

# Property modeling across transition temperatures in polymers: application to thermoplastic systems

C. A. MAHIEUX\*, K. L. REIFSNIDER

Virginia Polytechnic Institute and State University, Materials Response Group,  
120 Patton Hall, Blacksburg, VA 24060, USA

E-mail: celine.mahieux@power.alstom.com

The growing demand for virtual design of composite materials necessitates the development of comprehensive models relating the microstructure of the constituents to the macroscopic mechanical behavior. In this spirit, a new model was recently introduced that enables the computation of polymer stiffness over the entire range of use temperature (C. A. Mahieux and K. L. Reifsnider, *Polymer* **42**(7) (2001) 3281). A preliminary study stated the feasibility of the approach and the apparent possibility of applying this model to all polymers. The present study investigated the possibility of applying the model to some commercial thermoplastics: PMMA, PEEK, PPS and AS4/PPS composite. Cryogenic DMA were performed and the properties (crystallinity and molecular weight) of the composites were systematically varied. The model was applied to the different materials. The influence of the chemical nature, the molecular weight and the crystallinity content on the model input was carefully studied. The molecular nature and molecular weight were found to have little influence on the statistical parameters; the statistical parameter associated with the glass transition was found to vary linearly with crystalline content for the semi-crystalline samples. The model was found to successfully represent the behavior of all of the polymer based systems considered in the present study. © 2002 Kluwer Academic Publishers

## 1. Introduction

Temperature greatly influences the mechanical response of polymers and polymer matrix composites. Even unidirectional carbon reinforced polymer matrix composites are found to exhibit temperature dependent stiffness and strength in the fiber direction. Composite materials are used over a wide range of service conditions, including temperatures within the matrix transitions. To enable virtual design of composites, it becomes necessary to carefully establish models relating the microstructure of the composite's constituents and the service conditions to the mechanical response of the system. Previous literature only focuses on the different regions of the polymer (glassy, rubbery) and do not offer a consistent model enabling the description of the mechanical properties of the material over the entire range of temperatures. A new model was recently established that described the instantaneous polymer stiffness as an explicit function of temperature from glassy state to flow, including the transition [1–6]. This model [1] was validated using experimental data taken at random from the literature. The statistical model showed potential for modeling the behavior of polymers and co-polymers over wide temperature ranges. This preliminary study suggested that the input parameters (e.g., Weibull parameter associated with each transition) might be related to the details of the molecular

arrangement of the polymers. The present paper investigates the applicability of the statistical model to various commercial polymers with very different properties. The effect of the chemical nature of the polymer, molecular weight and crystallinity will be carefully studied and analyzed. It is very difficult to find data concerning polymers in the literature where only one parameter was changed (e.g. molecular weight or crystallinity) keeping all other parameters constants for very wide temperature ranges (cryogenic to flow). Therefore, cryogenic DMA were performed on 4 polymer based systems (PMMA, PEEK, PPS and AS4/PPS) of different molecular weights and crystallinity contents. Finally the feasibility of applying the model to all polymers for any temperature range will be discussed and the impact on composite life modeling will be assessed.

## 2. Background

Following Ashby's [7] idea that relaxation in polymers requires the breakage of secondary bonds (referred to as "melting" of the secondary bonds by Ashby), a new model was established by Mahieux and Reifsnider [1] to explicitly relate the instantaneous stiffness of a polymer to temperature and applied to various polymers and composites [2–6, 8]. The concept can be summarized as follows.

\*Present Address: Alstom (Switzerland) Ltd, Hydrogenerator Technology Center, CH-5242 Birr, Switzerland.

Any transition in the polymer (secondary relaxation, glass transition, flow) requires breakage of secondary bonds (e.g. Van der Waals, polar attraction). By breakage we mean cessation of the attractive interaction between the specific atoms involved in the molecular motion corresponding to the specific relaxation, i.e. rotation of a side group (e.g. beta transition), reptation of the main chains (e.g. glass transition) or global translations (e.g. flow).

A distribution of strengths exists for the bonds between the macromolecules due to the different nature of bonds present in the material (e.g. Van der Waals, cross-linking) and the spatial arrangement of the molecules (Van der Waals interactions depending on the proximity of the atoms). Failure of these bonds can be represented by Weibull statistics at the microscopic level. For a number of transitions varying from 1 to 3, the following equations were established [1]:

$$E = E_3 \exp\left(-\left(\frac{T}{T_3}\right)^{m_3}\right) \quad (1)$$

$$E = (E_2 - E_3) \exp\left(-\left(\frac{T}{T_2}\right)^{m_2}\right) + E_3 \exp\left(-\left(\frac{T}{T_3}\right)^{m_3}\right) \quad (2)$$

$$E = (E_1 - E_2) \exp\left(-\left(\frac{T}{T_1}\right)^{m_1}\right) + (E_2 - E_3) \times \exp\left(-\left(\frac{T}{T_2}\right)^{m_2}\right) + E_3 \exp\left(-\left(\frac{T}{T_3}\right)^{m_3}\right) \quad (3)$$

Where the subscripts 1, 2, 3 refer to a given transition (e.g. 1 for beta transition, 2 for alpha transition and 3 for flow),  $E_i$  is the instantaneous modulus in each region before the transition, and  $T_i$  is the transition temperature.

Values for  $E_i$  and  $T_i$  can be found in the literature for common polymers. The major discussion focuses on the statistical parameters  $m_i$ . These parameters were found to be almost constant ( $m_1 = 5, m_2 = 20, m_3 = 20$ ) except for the crosslinked thermoset. The purpose of the present paper is to establish if these coefficients remain constant if the nature (chemical composition) of the polymer remains unchanged but the properties are significantly varied.

### 3. Experimental work

#### 3.1. Material selection

The different polymers were arbitrarily chosen. Three thermoplastics: Poly(methyl methacrylate) (PMMA), Poly(ether ether ketone) (PEEK) and Poly(phenylene sulfide) (PPS), and one composite: AS4/PPS were selected.

PMMA is a linear amorphous thermoplastic and exhibits the presence of secondary relaxations. The beta transition occurs around 0°C. Two different grades of plexiglas were obtained from Rohm and Haas:

- plexiglas MC: Low molecular weight PMMA Mw around 150,000 g/mole.
- plexiglas G: very high molecular weight PMMA (around  $10^6$  g/mole).

