

# **MATERIALS SCIENCE AND TECHNOLOGY NEWSLETTER**

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## **FOCUSING ON HIGH PERFORMANCE POLYMERS: THE POLYIMIDES AND THEIR RELATIVES**

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## EDITORIAL COMMENTS

Since the main purpose of this issue of the newsletter is to announce the upcoming SIXTH INTERNATIONAL SYMPOSIUM ON POLYIMIDES to be held in November 2009, it seems an appropriate moment to review the past history of these materials as documented in previous symposia. We briefly discuss the evolution of this important class of materials in regard to the following attributes:

- ◆ Variant classes and synthesis methods
- ◆ Characterization and structure property considerations
- ◆ Applications

The polyimides sort into a variety of classes depending on the chemistry and physical architecture of the main chain. The physico-chemical properties that result cover a wide range of behavior. Specific formulations can be totally amorphous or exhibit substantial crystallinity, they can give rise to flexible or brittle films and they can exhibit a wide range of glass transition and melting temperatures. The task of predicting the final bulk properties of a given formulation based solely on chain structure is tricky at best since the final properties which can result from a given chain structure are very sensitive to the details of the method of preparation. The range of applications of these materials is quite remarkable though the most common uses arise in the electronics and aerospace industries. The November 2009 symposium will shift focus slightly in that we tend to include papers on all manner of high performance polymers that not only show good temperature stability but also exhibit outstanding mechanical, electrical and thermodynamic properties as well.

Finally, it is also our pleasure to announce that this symposium will be held in collaboration with Prof. Gordon Nelson of the Florida Institute of Technology and Dr. Martha Williams and Trent Smith of the NASA Kennedy Space Center. These individuals have been active in the area of high temperature polymers especially in regard to aerospace applications.

## POLYIMIDES, PAST PRESENT AND FUTURE

The polyimide materials were developed by the DuPont company starting in the mid 1950's and into the early 1960's with apparent first announcement in the technical literature in a

seminal paper by Sroog et. al.<sup>1</sup> The early activity during the 1950's in the DuPont company has been reviewed in an engaging article by Sroog<sup>2</sup>. The investigators at DuPont developed what is now recognized as the classic two-step poly(amic acid) to polyimide process which, even to this day, is the most widely practiced procedure in polyimide synthesis. It involves reacting a dianhydride and a diamine at ambient conditions in a dipolar aprotic solvent such as N,N-dimethylacetamide (DMAc) or N-methylpyrrolidinone(NMP) to yield the corresponding poly(amic acid), which is then cyclized into the final polyimide.

Among the earliest users were the electronics and aerospace industries. By the late 1960's the electronics industry was starting to seriously explore the advantages of integrated circuits which required an insulator material that could support fine wiring structures on top of a silicon chip containing an array of imbedded transistors and other circuit elements that needed to be properly wired together. The first material used in this application was fused silica which could be conveniently grown and deposited on top of silicon. One problem with the silica material, however, was that it gave strictly conformal coatings which closely followed the underlying surface topography. Thus, if one wanted to make a multilayer structure using silica, there was a problem in that after coating the first layer of metal lines a lumpy surface would result making deposition of the next layer highly problematic. Since the polyimide materials could be spin coated onto the silicon material as a liquid the thinking was that they would give a much more planar surface. This consideration in combination with the excellent insulating properties of the polyimides made them natural candidates to replace silica as an insulator in multilevel thin film wiring structures. As it turned out the polyimides came with their own set of problems, but that is a story for another time.

In the aerospace industry there was a need to replace rivets for fastening together the sections of high performance aircraft. It turns out, somewhat counter intuitively, that a joint properly made with an adhesive material is considerably stronger than

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<sup>1</sup>Sroog, C.E., Endrey, A.L., Abramo, S.V., Berr, C.E., Edward, W.M., and Olivier, K.L. ,*J. Polym. Sci. , Part A*, **3**, 1373 (1965)

<sup>2</sup> "History of the Invention and Development of the Polyimides", C. E. Sroog in Polyimides: Fundamentals and Applications, Ed. Malay K. Ghosh and K. L. Mittal (Marcel Dekker, New York 1996) p.1.

one made with rivets. The basic point is that in order to fasten with a rivet one needs to make a hole in the section to be fastened. The hole then becomes a sort of defect in the material in that it will act as a stress riser in the presence of an applied stress field. In fact the local stress field near any type of hole can be some 3 times larger than the global stress level which can make rivet holes quite dangerous defects indeed. This was not a particular problem in old style aircraft which were over engineered with a large margin of safety. However, high performance aircraft cut the safety margin considerably in order to save weight so all critical joints had to be much stronger than what could be achieved with rivets. In selecting a suitable adhesive, however, account had to be taken of the high temperatures which aircraft and space vehicles must endure and thus the polyimide materials came front and center as prime candidates.

## Early Polyimide Symposia

### Unveiling new chain structures

Apparently the first public presentation of the early Dupont work was given by Sroog and coworkers at the April 1964 meeting of the American Chemical Society in Philadelphia Pennsylvania. However, the first truly major meeting on polyimides was held in Ellenville New York, the week of November 10, 1982 and was organized by the Mid Hudson section of the Society of Plastics Engineers. MST's director Dr. Mittal had the pleasure of documenting that meeting in a two volume work<sup>3</sup> which will be the starting point for this review. The resulting volumes came to 1182 pages containing 71 papers reflecting the work of 164 authors from some 9 different countries. Just a cursory look at the papers documented in these volumes indicates that, already by the early 1980's the variety of polyimide materials had expanded greatly since the early DuPont work. The following is a brief list of the different polyimide systems which were in use or under development:

1. **Acetylene Substituted Polyimides:** The aircraft industry in trying to create high temperature adhesives were developing what came to be known as the Thermid materials. By using an acetylene substituted polyimide isomer a material could be synthesized which would be

soluble in common solvents and have a lower melting range making them more suitable as adhesives and binder materials in composite structures. (Work of Landis and Naselow, ref. 3 Vol 1, p. 39)

2. **Silicon Modified Polyimides:** Efforts to improve the processing properties of the polyimides while retaining their excellent thermal stability lead to the introduction of silicon and silicone groups into the main chain backbone. (work of Babu, ref. 1 Vol. 1 p.51 and Berger, ref. 1 Vol. 1 p.67)
3. **Thermoplastic Materials from Polyimidesulphones:** In an attempt to develop a material with the excellent thermoplastic properties of the polysulphones a hybrid material integrating both the sulphone and polyimide moieties into a single chain structure was developed at NASA. The resulting material showed great promise as a binder material for graphite fiber reinforced mouldings. ( Work of St. Clair and Yamaki, ref. 1 vol. 1 p. 99)
4. **Polyetherimides:** In yet another approach to achieving good processability while retaining the excellent thermal stability of the classic polyimides, researchers at the General Electric company inserted flexible ether linkages into the chain backbone. The result was a polyetherimide that was commercially introduced as the ULTEM<sup>®</sup> line of thermoplastics. In addition to showing good melt flow and processability these materials also exhibited high mechanical strength, inherent flame resistance and chemical and UV light stability. (work of Serfaty, ref. 1 vol. 1 p. 149)
5. **Electrically Conducting Polyimides:** In an effort to fabricate a material that could simultaneously serve as an insulator and a conductor, work was carried out to surface modify a polyimide with tin chloride materials. The resulting films showed a reduction of some 12 orders of magnitude in the surface resistivity compared to conventional polyimides. Such a material had obvious application in situations where there was a need to prevent charge buildup while simultaneously retaining insulator properties through the film thickness.

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<sup>3</sup> "Polyimides: Synthesis, Characterization, and Applications", Vols. 1 and 2 Ed. K. L. Mittal (Plenum Press, New York, 1984)

Thus already by the early 1980's at least 5 different varieties of the original DuPont materials were either being commercialized or were in

advanced stages of development. Given the large number of diamines and dianhydride precursors available coupled with several different backbone linkages and sidegroup variations the number of possible different chain structures was nearly limitless. However, in order to be of any use, a given material had to be readily processable and also give rise to desirable end properties such as mechanical strength, thermal-chemical stability and dielectric behavior. All this gave rise to the need to be able to properly characterize the plethora of new materials that were being synthesized and also, if possible, discover a way of knowing beforehand what physical properties would result from a given chain structure.

### Early characterization work and attempts at deriving structure property correlations

The need to characterize the burgeoning number of new polyimides gave rise to some 25 papers at the first Ellenville conference dealing specifically with this topic. Just about every analytical technique then available was applied to the problem including but not necessarily limited to the following:

1. Spectroscopes
  - a. Infra red spectroscopy (IR also FTIR)
  - b. Nuclear magnetic resonance (NMR, <sup>13</sup>C NMR)
  - c. X-ray Photoelectron Spectroscopy (XPS also ESCA)
  - d. Auger Spectroscopy
2. Thermal-mechanical analysis
  - a. Differential scanning calorimetry (DSC)
  - b. Thermal gravimetric Analysis (TGA)
  - c. Thermal Mechanical Analysis (TMA)
3. Electrical measurements
  - a. Dielectric relaxation
  - b. Resistivity measurements
  - c. Polarization measurements
  - d. Thermally Stimulated Discharge Currents (TSDC)
4. Elastic property measurements
  - a. Tensile modulus
  - b. Shear modulus
  - c. Ultimate tensile strength

5. Miscellaneous
  - a. Light scattering
  - b. Rheological measurements (Rheometry)
  - c. Vapor sorption and permeability
  - d. Ultrasonic measurements
  - e. Liquid chromatography
  - f. Internal friction, dynamic modulus
  - g. Internal stress measurements

Limitations of space allow us to elaborate on only a handful of the papers presented at the symposium of which we shall comment briefly on 4 of them:

### Light scattering measurements on PMDA-ODA polyimide (alias DuPont KAPTON®)

**Paper of P. Cotts<sup>4</sup>:** The main reason for commenting on this particular paper is the fact that one rarely comes across light scattering work focused on determining the colligative properties of polymer systems. Even under relatively favorable circumstances the light scattering technique is highly demanding due mainly to the rigors of sample preparation. In particular the sample holder and the solvents used have to be submicroscopically clean since any contaminant as large or larger than the polymer chains one is trying to measure will either swamp or drastically confound the light scattering signal from the sample material. A typical polymer molecule in solution will form a coiled blob on the order of 10<sup>-7</sup> meters in radius. Thus contaminants in this size range will cause serious problems. One would need to keep any contaminant particles to at least 10 times smaller than this number and in as low a concentration as possible. If this is not enough, one also has to consider the fact that there are almost no solvents for the PMDA-ODA material except concentrated sulphuric acid which was the solvent ultimately used for the measurements. Given the constraints Dr. Cotts measurements were a heroic effort indeed. All impediments aside, however, the paper amounts to a fairly standard light scattering study and in addition to the KAPTON material a substantial amount of data was obtained on the polyamic acid precursor material including intrinsic viscosity data. With both light scattering and intrinsic viscosity data in hand Dr. Cotts was able to show that the polyamic acid materials obeyed the classic Mark-Houwink relation as follows:

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<sup>4</sup> "Characterization of Polyimides and Polyamic Acids in Dilute solution", P. M. Cotts, Ref. 3. Vol 1, p.223

$$[\eta] = k M_w^a$$

$$k = 0.058$$

$$a = 0.74$$

Where:

$[\eta]$  = Intrinsic viscosity

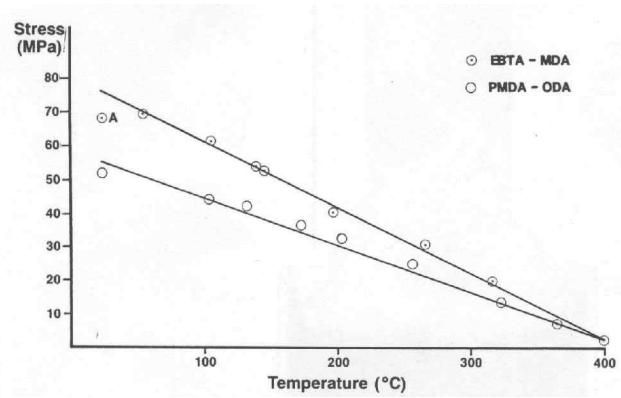
$M_w$  = Weight average molecular weight

The above relation is quite handy in that once established it allows one to get at the weight average molecular weight of a material by carrying out the much simpler intrinsic viscosity measurement as opposed to enduring the rigors of light scattering. Unfortunately, given the adverse conditions surrounding the KAPTON measurements no Mark-Houwink relation was derived for this material. However, a figure was arrived at for the molecular weight which came to  $20,000 \pm 5,000$ .

### Stresses in polyimide films

There was only one paper in the entire symposium dealing with stress buildup in polyimide films coated onto rigid substrates given by Geldermans et al.<sup>5</sup>. Though this was a rather lonely contribution to the symposium it was of significant interest to me since the laboratory I worked in at the time was struggling with a major problem in using the polyimide materials to build multilevel wiring structures for computer modules. The structures required the layering of one wiring level upon another with each layer separated by a film of polyimide which, due to the curing schedule required, happened to be in a significant state of stress.

Now one of the requirements for such a structure is that each level of wiring has to be connected to the one below by what are called via columns. This of course required that holes had to be etched in the polyimide layer to allow for metal to be deposited in the hole to form the required conducting via. Recall from above the problem with rivets used in aircraft structures which also required a hole to accommodate the rivet thus forming a stress riser in the section being



**Figure 1** Residual stress vs temperature for two polyimide coatings which were cured at 400 C. Adapted from Geldermans et al, Ref. 3 vol 2, p. 695.

fastened. The laws of physics dictated that the same would also be true for the via holes which had to be etched in the polyimide layers. This would not have been that big of a problem except for the fact that the film stress in the fully cured polyamide was already quite high as can be readily seen from figure 1. Referring to the curve for the PMDA-ODA material we see that the residual stress level for a blanket film at room temperature is already close to 55MPa which is quite substantial considering the fact the ultimate tensile stress of nearly all polyimides does not exceed 120MPa. Thus, already in the uniformly coated film, the residual stress in the material is nearly half way to the ultimate breaking stress. It does not take too much imagination to guess what will happen if a via hole is now etched in the coating given the fact that the local stress level near the hole will approach something like 3 times the already present uniform biaxial stress level. As it turned out, forming the required via holes in the coating unleashed mechanical mayhem at every via hole. The EBTA-MDA material which is also shown in figure 1 gave rise to radial cracks emanating from each hole due to a very high hoop stress. The PMDA-ODA material, however, showed no signs of cracking since this material proved to be astonishingly ductile as will be discussed below. This material nonetheless exhibited extensive delamination near each via due to the very high normal stress component at the edge of all the holes. In order to try and understand what was happening I did extensive finite element stress calculations to elucidate the nature of the stress state near the vias. Details of this work were published at a subsequent symposium<sup>6</sup>. The main

<sup>5</sup> "Measurement of Stresses Generated During Curing and in Cured Polyimide Films", P. Geldermans, C. Goldsmith and F. Bedetti (Ref. 3 vol. 2, p. 695).

<sup>6</sup> "Stresses in Thin Films: Relevance to Adhesion and Fracture", R. H. Lacombe, Surface and Colloid Science in Computer Technology, Ed. K. L. Mittal, Plenum (1987).



conclusion was that once residual stress levels go beyond a certain critical level they will be relieved by one mechanism or another. In essence, if you improve the mechanical strength then the coating will delaminate. Conversely, improving the adhesion will force the coating to crack. You are in essence "caught between the devil and the deep blue sea". It could be easily shown, in fact, that the stress levels shown in figure 1 were due primarily to thermal expansion strains since the expansion coefficient of the polyimides was in the range of 30 to 40 ppm/deg. and the coefficient for the silicon substrate material was on order 3 ppm/deg. giving a net mismatch close to 35 ppm/deg. This, coupled with the fact that the coating had to be cooled through a range of roughly 380 degrees, is what gave rise to the residual stress levels shown in figure 1. Thus the only way around the problem was to somehow avoid having to cure at 400 C or to switch to a material with a much lower thermal expansion coefficient.

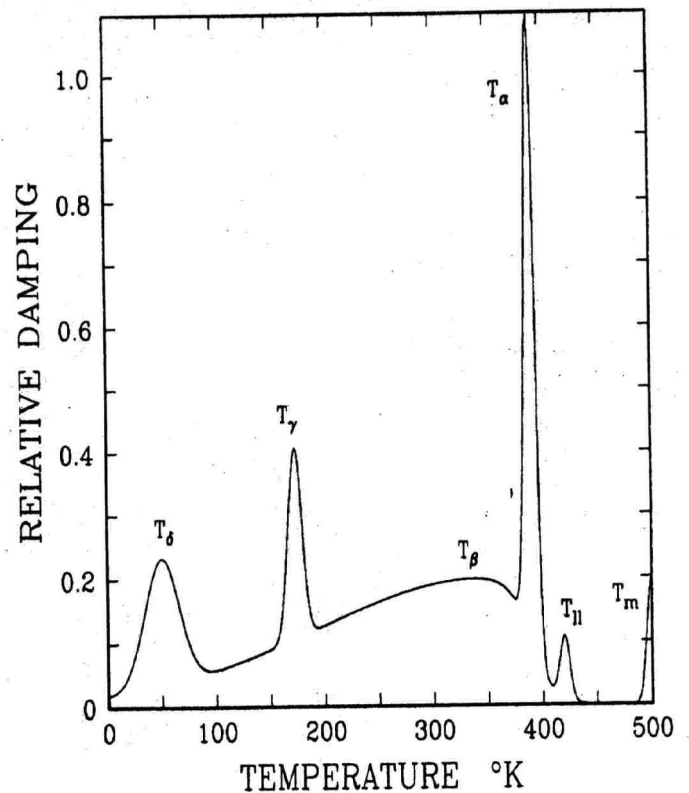
### Early attempts at determining structure property relations

The notion of somehow being able to determine the bulk properties of a material based on some limited knowledge of its molecular structure has always been something of a "Search for the Holy Grail" in materials science and especially so in the realm of polymer materials. However, an increment of progress was made on this problem in regard to correlating the glass transition temperature of a given material to its molecular structure in a paper by Michael Fryd<sup>7</sup>. Since the glass transition temperature is arguably one of the most important thermodynamic parameters of any amorphous polymer, any insight into predicting this property from some limited set of structural data can be regarded as a substantial achievement.

Fryd first points out that trying to correlate chain structure with the glass transition temperature in the polyimides is complicated by a number of confounding technical difficulties such as:

1. Variable molecular weight
2. Variable chain end groups
3. Degree of imidization
4. Processing atmosphere and curing schedule
5. Presence of absorbed moisture and retained solvents
6. Variability due to differing measurement

<sup>7</sup> "Structure -  $T_g$  Relationship in Polyimides", M. Fryd (Ref. 3, vol. 1, p.377)



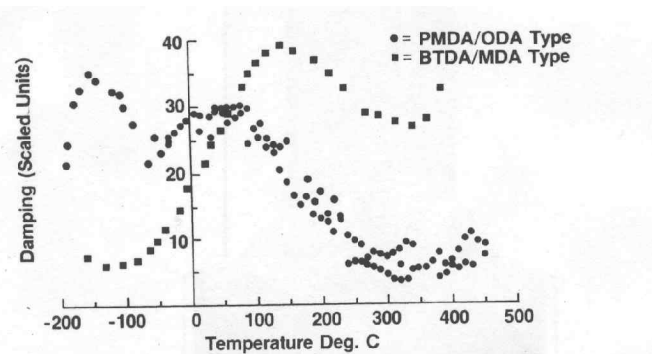
**Figure 2** Fictional plot of internal friction relaxation peaks that might be exhibited by a typical polymer material.

methods

Notwithstanding the above difficulties Fryd managed to obtain glass transition data on 15 different polyimides formed from combinations of 5 different dianhydride segments with 6 different diamines. The results of his analysis confirmed the well known fact that the glass transition has a strong dependence on chain flexibility. Introducing flexibilizing groups into the main chain decreased the glass transition by increasing rotational and translational mobility of the chain units. However, somewhat unexpectedly, interchain interactions also had a strong effect due to the electronic makeup of polyimides in general. Each polyimide is in fact an alternating sequence of diamine and dianhydride units. The anhydrides are known to be strong electron acceptors and the diamines electron donors giving rise to the possibility of forming strongly interacting charge transfer complexes which can greatly stabilize chain packing and thus raise the glass transition. This hypothesis was born out by the fact that introducing side groups and other modifications which tend to disrupt chain packing also greatly lowered the glass transition. Thus, chain flexibility which is an intra chain property and chain packing which is an interchain property combine to control the overall glass transition behavior of the polyimides.

## Mechanical properties through internal friction measurements

One further way of probing the mechanical behavior of solid materials is through internal friction measurements commonly also called dynamic mechanical measurements. This technique goes back at least 60 years and was one of the first experiments capable of elucidating atomic and molecular relaxation processes in solids<sup>8</sup>. The basic idea is to apply an oscillating stress field to the material and then measure the resulting energy dissipation as a function of applied frequency and temperature. There are many possible experimental setups, but one of the simplest is the vibrating beam method. In this approach a long slender beam firmly anchored at one end is set into vibration by applying an oscillatory load at the free end. By properly adjusting the load frequency one can set the beam oscillating in one of its normal modes of vibration which is a pure sinusoidal motion at a well defined frequency. After removing the load the beam will then exhibit a decaying oscillation due to external damping by air and also due to internal atomic and molecular motions. By suppressing or factoring out the external damping mechanisms the resulting energy loss can then be attributed to the internal atomic and molecular motions alone. A typical experiment consists of exciting the beam into vibration at some fixed frequency then turning off the applied load and counting the number of oscillations required for the vibration amplitude to decrease to half of its initial value. This then gives a direct measure of the energy loss per cycle, or the internal friction, at the prevailing conditions of temperature and frequency. With both frequency and temperature available as possible independent variables, there are basically two different types of experiments that can be carried out, one holding the frequency constant while varying the temperature and vice versa. Figure 2 shows a highly stylized plot of what might be observed for a polymer solid in a fixed frequency variable temperature experiment. The major peak labeled  $T_{\alpha}$  is the glass transition relaxation sometimes also labeled  $T_g$ . Of most interest for the solid material, however, are the lower temperature peaks labeled



**Figure 3** Internal friction vs temperature data for two different polyimide materials. Data adapted from Reference 9.

$\beta$ ,  $\gamma$  and  $\delta$  in order of decreasing temperature. The  $\alpha$  peak or glass transition is associated with large scale segmental motions of the polymer chain which become active as the increasing temperature starts to force the system into the liquid state. The  $\beta$  relaxation has been identified with smaller scale local motions that are still active below the glass transition where all large scale motion is now frozen out. Since these motions are the major degrees of freedom available to the solid material they have been closely associated with properties such as the fracture toughness and ductility. The  $\gamma$  and  $\delta$  peaks are associated with yet weaker processes such as diffusion of residual solvents and impurities.

Of most interest to my laboratory was the  $\beta$  relaxation due to its correlation with fracture toughness which was of great concern due to the wide spread cracking behavior we were seeing in many of the polyimide coatings we were experimenting with at the time. Thus, in my own contribution to the Ellenville symposium,<sup>9</sup> I was able to demonstrate the difference between a tough and a brittle polyimide as shown in figure 3. Shown in the figure is the internal friction behavior of two different polyimides. The PMDA-ODA material is essentially the classic DuPont KAPTON<sup>®</sup> only coated as a thin film as opposed to a cast sheet. The BTDA-MDA was a Monsanto material developed for the electronics industry under the trade name of SKYBOND 703<sup>®</sup>. Both of these materials had a glass transition in excess of 400 C which was essentially unmeasurable since heating the material to 400C caused these materials to further vitrify and thus move the glass transition to a higher value where they became thermally unstable. Thus there is no glass transition peak

<sup>8</sup> For metals and other inorganic solids the method has been covered in great detail in "Anelastic Relaxation in Crystalline Solids", A. S. Nowick and B. S. Berry, (Academic Press, New York, 1972). Polymeric solids are treated in "Anelastic and Dielectric Effects in Polymeric Solids", N. G. McCrum, B. E. Read and G. Williams (Wiley, New York, 1967).

<sup>9</sup> "Mechanical Properties of Thin Polyimide Films", Robert H. Lacombe and Jeremy Greenblatt (Ref. 3, Vol. 2, p 647).

evident in the figure except for a slight upturn in the data above 400 C most likely indicating the earliest onset of the glass transition which now is most likely above 500 C a temperature where these materials become thermally unstable.

Looking first at the data for the PMDA-ODA material given by the filled circles we see a broad  $\beta$  peak centered close to room temperature indicating that the small scale motions giving rise to this relaxation are active at room temperature. These still active degrees of freedom presumably gives rise to the exceptional ductility of this material which can show an elongation at break approaching 100% in a standard tensile test. Looking next at the BTDA-MDA material represented by the filled squares we see that the analogous  $\beta$  peak is now centered near 150 C fully 130 degrees higher than the what is observed for the PMDA-ODA. Not unexpectedly the BTDA-MDA behaves like a brittle glass at room temperature giving an elongation at break of at most 2% in a standard tensile test.

Trying to understand the above results on the basis of molecular structure is not straightforward but at least a few observations can be made using the general principles laid out in the paper by Fryd. Small angle X-ray data has shown that the PMDA-ODA material is not completely amorphous as might be expected but shows a significant degree of long range order apparently due to a high degree of chain regularity which allows long segments to pack together in such a way as to take advantage of the charge transfer complex mechanism discussed above. Thus a high level of chain stiffness coupled with denser packing associated with the charge transfer mechanism gives this material an exceptionally high glass transition. However, curiously enough, the the quasi crystalline structure brought about by the close chain packing also accounts for the high ductility of this material by allowing a mode of deformation in response to tensile loads which is normally not available in strictly amorphous polymers. Thus the first response of the material to a tensile load is to allow the closely stacked chains to slide past one another thereby giving rise to a localized yield behavior which relaxes the applied stress in a manner similar to that exhibited in metals. The chain structure of the BTDA-MDA material on the other hand apparently does not allow for the efficient chain packing achieved by the PMDA-ODA and thus this material is truly amorphous and therefore exhibits all the properties of a brittle glass.

## Sequels to the First Ellenville Symposium

So successful was the first symposium that the Mid Hudson Section of the Society of Plastic Engineers went on to sponsor 4 more symposia devoted to the polyimide materials all held as before in Ellenville New York. These subsequent symposia were documented in the following volumes:

### SECOND SYMPOSIUM

"Recent Advances in Polyimide Science and Technology", Eds. W. D. Weber and M. R. Gupta, (Society of Plastic Engineers, P. O. Box 1658, Poughkeepsie, New York, 1987).

### THIRD SYMPOSIUM

"Polyimides: Material Chemistry and Characterization", C. Feger, M. M. Khojasteh and J. E. McGrath, Eds.(Elsevier,Amsterdam, 1989)

### FOURTH SYMPOSIUM

"Advances in Polyimide Science and Technology",Eds. Claudius Feger, Mahmoud M. Khojasteh and Maung S. Htoo (Technomic Publishing Co. Inc. Lancaster, Pennsylvania,1993)

### FIFTH SYMPOSIUM

"Polyimides: Trends in Materials and Applications", Eds. Claudius Feger, Mahmoud M. Khojasteh and Steven E. Molis (Society of Plastics Engineers, Brookfield Connecticut, 1996).

## Novel synthesis methods

These subsequent symposia basically took up where the first symposium left off investigating yet newer formulations, processing methods and characterization techniques. Space constraints do not allow us to go into any detail as to the contents of the above volumes but a few comments are in order in regard to a few of the more innovative papers that were presented.

In the realm of synthesis methods perhaps the most innovative paper was the one presented by Sklitzkova et. al. which dealt with the fabrication of ultra thin polyimide coatings using the Langmuir-Blodgett monolayer deposition technique ("Investigation of Thermally Induced Structure Transformations in Langmuir-Blodgett Polyimide Film", V. P. