parameters for future commercial scale products:

– Morphology effects relating to differences in both specimen size and specimen preparation for the tests.
– Extrapolation from small loads and speeds, often from parameters determined in the linear range of material behavior, to nonlinear and even terminal behavior.
– Differences between synthesis results in lab scale, pilot scale, and commercial scale (in practice the first of these two steps is most relevant as it normally means going from a discontinuous—batch—to a continuous synthesis process).

Nevertheless, the facilitation of high-speed material development for both reactor-based synthesis and compounds or composites remains a relevant target. Dynamic-mechanical thermal analysis (DMTA), basically a technique of solid-state rheology, can generate data on modulus ($G'$), mobility (loss angle), and temperature dependence at the same time. While frequency and heating rate dependence limit an achievement of target (c) above, this allows a first full thermo-mechanical characterization of a new material. In this article, we will demonstrate the possibilities of DMTA-based predictions for a range of polypropylene-based materials. The target is to predict modulus- (stiffness-) and impact- (toughness-) related data as well as thermomechanical resistance.

Earlier uses of DMTA for modulus estimation in this area include the application to mineral-reinforced PP composites with wollastonite [4], for studying ageing and post-crystallization of PP [5, 6], and for blends of metallocene-based linear-low density polyethylene (MC-LLDPE) with PP, high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polystyrene (PS) [7]. Especially in the latter case, the problem of morphology effects in heterogeneous blend materials is quite evident, while the ageing studies point out crystallinity effects.

Also for toughness predictions, DMTA has been used before in several cases: Recently, Wang et al. [8] have investigated a series of ternary PP/MC-LLDPE/HDPE blends as model systems for high-impact PP copolymers, while our own working group [9] has tested the applicability for a number of PP homo- and copolymers.

Papers describing the use of DMTA for determining both stiffness- and toughness-related parameters include a recent study of metallocene-PP (MC-PP) copolymers in a wide composition range [10] and the application to PP blends with external ethylene-propylene rubber (EPR) in a broad composition window [11].

Other approaches for determining mechanics from small samples are scarce; an approach worth mentioning is the use of nanoindentation in combination with AFM. This has been attempted for different polymers; in the polyolefin area, e.g., for EP impact copolymers [12] and $\alpha/\beta$-crystal modification mixtures of isotactic PP [13]. The aforementioned problems are heightened here by the extremely local nature of modulus and damping information.

## Experimental work

Three different sets of polypropylene-(PP)-based materials were used in this study for examining the usefulness of DMTA in predicting standard mechanical parameters:

(1) A series of 10 different high-impact ethylene–propylene copolymers of heterophasic structure produced in a pilot plant with three serial reactors targeted at optimizing the stiffness/toughness balance.
(2) A series of (nano)composites based on reactive polypropylene/polystyrene (PP/PS) blends including nanoparticles of calcium carbonate or montmorillonite [14].
(3) Specimens of a high-crystallinity PP homopolymer with different thermal history, reflecting the effects of crystallization and post-crystallization [5, 6].

The melt flow rate (MFR) of the investigated materials was measured in accordance to ISO 1133 at a load of 2.16 kg using a temperature of 230 °C. The xylene cold soluble (XCS) content was determined according to

ISO 6427, representing the ethylene–propylene rubber (EPR) content for the high-impact copolymers and the polystyrene content for the nanocomposites. The propylene (C3) content of the dispersed EPR phase, C3(XCS), was measured according to EN 17025 with FTIR (Fourier transformations infrared spectroscopy) calibrated with 13C-NMR (nuclear magnetic resonance); FTIR was also used to determine the grafted styrene content for the PP part of the nanocomposites. The intrinsic viscosity (IV) of XCS (EPR) fraction was assessed by ISO 1628 in decahydronaphthalin at 135 °C. On selected samples, morphology investigations using transmission electron microscopy were performed on 100 nm ultrathin cuts after staining the specimen with ruthenium tetroxide [15]. The specimens were prepared from the compression-molded plates used for DMTA.