Little information could be obtained from the company concerning the molecular details of the material. The samples were supplied as  $10.15 \times 10.15$  mm ( $4'' \times 4''$ ) plates with a thickness of 3 mm.

PEEK is a linear aromatic polymer. PEEK also has a beta relaxation around  $-30^\circ\text{C}$  for the crystallized material. Different grades of PEEK were supplied by Victrex:

- 150 G: with a melt viscosity of  $0.150 \text{ kN} \cdot \text{s} \cdot \text{m}^{-2}$ .
- 450 G: with a melt viscosity of  $0.450 \text{ kN} \cdot \text{s} \cdot \text{m}^{-2}$ .

The molecular weight can be calculated from these values [9]:

- Mw (PEEK 150) = 27,222 g/mole.
- Mw (PEEK 450) = 38,331 g/mole.

The material was supplied as pellets.

PPS is a linear polymer. Two grades of PPS were supplied by Phillips Petroleum Company: PR09 and PR10X2. According to Phillips [10], the typical molecular weight for the grade PR09 is 65,000–70,000 g/mole. PR10X2 has a lower molecular weight, around 55,000 to 65,000 g/mole. These numbers were determined by exclusion chromatography. The supplier claimed that scatter of the results is typical and stated that these numbers can vary by as much as 10%. The PPS from Phillips was in a powder form.

Another grade of PPS (0320 PO) was supplied by Fortron Celanese. The molecular weight for this material could not be determined. The PPS Celanese was received as pellets.

For the last two thermoplastics, one must keep in mind that the molecular weights are approximate, considering the difficulties in measuring the molecular weight of these two materials (due to the poor solubility).

Unidirectional AS4/PPS composite was provided by Baycomp. The volume fraction of fibers was 50%. The material was supplied as a  $0.5'' \times 0.04''$  rolled tape.

#### 3.2. Materials processing and samples preparation

Unlike PMMA that did not need any further modification before testing, PPS and PEEK needed to be put into a plate form in order to be tested.

The PEEK samples were made by injection molding following a standard procedure [11]: the polymer was injected using an Arburg Allrounder Model 221-55-250 in a  $75 \times 80 \times 1.6$  mm mold. The injection pressure was held constant at 5 MPa, the holding pressure at 10 MPa and the flow at  $10 \text{ cm}^3/\text{s}$ . The temperature varied from the “solids conveying zone to the nozzle”: Zone 1 :  $380^\circ\text{C}$ , Zone 2 :  $400^\circ\text{C}$ , Zone 3 :  $400^\circ\text{C}$ , and Zone 4 :  $400^\circ\text{C}$ . The temperature of the mold was  $200^\circ\text{C}$ .

The PPS Celanese was received as pellets. The PPS from Phillips was received as powder straight from the reactor. The material was pelletized in an extruder at around  $290^\circ\text{C}$ . The PPS powders were injection molded following the same procedure than in the PEEK

case. The temperatures of the different zones were: Zone 1 : 250°C, Zone 2 : 290°C, Zone 3 : 280°C, and Zone 4 : 270°C. The mold was at 140°C.

For each material, the samples were made by sawing the plates using a band saw in dry conditions. The final samples had a size of 25.4 × 6.35 mm (1" × 1/4") for the DMA samples ("long samples"). Some extra smaller samples were also cut off the plates for DSC testing ("short samples"). The thickness of the final samples was approximately 3 mm for the PMMA and 1.5 mm for PEEK and PPS.

### 3.3. Crystallinity modifications

Each semi crystalline material: PEEK 150, PEEK 450, PPS PR9, PPS PR10, PPS Celanese, AS4/PPS composite, was tested as received. Then various heat treatments were applied to the samples in order to modify the crystallinity of the various polymers.

In order for the material to reach the highest crystallinity level possible, the specimens were annealed at elevated temperatures for relatively long times (PEEK and PPS are fast crystallizers). The PEEK samples (2 long samples, 1 short sample) of each grade were placed on an Aluminum plate in an oven (Fisher Scientific Isotemp Vacuum Oven Model 282A) at 180°C (crystallization temperature) for one hour. Similarly, the PPS samples were placed in the oven at 130°C for 1 to 3 hours (for Celanese material). The composite was placed at 130°C for several hours in the oven.

The process of getting amorphous polymers is more complex (PEEK and PPS are very fast crystallizers). Several attempts were necessary to achieve satisfactory results. One must also note that very high temperatures are involved and the use of a tube furnace (Labline model 4305, inner diameter: 78 mm) was necessary. The temperature was recorded by a thermocouple twisted on a screw attached to the aluminum plate. The temperature in the oven varies by 5°C when compared to the set point of the furnace.

For each type of material, 2 long specimens and 1 short specimen were placed on the 75 × 38 × 10 mm aluminum plate (the preheated mold was previously sprayed with release agent) at a temperature above melting for more than 1 hour then quenched in ice water. The exact procedure for each sample and observations is summarized in Table I.

The AS4/PPS composite as received had a very low crystallinity content and was considered as amorphous.

Intermediate crystallinity values were obtained for PEEK by placing the amorphous specimens in the oven at 180°C for one to two minutes then taking them out

of the oven, and letting them cool at room temperature. Crystallization of PEEK was very rapid. If the specimen was in the oven for more than 2 minutes, the sample became fully crystallized. But one minute was just enough for the specimen to get to temperature, and the percent of crystallinity was too close to the amorphous samples. For this reason, another scheme was used to obtain results on intermediate crystallinity values. The intermediate sample that was used later was obtained by running a DMA up to melting at 2°C/min then cooling the specimen down in air. The same sample was then placed again in the DMA. With this process, no crystallinity was measured for these samples.

Intermediate crystallinity PPS samples were obtained by placing the specimen in the oven at 130°C for 2 minutes and then air cooling at room temperature.

### 3.4. Crystallinity evaluation

In order to evaluate the crystallinity of all the samples, Dynamic Scanning Calorimetry (DSC) experiments were performed. Unfortunately, this type of testing is a destructive evaluation: the measurements were performed on the short specimens that were heated and quenched at the same time as the long specimens for DMA.

DSC of all the specimens was performed with a Dupont DSC model 910 at 20°C/min (standard heating rate to minimize molecular rearrangement). The DSC results are summarized in Table II.

We will keep in mind that the crystallinity and molecular weight measurements are extremely difficult for PEEK and PPS. The amorphous materials exhibit very low crystallinity in accordance with the heat treatment and the visual aspect of the samples (transparent). The crystallinity contents seem a little high for PPS as received (typical crystallinity of 30%). This can be due to the values of the theoretical melting enthalpy used in the calculations. Therefore the above values will be considered as indications for trends and not absolute values.

### 3.5. DMA

Dynamic Mechanical Analysis was performed on the different samples on a Polymer Laboratory MkII dynamic thermal analyzer (DMTA, DMA). The deformation geometry was a single cantilever. Each sample was tested from -100°C up to flow of the material at different frequencies: 50 Hz, 20 Hz, 10 Hz, 5 Hz and 1 Hz. Tangent delta and storage modulus were recorded in bending as a function of temperature. The samples were tested at a heating rate of 2°C/min. We will not deal in the present paper with rate effects. The results at 20 Hz were arbitrarily chosen and are shown in the following section.

## 4. DMA results and model validation

### 4.1. Effect of crystallinity

For the two thermoplastics (PEEK and PPS) and the composite it is possible to study the influence of crystallinity on the parameters used in Equations 1-3.

TABLE I Amorphous heat treatment of the semi-crystalline samples

Material	Oven T (°C)	Time in oven	Quenching	Resulting sample
PPS Celanese	330	1 h 30	Ice water	Transparent
PPS PR09	330	1 h	Ice water	Transparent
PPS PR10	330	2 h	Ice water	Brown opaque
PEEK 150	365	1 h 30	Ice water	Transparent
PEEK 450	365	2 h	Ice water	Transparent

TABLE II Crystallinity content of the different samples

Material	Crystallinity (%)	Material	Crystallinity (%)
PPS Celanese amorphous	2	AS4/PPS as received	2
PPS Celanese intermediate	30	AS4/PPS annealed	28
PPS Celanese as received	36	PEEK 150 amorphous	0
PPS PR09 amorphous	2	PEEK 150 intermediate	≈12
PPS PR09 intermediate	21	PEEK 150 as received	24
PPS PR09 as received	52	PEEK 450 amorphous	0
PPS PR10 amorphous	10	PEEK 450 intermediate	≈12
PPS PR10 intermediate	15	PEEK 450 as received	24
PPS PR10 as received	47		

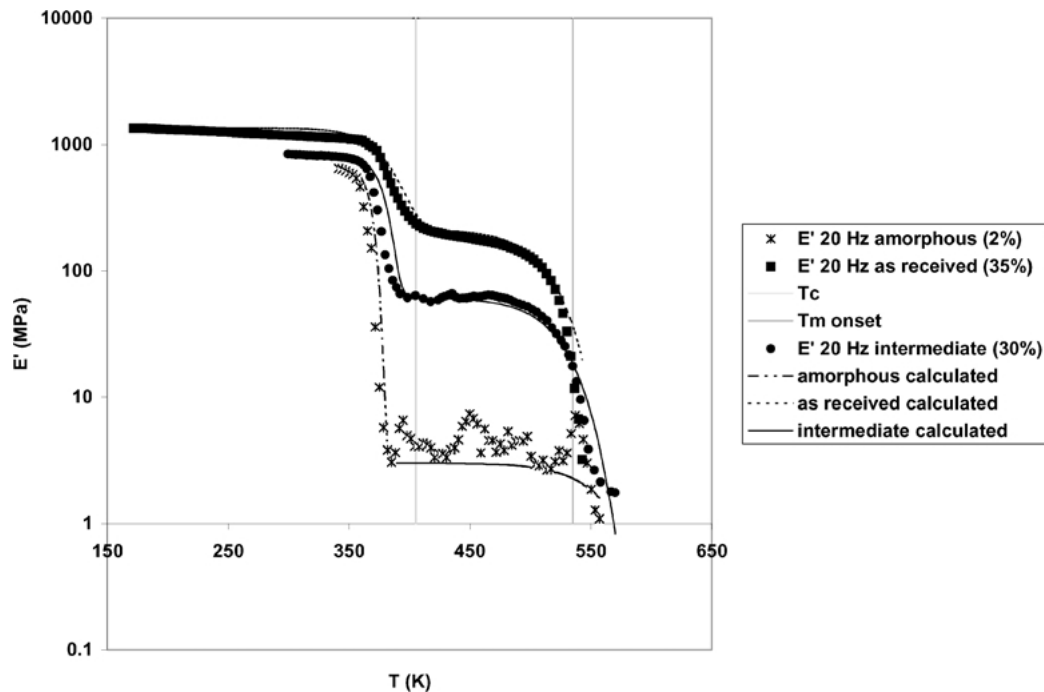


Figure 1 Experimental and theoretical results for various crystallinities of PPS Celanese.

#### 4.1.1. PPS Celanese

The experimental results and theoretical fit are shown in Fig. 1 for the amorphous material, the intermediate crystallinity and the sample as received. The results of the DMA for the different sample of PPS show the trend expected from the literature: the magnitude of the drops during the transition increases with a decreasing amount of crystallinity in the material. All the curves meet after the melting point of PPS Celanese (540 K). The melting and flow regions are not distinct. The material starts flowing immediately after the melting temperature. The amorphous sample exhibits the presence of a rise of the modulus right after the glass transition, due to the fact that the material reaches the crystallization temperature. The rate of the testing was slow (2°C/min) and therefore, the material was allowed to recrystallize. We only tried to fit our model to the section of the curve located before the crystallization temperature.

No secondary transition could be observed. Therefore Equation 2 was used to model the behavior. The necessary parameters for the model are the heights of the glassy and rubbery plateaus and the transition temperatures (glass transition and melting-flow as indicated by the DSC or tan delta). We also need the two Weibull moduli associated with the different transitions. All

TABLE III Parameters for PPS Celanese

Material	$T_2$	$T_3$	$E_2$ (MPa)	$E_3$ (MPa)	$m_2$	$m_3$
PPS Celanese amorphous	370	520	646	3	60	20
PPS Celanese intermediate	380	530	832	61	40	20
PPS Celanese as received	385	570	1348	212	20	20

these parameters are summarized in Table III. The glass transition temperature increases slightly with increasing crystallinity. The glass temperature varies between 97°C (amorphous) and 112°C (crystallized). The flow temperature is hard to define from our experimental results and the temperature chosen was the beginning of the final drop.

#### 4.1.2. PPS PR09

The results for the PPS PR09 samples are summarized in Table IV and Fig. 2. The intermediate crystallinity content was low and we can observe recrystallization for the amorphous sample as well as for the intermediate sample.

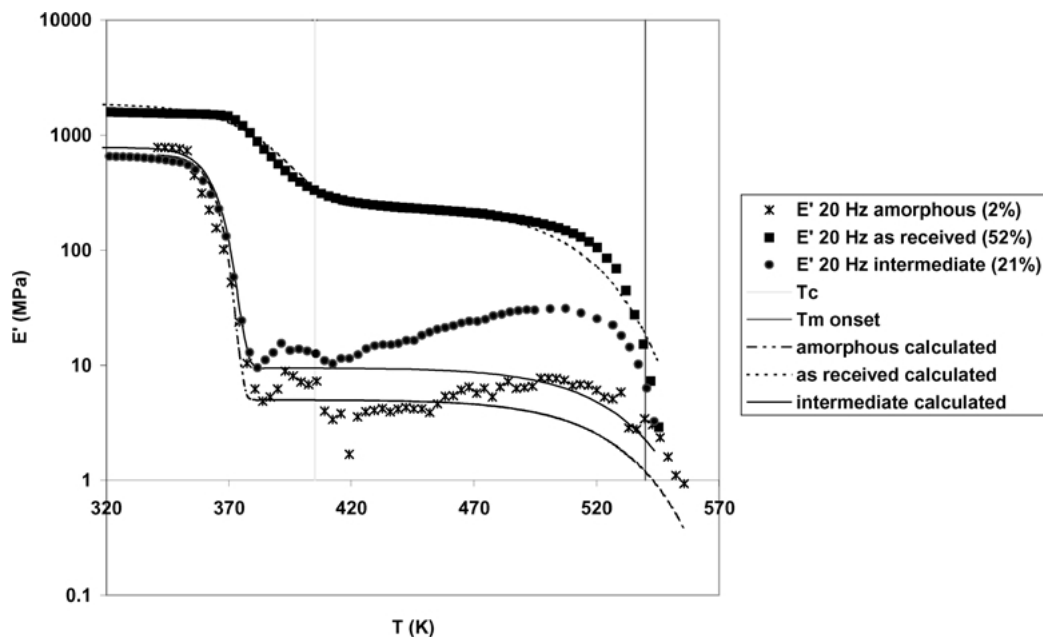


Figure 2 Experimental and theoretical results for various crystallinities of PPS PR09.

TABLE IV Parameters for PPS PR09

Material	$T_2$	$T_3$	$E_2$ (MPa)	$E_3$ (MPa)	$m_2$	$m_3$
PPS PR09 amorphous	365	530	682	5	60	20
PPS PR09 intermediate	365	530	780	9.5	50	20
PPS PR09 as received	385	515	1875	240	20	20

TABLE V Parameters for PPS PR10

Material	$T_2$	$T_3$	$E_2$ (MPa)	$E_3$ (MPa)	$m_2$	$m_3$
PPS PR10 amorphous	373	520	1543	280	60	20
PPS PR10 as received	373	520	841	32	20	20

#### 4.1.3. PPS PR10

The PR10 samples were also studied. However, during the experiments, strange behavior of the material indicated the presence of impurity in this sample (the material was very difficult to melt, a fully transparent material could not be obtained. . .). The intermediate samples exhibited low crystallinity contents and lead to a mechanical response similar to the amorphous sample. For a better clarity, only the DMA results on the amorphous and the as-received samples are shown in Fig. 3 and Table V. In the glass transition region, the behavior of the material as received is also surprising: the drop is very steep and a bump immediately follows. This, again, can be explained by the presence of impurities in the polymer.

#### 4.1.4. PEEK 150

A similar approach was used for the different crystallinities of the PEEK 150 samples (amorphous, intermediate, as received). PEEK exhibits the presence of a secondary relaxation at low temperatures. Therefore Equation 3 was used to model the mechanical response

of the polymer. Similar observations to the PPS samples can be made (Fig. 4):

- the magnitude of the glass-transition drop increases with decreasing crystallinity,
- the transition temperatures increase with increasing crystallinity,
- the beta transition temperature varies between  $-60^\circ\text{C}$  for the amorphous material to  $-30^\circ\text{C}$  for a crystallized material that corresponds to values given in the literature [12],
- the glass transition is between  $144^\circ\text{C}$  and  $157^\circ\text{C}$  that also corresponds to literature data [13],
- a modulus increase can be observed for the amorphous sample at the crystallization temperature.

The different parameters are summarized in Table VI.

#### 4.1.5. PEEK 450

The results for PEEK 450 are shown in Fig. 5 and Table VII.

#### 4.1.6. AS4/PPS composite

A DMA was also performed on the composite as received (almost amorphous) and crystallized (Fig. 6, Table VIII). As the DMA was performed in bending, we can observe a large temperature effect. For the crystallized sample, the glass transition disappears. This behavior was observed in other studies for highly crystalline materials [14]. In this case, we only need a “one transition” model (Equation 1).

## 4.2. Effect of molecular weight

We also investigated the effect of molecular weight on the different parameters by testing different grades of a same polymer.

