Journal of Thermal Analysis, Vol. 49 (1997) 491-498

SEMI-CRYSTALLINE POLYMERS
Two phases or three? An overview and perspective

R. J. Seyler

Eastman Kodak Company, Rochester, NY 14650-2158, USA

Workshop purpose

An international panel of scientists will conduct a workshop that will address evidence for the existence of an additional amorphous fraction(s) of significant quantity in semi-crystalline polymers. This fraction is constrained or rigid and unable to participate in the relaxations associated with the normal glass transition temperature interval. Additionally, the utility of using thermal analytical measurements in conjunction with other analytical techniques including dielectric, NMR, X-ray diffraction, etc. in such materials studies will be demonstrated.

Keywords: nanophase, PEEK, PET, rigid amorphous fraction, semi-crystalline polymer

Introduction

Semi-crystalline polymers like poly(ethylene terephthalate) – PET [1, 2] and poly(ether-ether ketone) – PEEK [3] have been well studied because of their commercial significance. Especially in the case of PET, much of the literature discusses changes in physical and mechanical properties that arise from alterations in the thermomechanical history imposed during processing. Until recently, these changes were attributed solely to crystallinity changes and the modeling of the effects assumed a simple two-phase morphology. This two-phase model included finite crystalline and finite amorphous regions each contributing additively to the final properties. Scientists did recognize certain polymer molecules along the crystal interfaces in semi-crystalline polymers such as tie molecules and chain folds would not fit the classic behaviors of the two-phase model. However, their population and contribution were considered negligible.

Advances in measurement technologies, including thermal analysis and calorimetry, over the past few years have led to observations of deviations from the two-phase model for semi-crystalline polymers. One such deviation is that there is not always a one-to-one correspondence between crystallinity and the jump in heat capacity in the glass transition interval. It has been suggested that such deviations are caused by molecules whose mobility has somehow been hindered, despite being at least partially located in the amorphous phase. Such observations originated the term "rigid amorphous" first coined by Professor Wunderlich [4]. This thinking has

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

led to proposals for a three-phase model of semi-crystalline polymer morphology that includes crystalline, mobile and rigid amorphous phases [5, 6].

The validity of these observed deviations, their significance, the magnitude of their effects, and the existence of a third (or more) phase(s) have all been questioned in the recent literature. Hence, the motivation for conducting this workshop.

Overview

The workshop was opened with a brief overview by Dr. R. J. Seyler in which he raised several questions directed at focusing the discussion on "What is the issue?" To further seed discussion he shared some original work that established a directional bias in the apparent glass transition temperature within oriented PET.

Where is the "missing" heat capacity?

As crystallinity is developed, the jump in heat capacity during the glass transition such as observed with differential scanning calorimetry diminishes. The breadth of the temperature interval during the glass transition and the temperature assigned to represent this interval tend to increase. Assuming the additivity of the two-phase model, the lessening of the heat capacity jump should be directly proportional to the increase in crystallinity. It often is not but most measurements are not recorded with sufficient care and accuracy to distinguish this discrepancy.

Are the words "amorphous" and "non-crystalline" one and the same?

In the two-phase model they are, yet as was noted in the introduction above, certain molecules could exist which do not behave like the remainder of the amorphous phase molecules and which do not belong to the crystals.

What is the magnitude of any additional phase(s)?

Any non-typical amorphous molecules were ignored and their population was considered to be a negligible fraction when the two-phase model is employed. Recent publications, including the works of several of these panel members, have indicated that as much as 20 to 90% [7, 8] of semi-crystalline polymers could behave differently than that of a classic crystalline or amorphous molecule. This fraction is more extensive than simply tie molecules and chain folds along crystal boundaries and has become the basis for discussions of a constrained, rigid, or immobile amorphous phase.

Are there aging consequences?

Aging of any polymer has consequences, the extent of which and the manner in which it is manifested will be temperature dependent. The effect of aging on a rigid amorphous phase is just beginning to be elucidated.

Is there any impact on mechanical or physical properties?

