

Determination of Dynamic Mechanical Properties of Engineering Thermoplastics at Wide Frequency Range using Havriliak–Negami Model

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ABSTRACT: Using Havriliak–Negami (HN) model of time–temperature superposition, dynamic mechanical properties for two thermorheologically simple engineering thermoplastics, viz., polyether ether ketone (PEEK) and polycarbonate (PC) were determined. Calculations have been made with respect to (i) temperature-independent HN parameters from dynamic mechanical analysis (DMA) and (ii) activation energies of the deformation processes involved. Viscoelastic properties, over a wide frequency range, were predicted

from the HN model, which were further correlated with the experimentally determined quantities and chemical structure of the polymers. The mathematical calculations were done using Matlab[®] software. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 677–683, 2006

Key words: dynamic mechanical analysis; time–temperature superposition; thermoplastic; activation energy; Matlab[®]

INTRODUCTION

Viscoelastic properties of polymers are both temperature- and time/frequency-dependent. However, the effects of these variations may be interconverted by using the fact that the time scales of the motions or relaxations of the constituent molecules of a polymer are affected by temperature. For critical application, informations on the changes of the dynamic properties over a long period of time or exposure to high frequencies are necessary. The response time required in a laboratory experiment to simulate such field conditions is quite long and sometime lies beyond the capability of available thermoanalytical instruments. However, by using empirical models based on the time–temperature superposition principle, the desired evaluation can still be accomplished. Many models like Cole–Cole,¹ KWW,² WLF,³ and Havriliak–Negami (HN)⁴ have occasionally been used for the purpose. The HN model, however, has the distinct advantage over the other models for its simplicity and capability to accurately predict the results. Szabo and Keough,⁵ using HN model, have studied the thermophysical behavior of plasticized polyvinyl chloride (PVC) and of polychloroprene elastomer (CR). Particularly, in case of CR, which shows deviation from HN model both at lower as well as at higher moduli, the authors

have reported that the validity of the HN model analysis procedure can still be justified through calculation of shift factor for time–temperature superposition by applying a complex plane fitting method and choice of appropriate experimental conditions. Dynamic relaxation behavior of the solvent-crystallized polyether ether ketone (PEEK) has been reported by Kalika et al.⁶ Secondary relaxation behavior of the blends of PEEK and polyether imide (PEI) has been investigated by Goodwin and Marsh.⁷ Adams and Gaitonde⁸ have reported on the low-temperature transitions and their effect on the modulus and mechanical damping properties of PEEK. The influence of microstructure on elastic and viscoelastic properties of PEEK has again been investigated by Ogale and McCullough.⁹ The authors have reported that at temperatures below 140°C the shifting parameters are approximately equal for all levels of crystallinity of PEEK. For the materials which are partially crystallized (such as PEEK) and show a nonlinear behavior even at lower applied stress, an efficient method is to isolate the extent of dynamic stress raised due to linear viscoelastic contribution at low strain levels.¹⁰ A laboratory dynamic mechanical analyzer produces a very low excitation strain (~20 nm) and could only marginally influence the dynamic strain signal by irrecoverable deformation process. The amount of irrecoverable strain during such a dynamic cycle is almost negligible. Liu et al.¹¹ have studied the viscoelastic properties of linear and branched polycarbonates (PCs). They have shown that PCs with a long branched chain variety exhibit

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TABLE I
Physical Properties of PEEK and PC

Properties	PEEK	PC
Density (g cm^{-3})	1.30	1.19
Heat-deflection temperature ($^{\circ}\text{C}$) at 455 kPa	160	138
Melting point, T_m ($^{\circ}\text{C}$)	334	—
Glass-transition temperature, T_g ($^{\circ}\text{C}$)	143	154
Flexural modulus at 23°C (GPa)	4.1	2.34
Tensile strength at 23°C (MPa)	97	66
Elongation-at-break (%)	150	110

higher flow activation energy and much longer relaxation time than their linear version. In these studies, limited laboratory testing using multifrequency and accelerated temperatures were conducted. The results were found to be adequate to predict the long-term properties. Empirical approaches were also made where the constant temperature data segments were shifted along the log frequency axis and a master curve was generated. Thus, viscoelastic changes, which occur relatively quickly at higher temperatures, can be made to appear as if they occurred at longer