TABLE VI Parameters for PEEK 150

Material	$T_1$	$T_2$	$T_3$	$E_1$ (MPa)	$E_2$ (MPa)	$E_3$ (MPa)	$m_1$	$m_2$	$m_3$
PEEK 150 amorphous	213	417	570	824	661	10	5	60	20
PEEK 150 intermediate	230	430	570	900	780	93	5	30	20
PEEK 150 as received	254	431	570	1875	1470	275	5	20	20

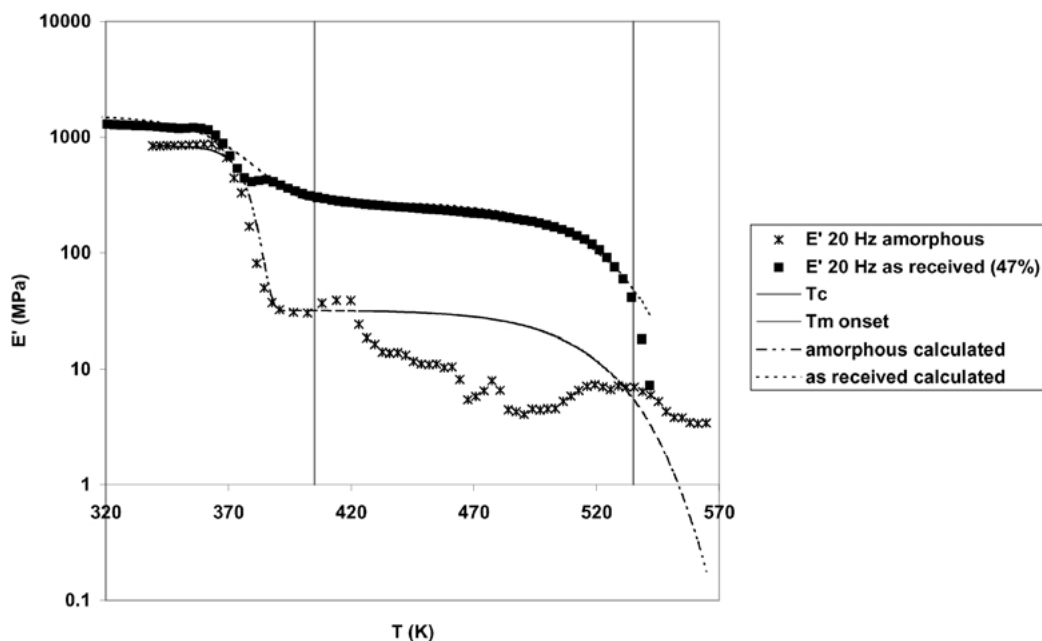


Figure 3 Experimental and theoretical results for various crystallinities of PPS PR10.

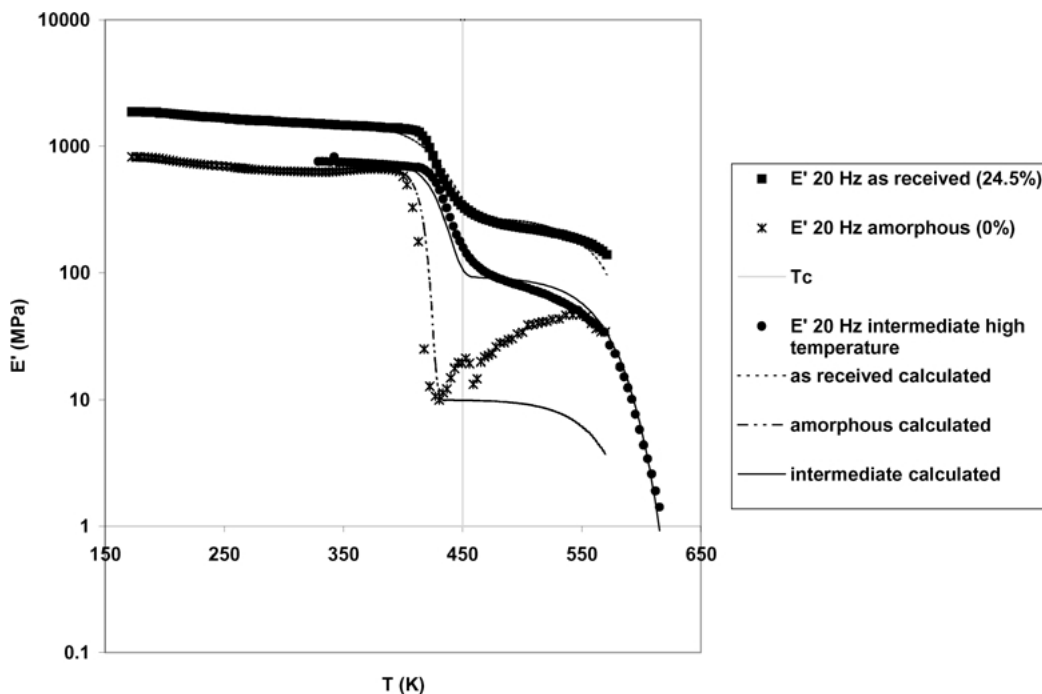


Figure 4 Experimental and theoretical results for various crystallinities of PEEK 150.

#### 4.2.1. PMMA

To investigate the effect of molecular weight on our model, a completely amorphous material was chosen. The two molecular weight samples of PMMA were tested and experimental results are reported in Fig. 7. The different parameters are summarized in Table IX. As expected the high molecular weight material was slightly stiffer than the low molecular weight sample.

The different transitions also occurred at higher temperatures for the high molecular weight specimen.

#### 4.2.2. PPS

For comparison purposes, the DMA of the PPS samples with different molecular weights were plotted on the same graph (Fig. 8). The samples “as-received” are

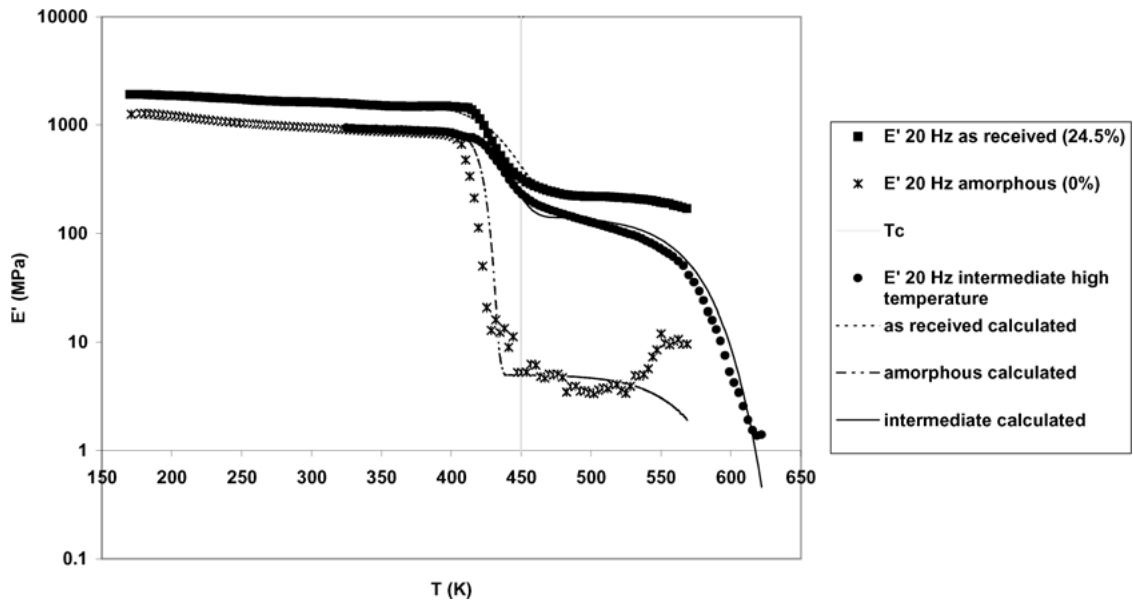


Figure 5 Experimental and theoretical results for various crystallinities of PEEK 450.