It is not clear to what extent a rigid amorphous phase will impact physical and mechanical properties nor how it would affect them. It would, however, seem reasonable that if greater than 20% of the material is vitrified above the glass transition temperature of the mobile amorphous phase, some effects on material properties should be noted. One possibility is that the modulus may be higher than expected on the basis of crystallinity alone. Attempts to optimize properties of several commercial semi-crystalline polymers have encountered some unusual outcomes which may well be the result of a rigid amorphous phase.

Is there path dependent differences in the behavior of specimens of the same resin taken to equivalent crystallinities or densities?

This question may not have been the intent of any work published in the open literature but one can gather a sense for this from a survey of the literature for any given semi-crystalline polymer. The many different process conditions reported for PET, as an example, do suggest that for nominally equivalent density specimens, some effects of the thermomechanical pathway exist. How this relates to a third rigid phase is under study.

Is the glass transition sensitive to constraint?

The observance of deviations in the expected heat capacity jump during the glass transition as well as, shifts in the glass transition interval would support this. Constraint is the operative word in discussions accounting for a second amorphous phase that does not participate in the "traditional" glass transition.

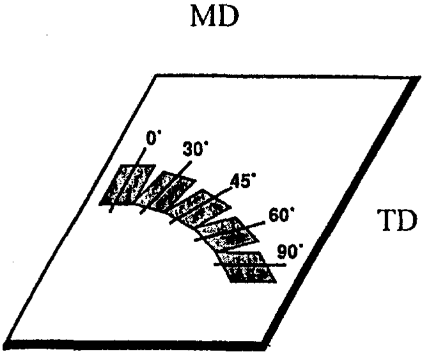
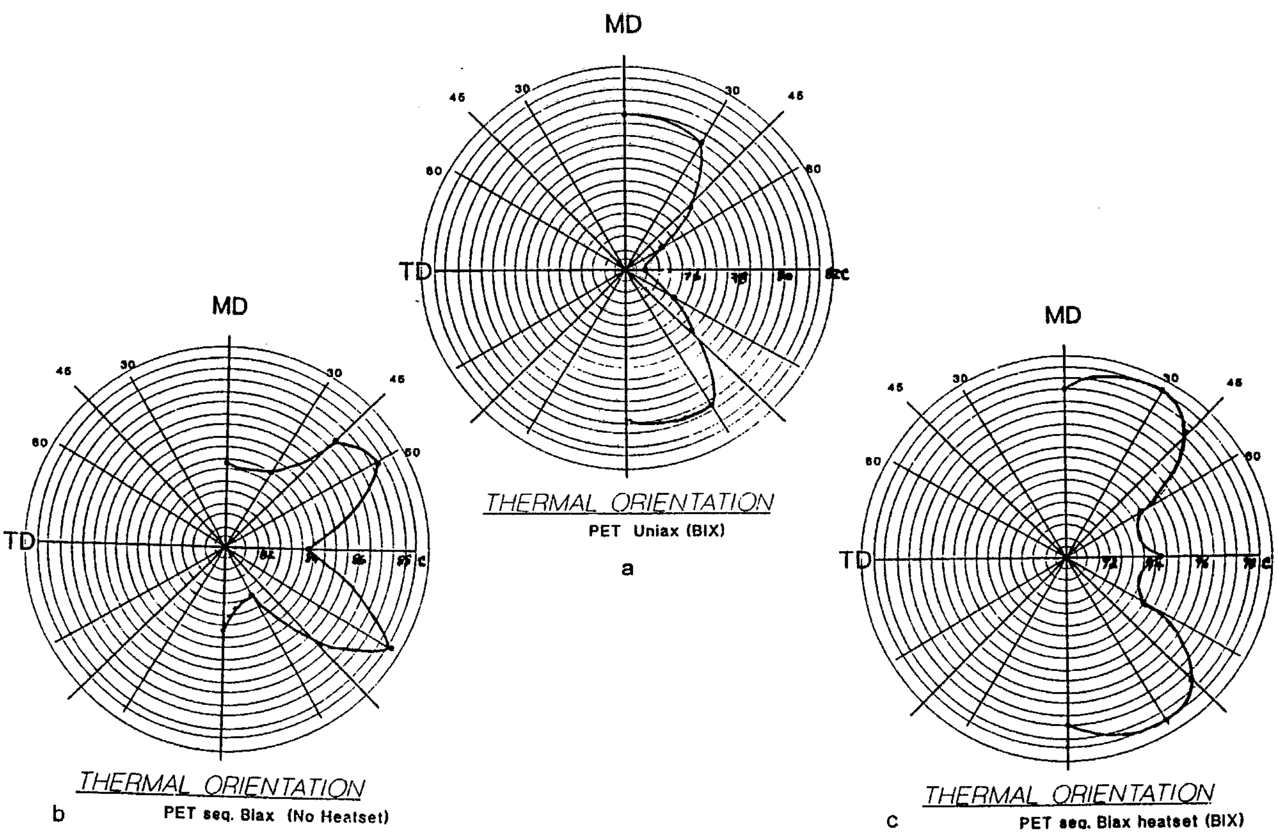