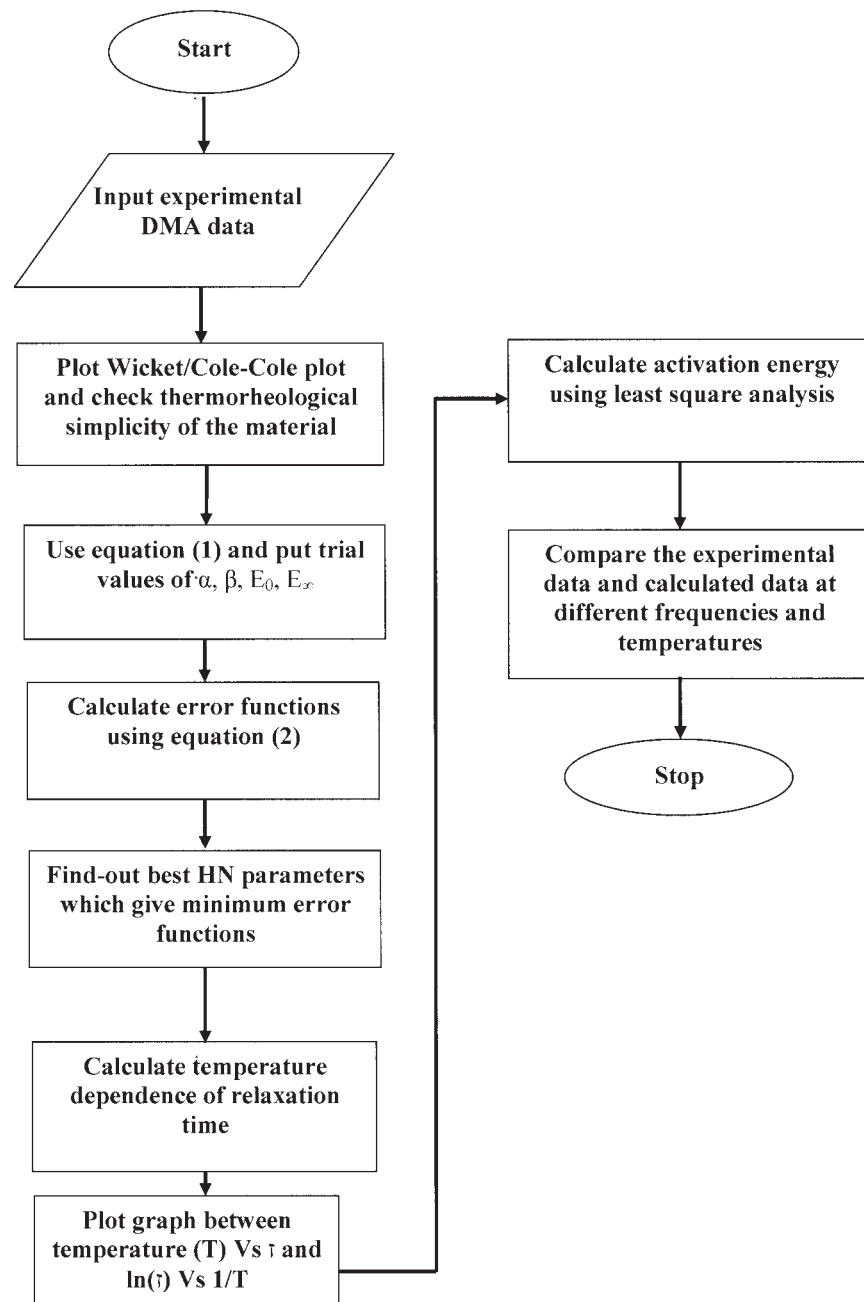


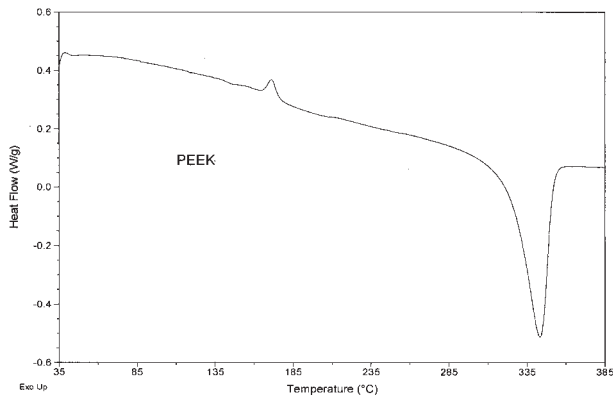
Figure 1 Process diagram for selection of HN parameters and validity tests.

times or lower frequencies simply by shifting the data with respect to time or frequency.

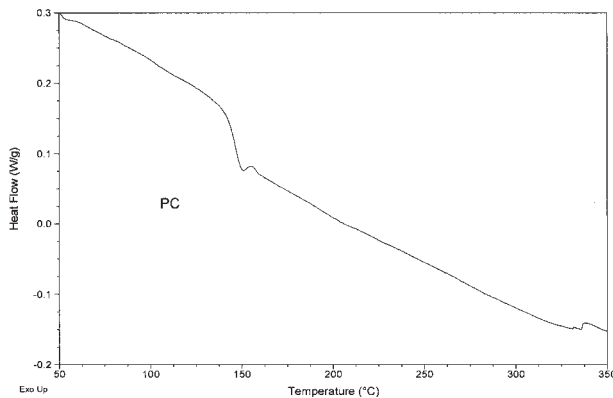
In the present study, we have experimentally evaluated the HN model parameters and carried out computational data fitting exercise through Matlab® software. Two valued engineering thermoplastics, PEEK and PC, have been considered. Matlab is a high-performance language and interactive system for technical computing. This software has been chosen because of its capability of handling of a huge data matrices arising out of dynamic mechanical analysis (DMA).

EXPERIMENTAL

PEEK (Victrex 450G) was obtained from ICI Chemicals and Polymers Ltd., Wilton, Cleveland, UK, and PC (Lexan) was obtained from GE Plastics, Gurgaon, Haryana, India. The physical properties of the PEEK and PC collected from trade literature are listed in Table I. The granules of these polymers were molded into sheets (thickness 3 mm) by a hydraulic press at 400°C for PEEK and 155°C for PC. The test specimens (dimension 35 × 15 × 3 mm³) were cut out from the molded sheets. Differential scanning calorimetry (DSC) studies of PEEK and PC were done in a DSC

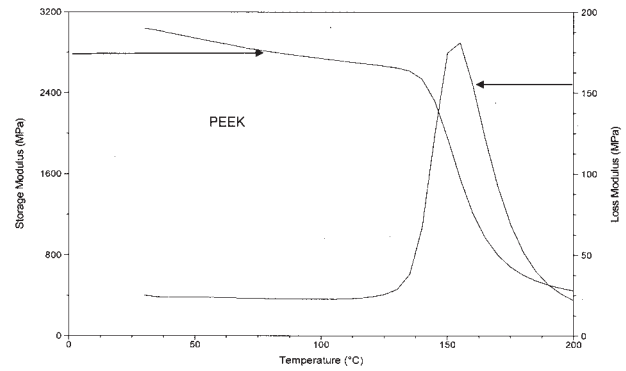


(a)

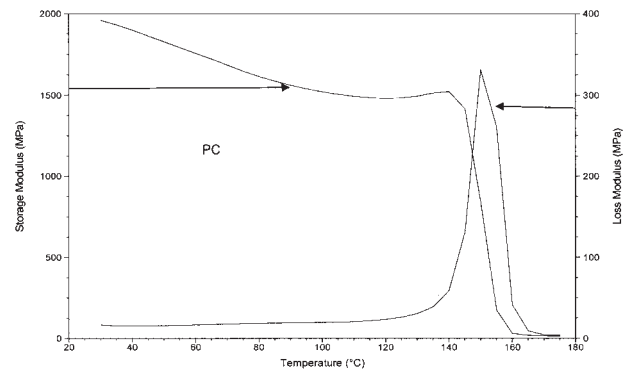


(b)

Figure 2 (a) DSC plot of PEEK. (b) DSC plot of PC.



(a)



(b)

Figure 3 (a) Storage/loss moduli versus temperature plot of PEEK. (b) Storage/loss moduli versus temperature plot of PC.

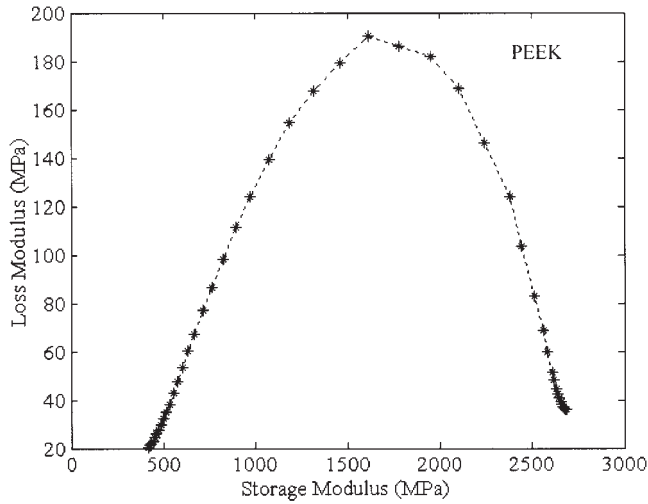
2910 module of TA Instruments Inc., New Castle, DE at a heating rate of 10°C/min in nitrogen flow of 50 mL/min. The heat of fusion (ΔH) of the polymers was determined from the area of melting endotherm. Percent crystallinity (X_c) was calculated as

$$X_c = \Delta H / \Delta H_0 \times 100\% \quad (1)$$

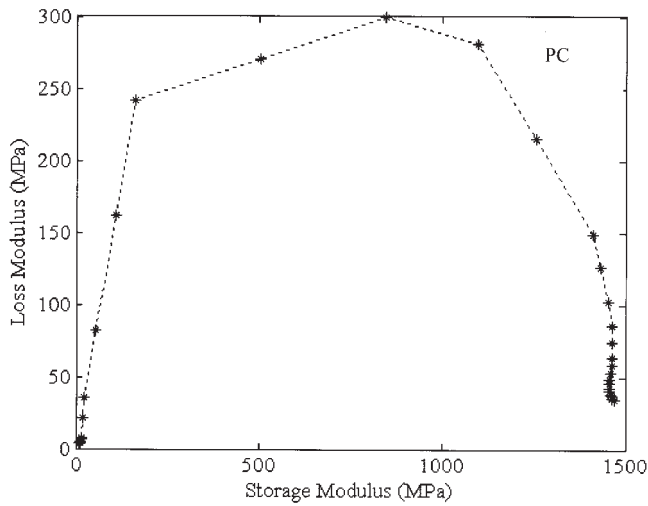
where ΔH_0 is the heat of fusion of 100% crystalline material.

A dynamic mechanical analyzer (DMA 2980 of TA Instruments Inc.) was used for evaluation of dynamic properties, e.g., storage modulus, loss modulus, $\tan \delta$, etc., of the specimen. The experiments were conducted with a dual cantilever clamp in a temperature sweep program from ambient to 200°C in steps of 3°C/min with varied frequencies ($f = 0.1, 0.2, 0.3, 0.5, 0.6, 1.0, 2.0, 3, 5, 6, 10, 20, 30, 50, 60, 100, 125, 150,$ and 175 Hz). Prior to data collection, it was ensured that the samples were attained a thermal equilibrium at a particular temperature until frequency sweep was applied.

The mathematical calculations and graphs were programmed using Matlab software (version 6.5 Release 13) and its statistical toolbox. The experimental DMA data, matrix variables, and scalar matrix vari-



(a)



(b)

Figure 4 (a) Cole–Cole plot of PEEK. (b) Cole–Cole plot of PC.

ables were stored in the Matlab workspace initially. A separate module program was used for preliminary verification of the behavior of the materials, i.e., to testify the thermorheological simplicity by generation of Cole–Cole plot,¹ Wicket plot, etc., as described by Jones.¹² Another module was applied to obtain the HN parameters with least error. The process diagram of these operations is given in Figure 1.

CALCULATIONS

The basic equation of HN model is as follows:

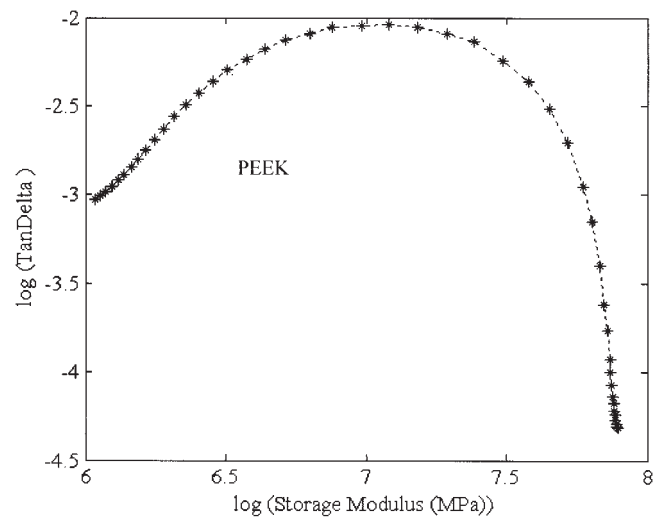
$$E^* = (E_0 - E_\infty) / \{1 + (i\omega\tau)^\alpha\}^\beta + E_\infty \quad (2)$$

The complex modulus E^* , measured at radian frequency $\omega = 2\pi f$, is equal to $E^* = E' + iE''$, where $i = \sqrt{-1}$ (a unit imaginary number). E' and E'' are the