For an overall thermomechanical profile, dynamic-mechanical analysis (DMTA) was performed in accordance with ISO 6721 with $50 \times 10 \times 1 \text{ mm}^3$ compression-molded samples, as a function of temperature at a test frequency of 1 Hz with a heating rate of $2 \text{ K min}^{-1}$. Measurements were carried out under forced oscillation in a torsion mode ($\varepsilon = 0.04\%$) with an ARES rheometer (Rheometrics). Temperature dependence of storage modulus G′ and loss angle tangent tan($\delta$) were used for evaluation as outlined earlier [9]. All standard mechanical data were determined on $80 \times 10 \times 4 \text{ mm}^3$ specimens. All the materials were injection molded under the same standard conditions in line with EN ISO 1873-2. The parts were not conditioned prior to testing, which was done at least 96 h after molding. Charpy notched impact strengths (NIS) were measured at +23 and −20 °C according to ISO 179/1eA (test speed of about $3 \text{ ms}^{-1}$), flexural elastic moduli were recorded at 23 °C according to ISO 178 at a flexural test speed of $1 \text{ mm min}^{-1}$.

## Results and discussion

### PP high-impact copolymers

Tables 1 and 2 summarize the composition and properties for the copolymers investigated for this study. Each of the series represents a variation of the molecular weight of the EPR phase at a certain EPR composition, as described before in a more limited range [16]. The most striking effect in the DMTA results is the development of a double maximum in tan($\delta$) for the higher C3-content in the EPR phase; Fig. 1 compares materials P1/6 and P2/4 in that respect. As a separation of these two contributions is not straightforward, only the total integral peak area was used for further evaluation.

As Figs. 2 and 3 clearly show, acceptable correlations can be established within each series of similar

**Table 1** Part 1 of PP impact copolymer series; results of analytics, mechanics and DMTA (IV—intrinsic viscosity)

| Material | MFR | Analysis | | DMTA | | | | Charpy ISO 179 1eA | | Flex. mod. |
|---|---|---|---|---|---|---|---|---|---|---|
| | 230 °C/ 2.16 kg/g 10 min$^{-1}$ | IV(XCS)/ dL g$^{-1}$ | C3(XCS)/ mol% | $T_g$ (EPR1)/°C | $T_g$ (EPR2)/ °C | ATD (EPR) | G′ (+23 °C)/ MPa | NIS (+23 °C)/ kJ m$^{-2}$ | NIS (−20 °C)/ kJ m$^{-2}$ | ISO 178/ MPa |
| P1/1 | 12 | 1.34 | 69.1 | – | −45.1 | 0.269 | 630 | 5.5 | 1.2 | 1004 |
| P1/2 | 7.3 | 2.05 | 68.4 | −58.6 | −42.9 | 0.348 | 591 | 7.4 | 1.9 | 1079 |
| P1/3 | 5.7 | 3.01 | 67.0 | −58.4 | −42.6 | 0.395 | 583 | 10.2 | 3.5 | 1119 |
| P1/4 | 3.9 | 4.38 | 68.7 | −56.5 | −40.2 | 0.475 | 620 | 13.3 | 4.9 | 1121 |
| P1/5 | 3.2 | 5.24 | 69.9 | −56.4 | −39.5 | 0.495 | 618 | 13.8 | 5.1 | 1129 |
| P1/6 | 2.0 | 6.24 | 68.8 | −56.8 | −39.9 | 0.530 | 585 | 13.6 | 4.8 | 1150 |