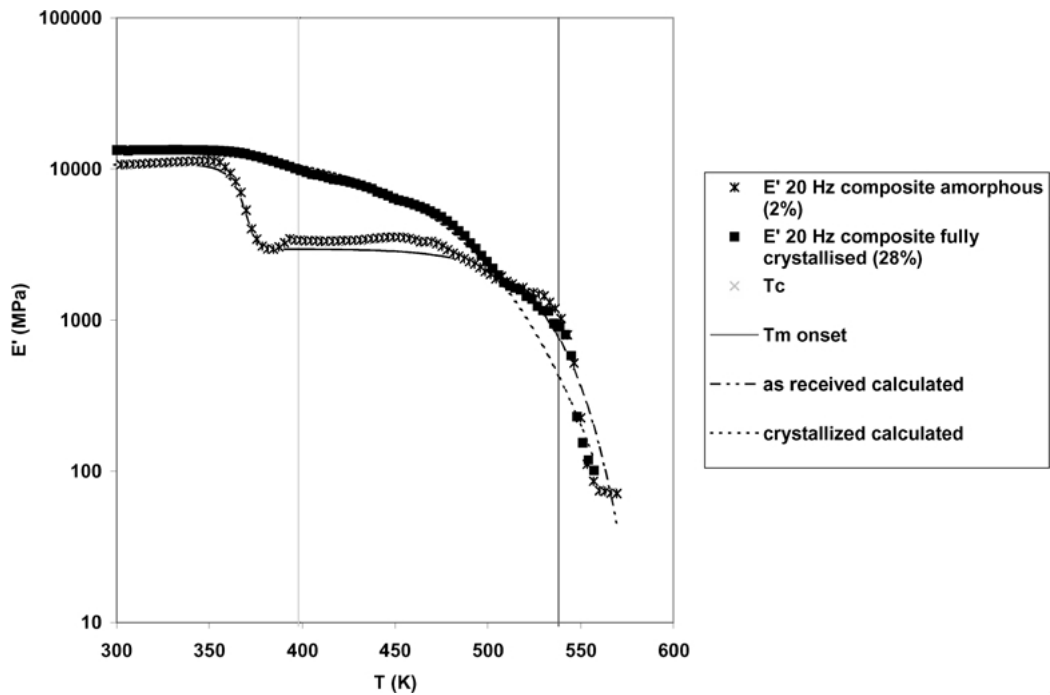


Figure 6 Experimental and theoretical results for various crystallinities of AS4/PPS composite.

TABLE VII Parameters for PEEK 450

Material	$T_1$	$T_2$	$T_3$	$E_1$ (MPa)	$E_2$ (MPa)	$E_3$ (MPa)	$m_1$	$m_2$	$m_3$
PEEK 450 amorphous	22	42	570	1279	920	5	5	60	20
PEEK 450 intermediate	22	43	570	1300	950	143	5	30	20
PEEK 450 as received	25	43	600	1920	1600	220	5	20	20

TABLE VIII Parameters for AS4/PPS composite

Material	$T_2$	$T_3$	$E_2$ (MPa)	$E_3$ (MPa)	$m_2$	$m_3$
PPS/AS4 composite as received	368	530	10690	2957	60	20
PPS/AS4 composite crystallized		469		11335		9

compared. One should note that the crystallinities are slightly different from one grade to the other. The higher molecular weight material is a little bit stiffer and flows at slightly higher temperatures. The PR10 grade (lower molecular weight) crosses the other molecular weight

curve. This phenomenon has been observed in other studies [15] but is not yet well understood.

#### 4.2.3. PEEK

The two grades of PEEK were plotted on a same graph (Fig. 9). The as-received samples had similar crystallinities. Higher molecular weight PEEK is slightly

TABLE IX Parameters for PMMA

Material	$T_1$	$T_2$	$T_3$	$E_1$ (MPa)	$E_2$ (MPa)	$E_3$ (MPa)	$m_1$	$m_2$	$m_3$
PMMA MC ( $10^5$ g/mol)	273	375	480	1080	867	1.4	5	20	20
PMMA G ( $10^6$ g/mol)	273	385	530	1347	1150	2	5	20	20