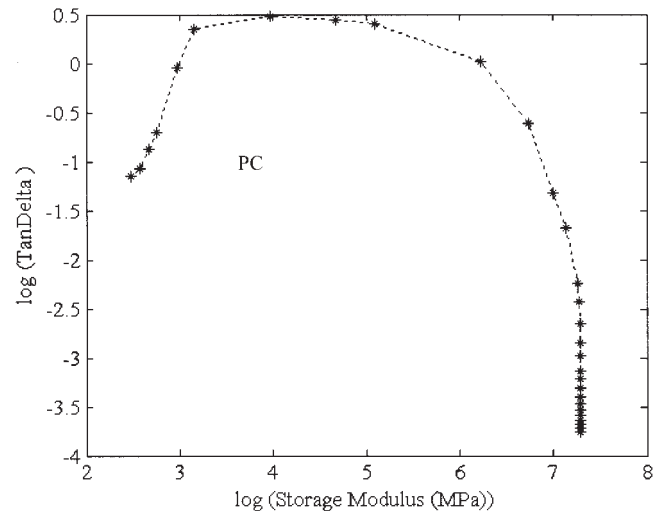
storage modulus and the loss modulus, respectively. E_0 represents the modulus at low frequency and E_∞ is the modulus at high frequency. α is related to the width of the loss peak, while β is related to the asymmetry of the loss peak and τ is the relaxation time. The parameters α and β can have values between 0 and 1.

Our approach involves fitting of four temperature-independent HN parameters viz., α , β , E_0 , and E_∞ , and also the calculation of temperature-dependent relaxation time $\tau(T)$. Trial values for α , β , E_0 , and E_∞ were used by setting $\tau = 1$ in eq. (2). These enable us to calculate $E^*(\omega)$ for frequency range between 10^{-2} and 10^5 Hz. Comparison of calculated complex modulus with the experimental values was carried out for each set of trial parameters to evaluate the degree of fit using both Cole–Cole and Wicket plots. The error function was calculated using the following function,

$$f = \sum E' [\log(\tan \delta_{\text{exp}}) - \log(\tan \delta_{\text{cal}})]^2 / \sum E' [\log(\tan \delta_{\text{exp}})]^2 \quad (3)$$



(a)



(b)

Figure 5 (a) Wicket plot of PEEK. (b) Wicket plot of PC.

where, $\tan \delta_{\text{cal}}$ and $\tan \delta_{\text{exp}}$ are the calculated and the experimental values of the loss factor, respectively. The values of α , β , E_0 , and E_∞ were chosen having minimum error function. The method also allowed us to calculate the HN parameters even from single-frequency DMA data and complex modulus over a wide range of temperatures as well as frequencies.

RESULTS AND DISCUSSION

The DSC plots of PEEK and PC are presented in Figures 2(a) and 2(b), respectively. The percent crystallinity (X_c) was calculated using eq. (1). For PEEK, X_c has been found to be 35% while PC shows no crystallinity. This is in agreement with trade literature of these materials. Viscoelastic properties of polymeric materials show both time as well as temperature dependence, as they experience molecular transition involving relaxation at characteristic, e.g., glass-transition temperatures. An assumption is made that all the relaxation times have the same temperature dependence. The material would then behave like a thermorheologically simple species. To obviate the difficulty encountered in case of a partially crystalline material, which shows poor fit in inverted U-shaped Cole–Cole or Wicket plots, some authors have adopted a vertical shift method for the construction of a master curve. The time–temperature shifting arising out of molecular transitions at varied temperatures is anomalous. This is because of different temperature effects on relaxation times above and below the transition and also the relaxed and unrelaxed moduli, which are temperature dependent.^{13,14} However, for the temperature region prior to occurrence of a gross phase transition, e.g., glass transition, even if the material is partially crystalline, its relaxation effects are relatively small, and therefore, vertical shifts can be neglected.^{15,16} The storage and loss moduli *versus* temperature plots for PEEK and PC are shown in Figures 3(a) and 3(b), respectively. The secondary transitions for both PEEK and PC are only relevant at low temperatures or high strain rates. Since no other transition except glass transition is observed above ambient temperatures, they can possibly be described as thermorheologically simple materials. Cole–Cole and Wicket plots for PEEK and PC are represented by Figures 4(a) and 4(b) and 5(a) and 5(b), respectively. It is apparent