Fig. 1 Sampling protocfol for T_g mapping of PET sheets

Recent comparison of the glass transition temperature assigned to PET specimens of different thermomechanical history using differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA) techniques by Moscato and Seyler [9] noted a difference between the draft and tenter directions in oriented sheets. The differences in the assigned T_g using TMA in the tensile mode were thought to be the result of orientation. Subsequent samplings were taken at intermediate in-plane angles according to Fig. 1 and measured with tensile TMA such that the long axis of the 3×8 mm specimens was the direction of load and response. A plot of the temperature assigned as the glass transition for specimens at each in-plane angle as a polar plot (Fig. 2) results in a unique profile. Comparison of this profile with the in-plane polarized fluorescence map of Fig. 3 by Gohil and Salem [10] for a uniaxially oriented specimen shows a similar appearance. A much different appearance occurs when the same comparison is made for a biaxially oriented or a biaxially oriented and annealed (heatset) specimen. Since the polarized fluorescence occurs only in the amorphous regions of PET, the fluorescence map is taken to be indicative of the amorphous orientation. That the T_g map from TMA data does



THERMAL ORIENTATION
PET Uniax (BIX)
a

THERMAL ORIENTATION
PET seq. Biax (No Heatset)
b

THERMAL ORIENTATION
PET seq. Biax heatset (BIX)
c

Fig. 2 Thermal orientation - assigned glass transition temperature as a function of in-plane angle: a) uniaxial stretch, b) sequential biaxial stretch, and c) sequential biaxial stretch with heatset

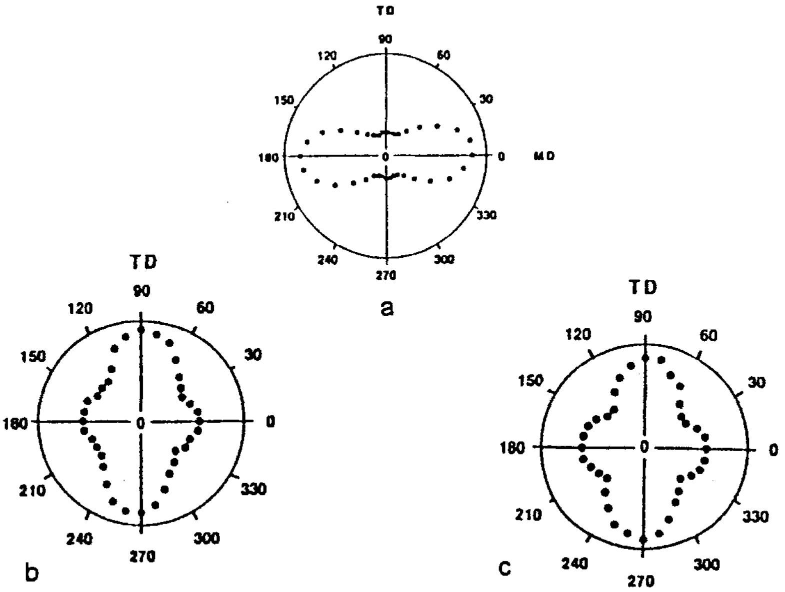


Fig. 3 In-plane angular distribution of polarized fluorescence intensity of PET film: a) uniaxial stretch, b) sequential biaxial stretch, and c) sequential biaxial stretch annealed