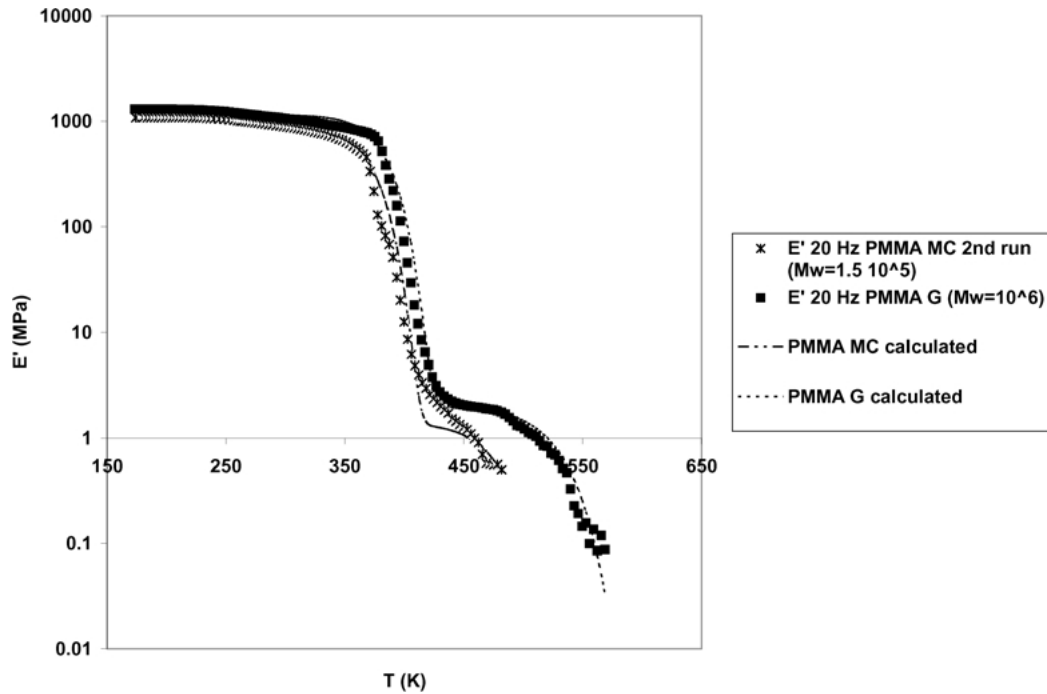


Figure 7 Experimental and theoretical results for PMMA.

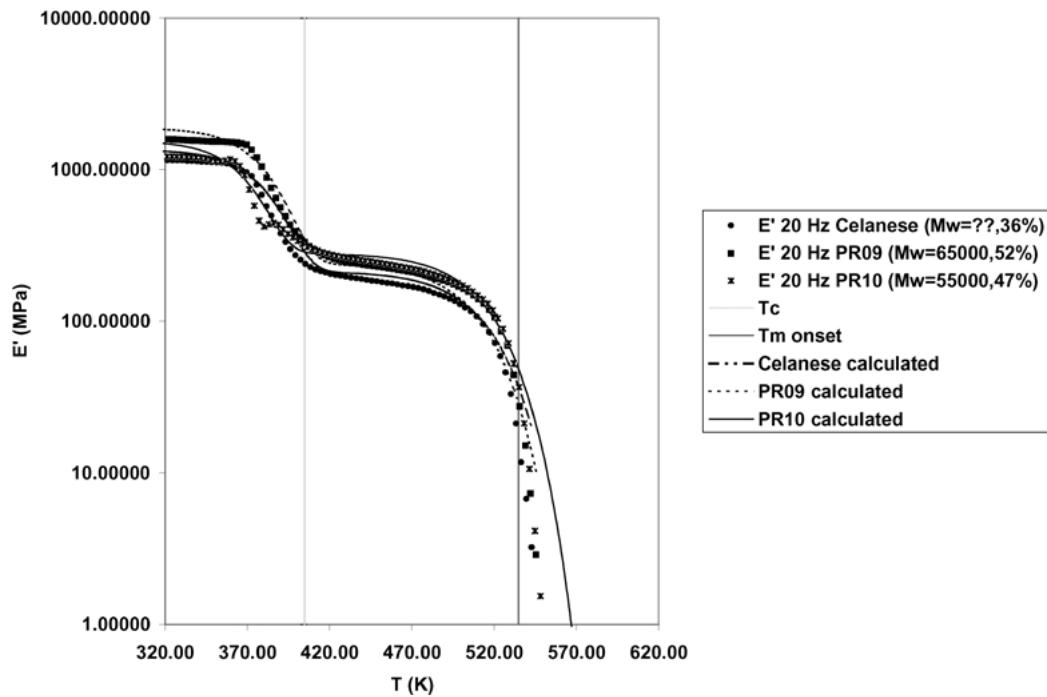


Figure 8 Experimental and theoretical results for various molecular weights of PPS.

stiffer and flows at temperatures slightly higher than the lower molecular weight. However, the difference between these two curves is not clearly significant.

## 5. Discussion

Using the model summarized in Section 2 leads to a fairly successful representation of the various polymers

having different chemical nature, molecular weights and crystallinity contents. We could also successfully represent the behavior of the polymers in the different regions and transitions, from glassy state to melting and flow. However, the behavior of the amorphous polymers can only be analytically represented up to the crystallization temperature. After this temperature and



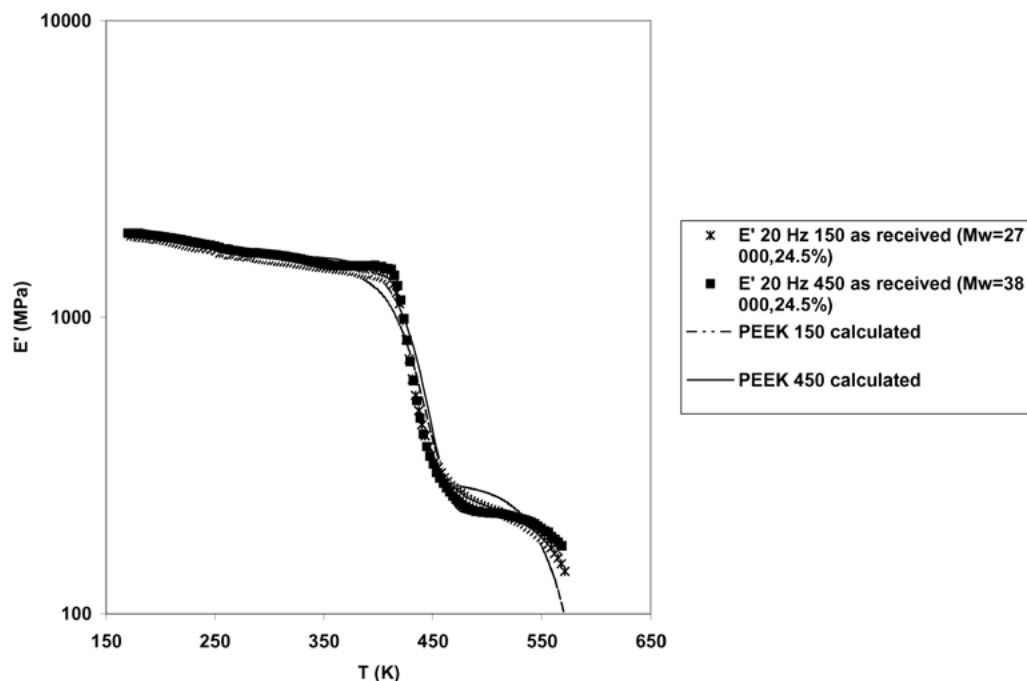


Figure 9 Experimental and theoretical results for various molecular weights of PEEK.

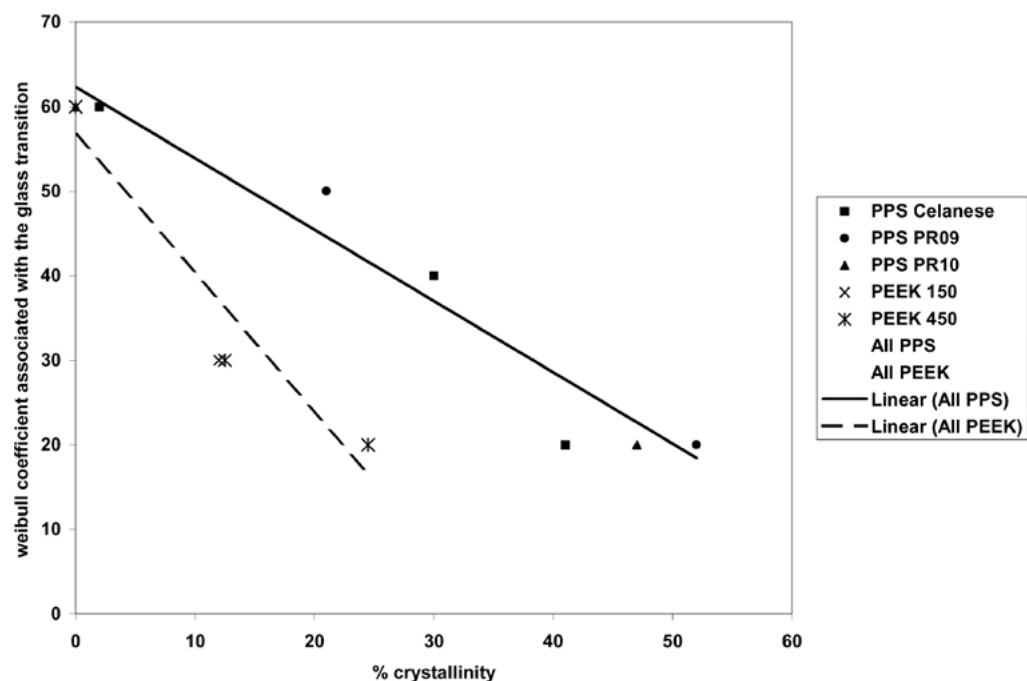


Figure 10  $m_2$  versus crystallinity content.

at low heating rates, the material recrystallizes during the measurements leading to a rise in the modulus. At the present point, the model does not allow for bond re-formation.

The parameters needed to apply this equation are of two types: physical parameters and the statistical parameters. All of the physical parameters can be determined by independent experiments (e.g. transition temperatures, instantaneous moduli) and several models exist in the literature that relate these values to the microscopic details of the polymers (e.g. Tg-molecular weight relationship [16], magnitude of the glass transition drop-crystallinity relationship [17]). Therefore the main discussion will focus on the statistical parameters,

the new feature of this study. The different parameters were obtained by fitting the model to the experimental data, in order to obtain the best fit for the shape of the curve (which does not necessarily correspond to the fit that minimizes the error).

The Weibull parameter associated to the secondary relaxations was found to be equal to 5 in the previous study. The fact that this number was smaller than the coefficients associated with the other transitions was attributed to the fact that the number of molecular segments involved in the beta relaxation was small compared to the glass transition. For the different grades of PEEK and PMMA  $m_1$  was also found to be equal to 5.

In the glass transition, we were expecting the Weibull coefficient  $m_2$  to increase, as the number of molecular segments involved increases and the distribution of bond strength broadens. Large Weibull coefficients indicate a very simultaneous relaxation process and leads to a very abrupt glass transition. Lower values ( $m_2 = 5$ ) broaden the transition. The Weibull coefficients were found to be equal to 20 for amorphous PMMA and the thermoplastics as-received. This coefficient does not seem to depend on molecular weight. Only the physical parameters ( $T_i$ ,  $E_i$ ) change according to already-known rules [16]. However, the Weibull coefficient ( $m_2$ ) increases significantly with decreasing crystallinity: as the polymer becomes more homogenous, the distribution of bond failure mechanisms narrows, leading to higher values of the Weibull modulus. The variations of  $m_2$  with crystallinity content is illustrated by Fig. 10. For the intermediate crystallinity PEEK samples, the content was assumed to be half of the maximum crystallinity. For a given material, the relationship between these two parameters appears to be linear. However, as already discussed, the crystallinity contents are only indicators for these materials and can not be taken as absolute value. A theoretical relationship between this coefficient and the percent of crystallinity still needs to be established, based on more extensive experiments, but is beyond the scope of the present paper.

The last coefficient related to melting and flow ( $m_3$ ) was kept equal to 20. The flow region was not studied in detail in the present paper. However, the statistics of bond breakage seems to be applicable to this region of the material. It is remarkable that our model enables the curves associated with the different crystallinity degrees to meet after the melting temperature of the polymer. We will underline the fact that  $m_3 = 1$  corresponds to a crosslinked polymer (random distribution of bond strength). Experiments on polymers with varying crosslinking content would enable the systematic study of this last parameter.

## 6. Conclusions

The statistical model was found to represent the four commercial thermoplastic systems used in the present study. The chemical nature of the polymer and the molecular weight appeared to have little influence on the statistical coefficients and only seemed to influence the height of the different plateaus and the transition temperatures (expected from the literature). The crys-

tallinity, however, greatly influenced the Weibull coefficients associated with the glass transition. The relationship between that statistical parameter was found to vary linearly with the crystallinity content for the two thermoplastics. We expect cross-linking and fillers to act similarly to crystallinity. Further studies are required on thermosets to validate this statement. The presented equations can be easily introduced into micromechanical models for stiffness, strength, and stress-rupture of polymer matrix composite. The contribution of the matrix to the mechanical response of the overall composite becomes a function of temperature, enabling the modeling of the behavior of the composite at any temperature and in the transition regions. Life prediction models for composites can finally be made explicit in temperature (from the glassy to flow region, including the transition regions) for any polymer.

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