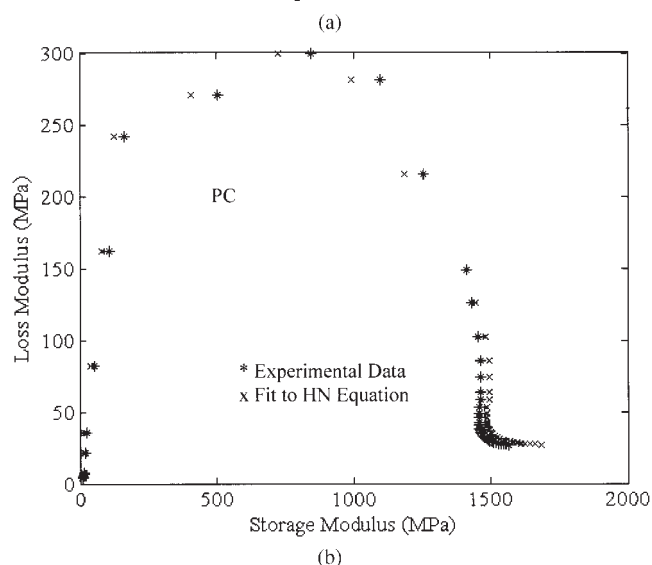
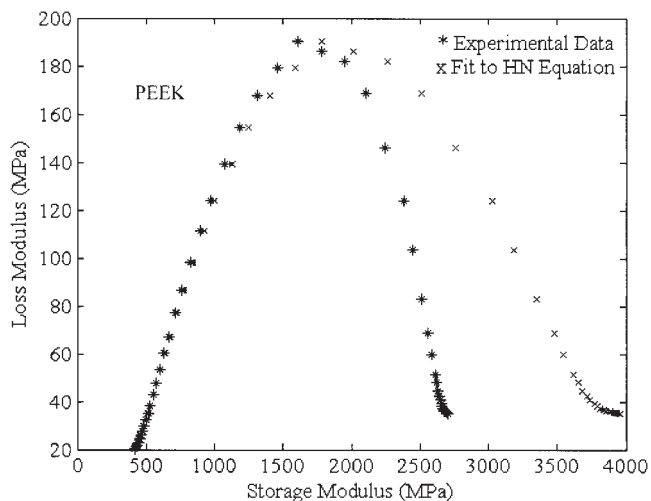


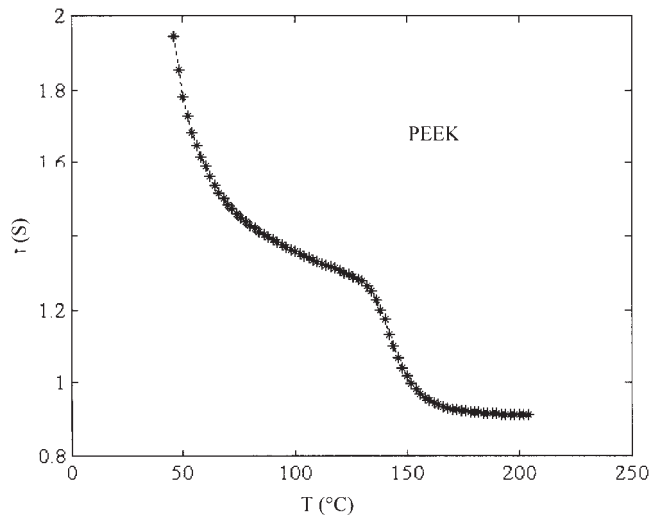
Figure 6 (a) Comparison of experimental and calculated Cole–Cole plot of PEEK. (b) Comparison of experimental and calculated Cole–Cole plot of PC.

from these figures that both PEEK and PC are thermorheologically simple, as they provide an inverted U-shaped graph, and this is supported by observations reported earlier.^{17–19} Thus, the HN model of time–temperature superposition principle can be applied for these materials.

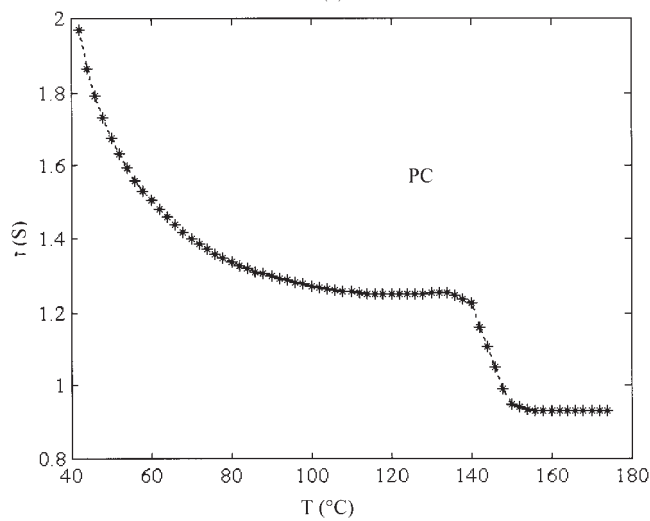
The best fit values of α , β , E_0 , and E_∞ having error function as minimum have been calculated as per process diagram given in Figure 1 and the values are enumerated in Table II. Figures 6(a) and 6(b) represent the comparison of Cole–Cole plot using the calculated values of HN parameters and the experimental values for PEEK and PC, respectively. In case of PEEK [Fig. 6(a)], the calculated values deviate from those of the experimental results after a modulus of 2000 MPa. This is perhaps due to a poor fit of HN equation outside the phase-transition region of PEEK. However, it can be seen from Figure 6(b) that the model

TABLE II
Values of Temperature-Independent HN Parameters

Parameter	PEEK	PC
α	0.093	0.078
β	0.062	0.052
E_0	4.83×10^8	9.81×10^6
E_∞	2.96×10^9	1.90×10^9



(a)

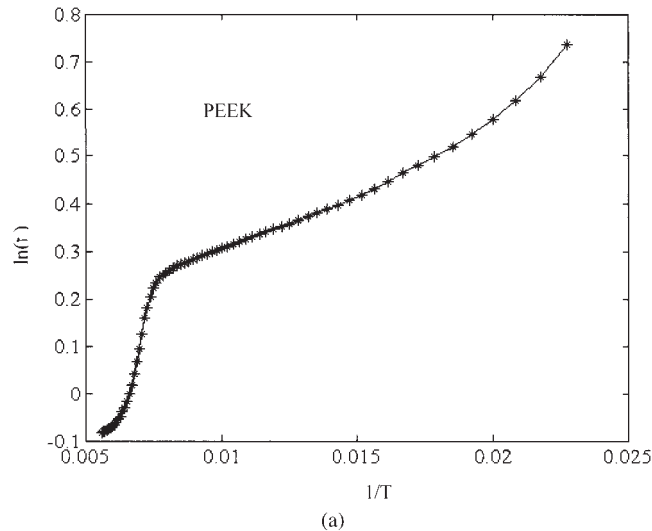


(b)

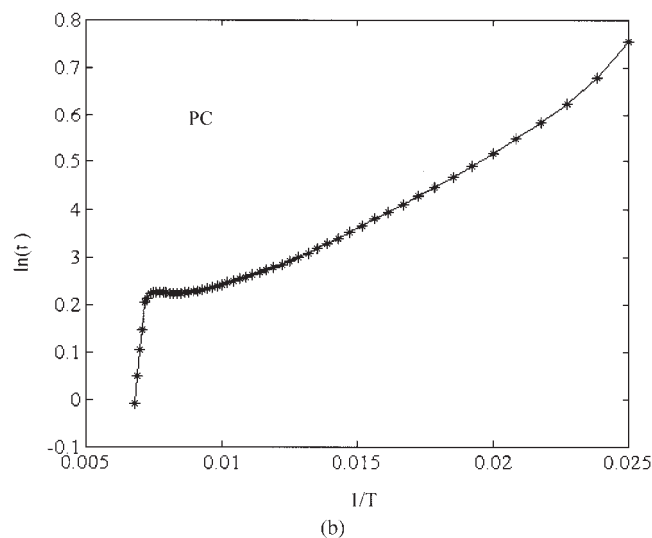
Figure 7 (a) Relaxation time *versus* temperature plot of PEEK. (b) Relaxation time *versus* temperature plot of PC.

parameters, as represented in Table II, gives good quantitative description of the complex modulus over the wide range of frequency selected for PC.

Using the HN parameters from Table II and experimentally obtained values of complex moduli, the relaxation time τ has been calculated from eq. (2). The graphs of relaxation time *versus* temperature are shown in Figures 7(a) and 7(b) for PEEK and PC, respectively. It can be seen that at $\sim 142^\circ\text{C}$ [for PEEK, Fig. 7(a)] and at 155°C [for PC, Fig. 7(b)] relaxation time *versus* temperature plots show a step transition. This corresponds to the state of increased molecular mobility and the onset of main chain segmental motion of the polymers. As no other step transition is observed, it can be assumed that PEEK and PC behave thermorheologically simple. This is in agreement with our earlier observations given in Figures 4 (a) and 4(b) and 5 (a) and 5(b).



(a)



(b)

Figure 8 (a) Calculation of activation energy for PEEK. (b) Calculation of activation energy for PC.

The temperature dependence of the relaxation time (τ) also follows the Arrhenius type of relationship as given below:

$$\tau = A \exp(-E_a/RT) \quad (4)$$

where, T is the absolute temperature (K), R is the gas constant (8.314 kJ/mol K), and E_a is the activation energy (J/mol) and A is the constant.

The plots of $\ln(\tau)$ against $1/T$ are shown in Figures 8(a) and 8(b) for PEEK and PC, respectively. The val-

TABLE III
Characteristic Properties of the Relaxation Process

$\tau = A \exp(-E_a/RT)$	PEEK	PC
Slope	38.07	33.06
Activation energy (E_a)	3.16×10^2 J/mol	2.74×10^2 J/mol

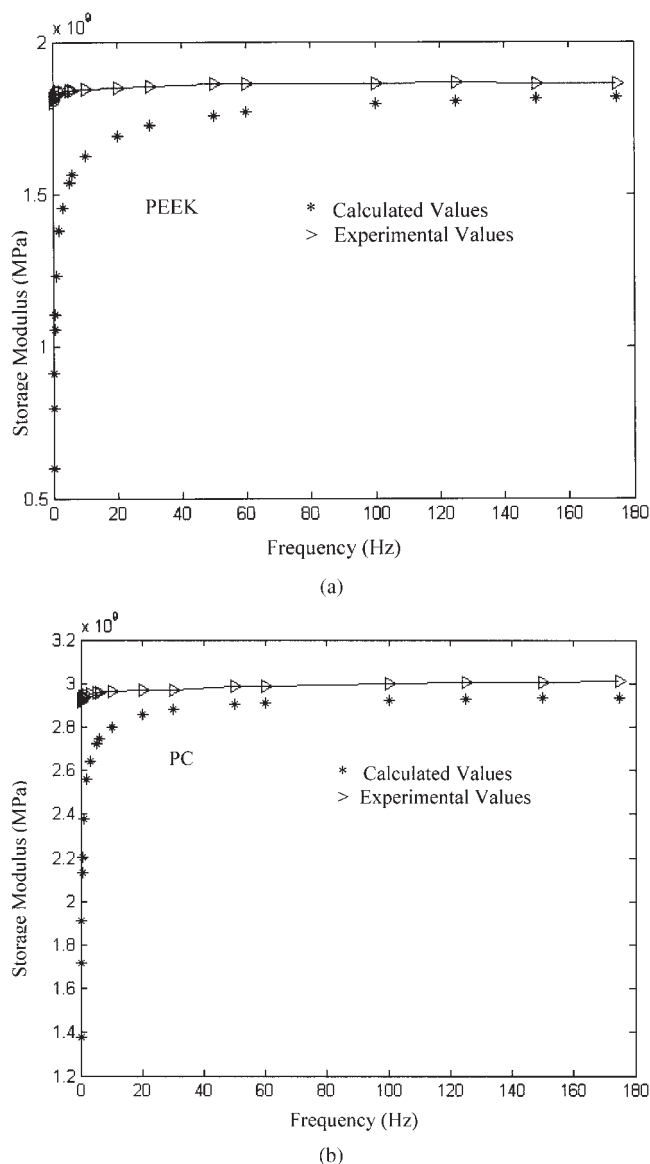


Figure 9 (a) Comparison of experimental and calculated storage moduli data at 50°C and at different frequencies of PEEK. (b) Comparison of experimental and calculated storage moduli data at 50°C and at different frequencies of PC.

ues of E_a have been calculated using least square analysis and the results are summarized in Table III. The value of the activation energy involved in the relaxation process of PEEK is higher than that of PC, and can be correlated to the rigid and bulky structure of PEEK compared to PC.

Figure 9(a) represents the experimental storage moduli (solid line) of PEEK for the frequency range of 0.1–175 Hz and at 50°C. The calculated moduli values obtained from eq. (2) using relaxation time from Figure 7(a) are also cited for comparison. Similarly, for PC, comparisons are made in Figure 9(b). It is clear from Figures 9(a) and 9(b) that there is good agreement between experimental and calculated data. The

HN model approach is, therefore, justified for complex plane analysis in case of both PEEK and PC. The calculation of complex modulus at a given temperature and frequency using eq. (2) become straight forward with the available α , β , E_0 , E_∞ and τ values.

CONCLUSIONS

1. From this study it can be concluded that both PEEK and PC behave thermorheologically simple and application of viscoelastic HN model is appropriate.
2. The predicted values of complex modulus from the HN model are in good agreement with the experimental data and four temperature-independent HN parameters, viz., α , β , E_0 , and E_∞ can collectively describe the complex plane behavior of both PEEK and PC.
3. The activation energy calculated for the PEEK is higher than that for PC and the same can be attributed to the rigid and bulky structure of the PEEK compared to PC.
4. It has also been found that the complex modulus can be predicted at any frequency, provided the temperature is within the experimental range.

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