not coincide with the amorphous orientation, nor with X-ray diffraction pole figures, it must be indicative of another parameter that introduces a heterogeneous response in the relaxations associated with the glass transition. Is this a map of the molecular constraint imposed by crystallinity and the molecular extensions created by stretching above the strain hardening point? What is the relationship, if any, between a directional dependence of the glass transition and a rigid amorphous phase?

Workshop Perspective

The following discussion is an attempt to capture some of the salient points offered by the panel members during their presentations and responses to audience questions. In no way should this be considered a complete summary but rather it is offered as one perspective of the outcome of this workshop. Readers are strongly advised to review publications from the panel members and some of the key references they cited.

Each panel member gave an approximately 20 minute presentation which was followed by exchange with the audience and other panel members. The following topics and order were followed:

"A Rigid Amorphous Fraction in Polymers: A Three-Phase Model" by V. B. F. Mathot

"The Phases of Polymers as Determined By NMR" by J. B. Miller

"Detection of Multiple Nanophases by DSC" by B. Wunderlich

"Separation of Components of Different Molecular Mobility by Calorimetry and Dielectric Spectroscopy" by C. Schick

"Modulated DSC and X-ray Scattering Study of Polymers with Constrained Amorphous Phases" by P. Cebe

"Morphological Contributions to Constrained Relaxations: Comparisons of Stiff Aromatic Versus Flexible Semi-Crystalline Polymers" by B.B. Sauer

The question of the equivalence of non-crystalline and amorphous was addressed at the outset. If one accepts that some portion of a semi-crystalline polymer exists outside of the crystalline lamellae yet is unable to relax during the glass transition, than non-crystalline cannot be equivalent to amorphous. It must correspond to a greater weight fraction of the resin. When careful measurements are made, one must determine the weight fraction of crystals (w^c) using the non-crystalline rather than the amorphous content, i.e., $w^c = 1-(w^a + w^r)$. This would, of course, necessitate the acceptance and use of a three-phase model for a semi-crystalline polymer. If the weight fraction (w^r) of the hindered, rigid, constrained, or immobile molecules becomes small, the results of the three-phase model collapses to that of the two-phase model.

There appears to be sufficient credible data available to substantiate the existence of portions of semi-crystalline polymers that are non-crystalline and which do not participate in the glass transition. Reluctance to accept this concept of a rigid or constrained amorphous phase appears to have settled around a nomenclature issue – it cannot be a phase! This is correct if we are talking about an equilibrium condition. For semi-crystalline polymers it was pointed out that they are not in equilibrium. Arguments around a nomenclature issue are non-productive and detract from the significant issues associated with understanding constraint in semi-crystalline polymers. The panel appears to have agreed upon the use of an alternative terminology by referring to the "rigid amorphous fraction."

With a nomenclature issue resolved, there remains much to be resolved regarding the rigid amorphous fraction. A major point of discussion is just what is the rigid amorphous fraction? A number of concepts and physical or morphological descriptions have been offered including: material vitrified during crystallization, material whose relaxation time is retarded to times in excess of those associated with T_g, intercrystalline regions, nanophases, interlamellar non-crystalline regions, etc. The residual X-ray diffraction pattern shown for a PET fiber had the appearance of a liquid crystalline material suggesting an oriented amorphous structure. While a simple description may not be possible, it is clear that constraint can be manifested in a number of ways and its effect is to inhibit relaxation at normal, characteristic times or temperatures. Perhaps the nanophases suggested by Professor Wunderlich if considered as a collective that is distributed throughout the semi-crystalline polymer is a reasonable phenomenological description of the "rigid amorphous fraction." Solid state NMR data demonstrates three relaxation times. However, it is not clear whether these are singular or distributions. Were they truly singular, one might anticipate a second glass transition unless the crystal relaxation time was shorter than that for the rigid amorphous fraction. If the rigid amorphous fraction were a collection of nanophases, then one would expect a distribution of relaxation times.

Another point of debate is the extent of the rigid amorphous fraction. Weight fractions of 20 to 90% have been given depending upon the polymer studied, its thermomechanical history, and the measurement technique(s) employed. Solid state NMR results can be biased by oriented components in the crystalline relaxation peak, which leads to a larger value of w^c than other techniques. There are difficulties with the other techniques as well.

Additional resins where a rigid amorphous fraction has been reported include poly(phenylene sulfide) – PPS [7], poly(butylene terephthalate) – PBT [8], poly(oxymethylene) – POM [11], poly(ethylene naphthalene-2,6-dicarboxylate) – PEN [12] and polyethylene – PE [6] elaborated upon at this workshop by Professor Wunderlich. In the case of polyethylene, there remains skepticism about the existence of a rigid amorphous fraction.

Annealing was reported to have an effect upon the rigid amorphous content. Thermal treatment can be used to both reduce and restore the rigid amorphous fraction. This result indicates the rigid amorphous fraction can be tailored to a desired level. It was also noted that the rigid amorphous fraction does influence T_g independent of crystallinity (w^c maintained constant). Consequently, optimization of properties of fabricated components from semi-crystalline polymers is best achieved when both the crystalline and rigid amorphous fractions are optimized. There are reversing and non-reversing signatures observable at the annealing temperature on a subsequent heating. These could afford us additional insight into the thermome-chanical history!

One final point made that warrants additional consideration and study is that of the dimensions of relaxing regions. This point may have been understated in that it could be the basis for better understanding the glass transition and it may be the basis for defining conditions beyond which cooperativity is no longer possible [13]. In other words, assuming the glass transition occurs because of cooperativity among a number of chain segments, then reducing the volume of a region below a critical size will constrain that portion of the molecule from relaxing in the same fashion as the mobile amorphous fraction. This may be the basis for the occurrence of vitrification with crystallization mentioned by Professor Schick and could thereby serve as one explanation for the existence of a rigid amorphous fraction. It is clear that a better understanding of either the glass transition or the rigid amorphous fraction will provide a better understanding of the other.

References

1 C. Roland, J. Walton and J. Miller, Magn. Reson. Chem., 32 (1994) 36.
2 Y. Fu et al., J. Polym. Sci.: Part B: Polym. Phys., 32 (1994) 2289.
3 B. Sauer and B. Hsiao, Polymer, 36 No. 13 (1995) 1553.
4 H. Suzuki, J. Grebowicz and B. Wunderlich, British Polymer Journal, 17 (1985) 1.
5 M. Alsleben and C. Schick, Thermochim. Acta, 238 (1994) 203.

6 V. Mathot, in Calorimetry and Thermal Analysis of Polymers, Ed. V. B. F. Mathot, Hanser Publishers, 1994, p. 231.
7 P. Huo and P. Cebe, J. Polym. Sci.: Part B: Polym. Phys., 30 (1992) 239.
8 S. Cheng, R. Pan and B. Wunderlich, Makromol. Chem., 189 (1988) 2443.
9 M. Moscato and R. Seyler, in Assignment of the Glass Transition – STP 1249, Ed. R. J. Seyler, ASTM, Philadelphia 1994, p. 239.
10 R. Gohil and D. Salem, J. Appl. Polym. Sci., 47 (1993) 1989.
11 H. Suzuki, J. Grebowicz and B. Wunderlich, Makromol. Chem., 186 (1985) 1119.
12 L. Abis, E. Merlo and R. Po', J. Polym. Sci.: Part B: Polym. Phys., 33 (1995) 691.
13 C. Schick and E. Donth, Physica Scripta, 43 (1991) 423.