**Table 2** Part 2 of PP impact copolymer series; results of analytics, mechanics and DMTA (IV—intrinsic viscosity)

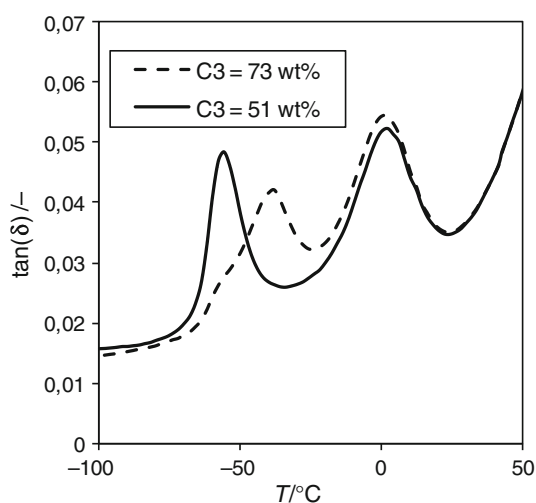| Material | MFR | Analysis | | DMTA | | | | Charpy ISO 179 1eA | | Flex. mod. |
|---|---|---|---|---|---|---|---|---|---|---|
| | 230 °C/ 2.16 kg/g 10 min$^{-1}$ | IV(XCS)/ dL g$^{-1}$ | C3(XCS)/ mol% | $T_g$ (EPR1)/°C | $T_g$ (EPR2)/°C | ATD (EPR) | G′ (+23 °C) | NIS (+23 °C)/ kJ m$^{-2}$ | NIS (−20 °C)/ kJ m$^{-2}$ | ISO 178/ MPa |
| P2/1 | 12.8 | 1.15 | 18.3 | 52.4 | −59.0 | 0.203 | 645 | 4.8 | 1.9 | 1163 |
| P2/2 | 6.9 | 2.15 | 19.4 | 48.3 | −58.5 | 0.282 | 641 | 6.4 | 2.2 | 1239 |
| P2/3 | 4.8 | 3.38 | 17.2 | 47.8 | −58.5 | 0.309 | 601 | 9.9 | 4.8 | 1215 |
| P2/4 | 2.3 | 6.3 | 17.4 | 50.0 | −55.2 | 0.438 | 609 | 11.7 | 5.2 | 1202 |



**Fig. 1** DMTA results: temperature dependence of loss angle tangent comparing materials with identical EPR molecular weight (iV(XS) ∼ 6.3) but C3-rich EPR (P1/6) and C2-rich EPR (P2/4)



**Fig. 2** Correlation between notched impact strength (NIS) at +23 °C and integral of the EPR glass transition peak in the loss angle tangent curve (ATD) for both copolymer series

composition only, but for both ambient and low temperature impact strength. This points out that the matrix contribution to toughness is already quite limited at the chosen EPR content and in this range of fracture resistance.

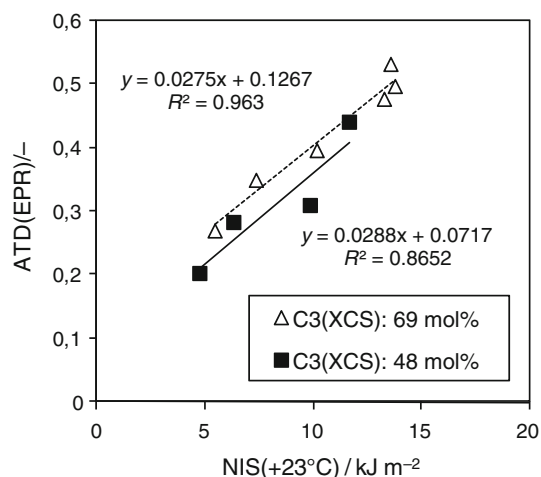A closer look reveals that in fact both impact strength and glass transition integral are closely related to molecular weight of the EPR phase (see Fig. 4). A similar correlation has been demonstrated before [16]. In detail, however morphology effects [17] have to be considered, which are also thought to differentiate the two series from each other.

The flexural modulus variation within these series was found to be too small to be correlated effectively to the storage modulus from DMTA.
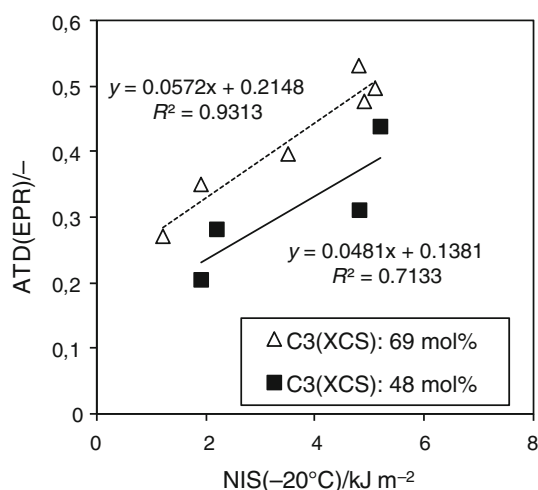
**Fig. 3** Correlation between notched impact strength (NIS) at −20 °C and integral of the EPR glass transition peak in the loss angle tangent curve (ATD) for both copolymer series
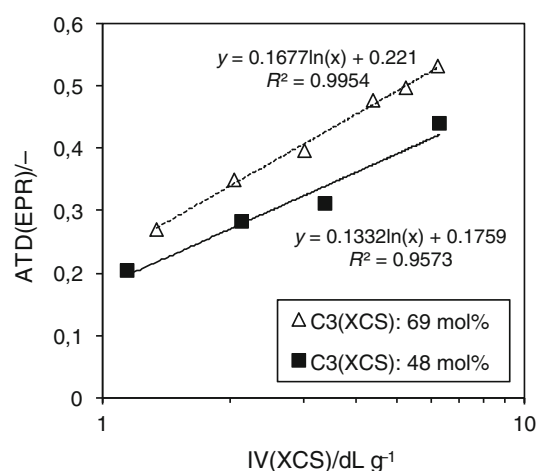


**Fig. 4** Correlation between EPR molecular weight expressed as iV(XS) and integral of the EPR glass transition peak in the loss angle tangent curve (ATD) for both copolymer series

Ternary PP/PS nanocomposites

For these materials, Table 3 summarizes the investigated compositions and their properties. Two routes for preparing the nanocomposites were employed, which have been outlined in more detail before [14]:

– The reactive compounds (RC) were prepared by grafting styrene or a mixture of styrene and maleic anhydride onto PP homopolymer powder in solid state at 125 °C. Grafting was performed under nitrogen in a 5 L stirred powder reactor in the presence of *tert*-butyl peroxybenzoate (Trigonox C by Akzo Nobel, The Netherlands), and optionally a mineral nanofiller; the resulting material was homogenized in a 24 mm twin screw extruder (Prism TSE24) at 200–210 °C.

– The conventional compounds (CC) were prepared by blending the same PP homopolymer with Polystyrene 168 N (BASF AG, Germany) and optionally a styrene elastomer (styrene–ethylene–butene–styrene triblock copolymer, Kraton 1501 from Kraton Inc., UK) as compatibilizer and a mineral nanofiller in a 24 mm twin screw extruder (Prism TSE24) at 200–210 °C.

Two typical DMTA curves for these composites are shown in Fig. 5, giving the results for CC1 and CC2, pure PP/PS-blends without and with the SEBS compatibilizer. Two or—in case of the composition with the compatibilizer—three glass transitions are visible, namely at $\sim -50$ °C (elastomer block of the SEBS), at $\sim 0$ °C (PP) and at $\sim 108$ °C (PS). For toughness considerations, the lower two of these transitions have been evaluated, however, without too much success. As the two diagrams in Fig. 6 show, the integral of PP glass transition correlates only to the relative PP amount and not to the room temperature impact strength. This can most likely be explained by the predominant influence of phase morphology and particle size on impact strength frequently found in the case of nanocomposites [18, 19].

A positive result was obtained for these nanocomposites when correlating the storage modulus at +23 °C to the flexural modulus (see Fig. 7). The relating equation is not quite linear but has a high correlation coefficient, definitely sufficient for first prediction purposes. Generalizations of such relations even within the propylene polymer "family" should, however, be considered critically. Earlier investigations in our own group [20] have already demonstrated that the equations remain valid only within a limited group of compositions, and that even seemingly small differences like the addition of a nucleating agent can result in significant deviations.

Ageing study

The use of DMTA to study ageing and annealing effects on the mechanical properties of PP, especially to understand the effect of the $T_{\alpha,c}$-transition occurring in the range of +50 to 100 °C for PP homopolymers, has been reported in our group before [5, 6]. At this time, deviations had appeared when trying to correlate results from compression molded specimens of 1 mm thickness (for DMTA and from injection molded specimens of 4 mm thickness (for flexural or tensile modulus). Modern rheometers, however, allow doing solid-state testing also on thicker samples and attempt was now made to better understand the transition changes in annealing by directly using sections from injection molded test bars (4 mm thickness) in DMTA.

Figure 8 summarizes one of various series investigated; in this case, a combination of high temperature annealing

**Table 3** PP nanocomposite series; composition and results of mechanics and DMTA (PP-g-SMA—PP grafted with styrene-maleic anhydride copolymer, PP-g-PS—PP grafted with PS)

| Material | PP/ wt% | PS/ wt% | Compatibiliser | | Mineral filler | | MFR | Flex. mod. | ISO 179 | HDT | DMTA | ATD (PP) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Type | Amount/ wt% | Type | Amount/ wt% | 230 °C/2.16 kg/g 10 min$^{-1}$ | ISO178/ Mpa | NIS + 23 °C/ kJ m$^{-2}$ | ISO75B/ °C | G′ (23 °C)/ MPa | |
| RC1 | 70 | 13 | PP-g-SMA | 7 | CaCO$_3$ | 10 | 17.9 | 1879 | 3.23 | 91 | 951 | 0.6181 |
| RC2 | 70 | 15 | PP-g-PS | 5 | MMT | 10 | 0.5 | 2068 | 4.65 | 90 | 987 | 0.6175 |
| RC3 | 70 | 13 | PP-g-SMA | 7 | MMT | 10 | 0.4 | 2203 | 3.21 | 103 | 1002 | 0.6093 |
| RC4 | 80 | 20 | PP-g-PS | 5 | None | 0 | 16.8 | 1618 | 1.51 | 89 | 905 | 0.6224 |
| RC5 | 80 | 12 | PP-g-SMA | 7 | None | 0 | 11.7 | 1786 | 1.95 | 90 | 936 | 0.6243 |
| RC6 | 80 | 20 | None | 0 | None | 0 | 3.2 | 1917 | 1.52 | 90 | 958 | 0.6155 |
| CC1 | 100 | 0 | None | 0 | None | 0 | 9.2 | 1258 | 2.37 | 102 | 785 | 0.7045 |
| CC2 | 80 | 15 | SEBS | 5 | None | 0 | 12.5 | 1848 | 3.61 | 98 | 952 | 0.6224 |
| CC3 | 67.5 | 20 | SEBS | 2.5 | CaCO$_3$ | 10 | 7.0 | 2010 | 1.26 | 95 | 974 | 0.5892 |
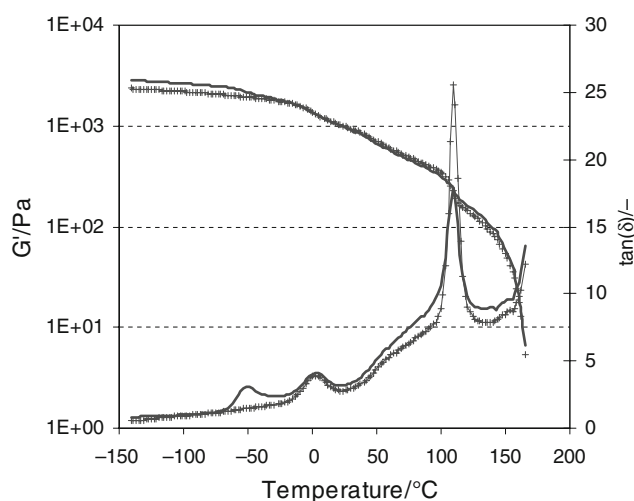


**Fig. 5** DMTA results: temperature dependence of loss angle tangent comparing materials pure PP/PS-blends without (CC1) and with SEBS compatibilizer (CC2)



**Fig. 7** Correlation of storage modulus G′ at +23 °C to the flexural modulus for blend/nanocomposite series

and room temperature storage. Earlier investigations on homopolymers had exhibited an improvement of both modulus and impact strength right after annealing with a decay of the toughness and a further increase of the stiffness in storage [5]. When looking at the transition temperatures and the storage modulus determined in DMTA

(see Table 4), this can be only partly related to the standard tests and the earlier results. Especially the modulus decrease in DMTA after annealing appears confusing, while the increase in glass transition is in line with a recent result of Androsch' group in Germany [21].

**Fig. 6** Correlation between notched impact strength (NIS) at +23 °C (left) as well as the overall PP content (right) and integral of the PP glass transition peak in the loss angle tangent curve (ATD) for blend/ nanocomposite series
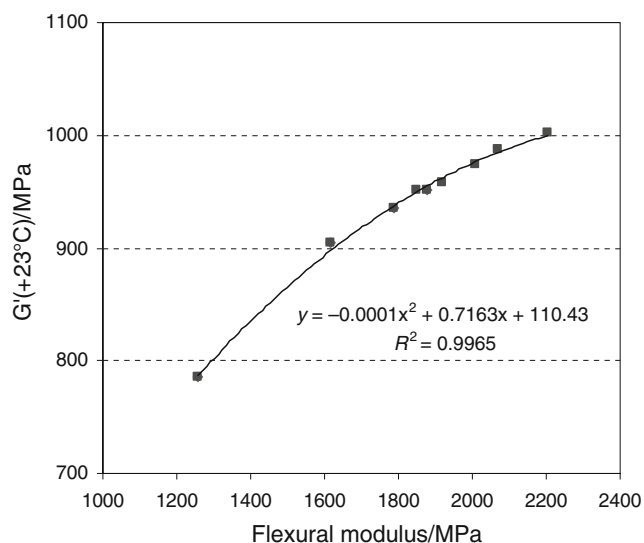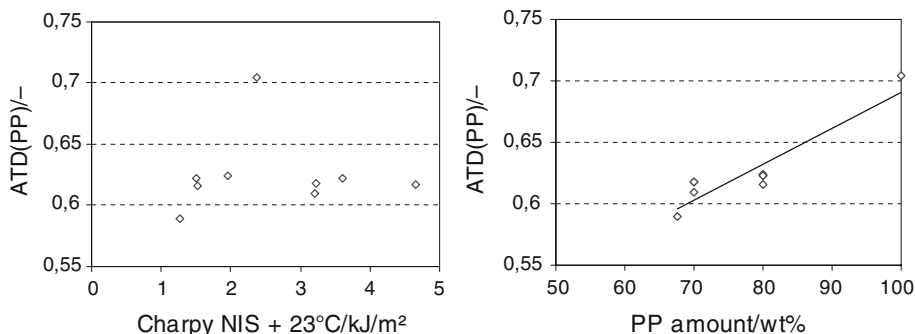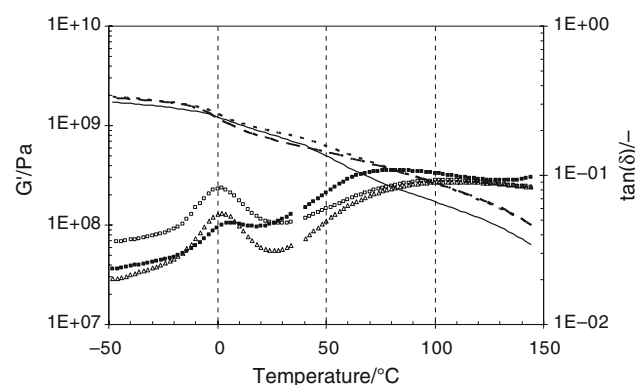
**Fig. 8** DMTA results: annealing/ageing effects on storage modulus G′ and loss angle tangent curves (as processed: *full line* and *filled square*; after annealing 145 °C/1 h: *long dashes* and *open square*; after annealing and storage 23 °C/96 h: *short dashes* and *open triangle*)

**Table 4** Results of ageing/annealing of HCPP homopolymer

| | $T_g(PP)/$ °C | $T_{\alpha,c}/$ °C | $G'(23\,°C)/$ MPa | Flex. mod./ MPa |
|---|---|---|---|---|
| Molded | 6 | 80 | 836 | 2030 |
| Annealed 1 h/145 °C | 2 | 104 | 749 | 2140 |
| Annealed and stored 96 h/23 °C | 2 | 108 | 911 | 2380 |

## Conclusions

The main challenges in trying to correlate DMTA tests to standard mechanics clearly result from the morphology effects at different scales, both in crystallinity and flow-induced superstructures (orientation) and in multiphase impact copolymers or composites. It is clearly more critical for polymers with high sensitivity to processing effects; limitations for complex systems have recently been exemplified in another study of our group [22].

Another more elementary problem lies in the present standard for DMTA testing, ISO6721-7. While specifying sample dimension, frequency and heating rate, it is not sufficient in terms of describing or specifying the sample preparation. For practical use of correlations to both modulus and impact strength, calibration with comparable materials is required in any case. While a relative scaling is easy, absolute prediction is difficult and can—as shown for the case of ageing—even be misleading.

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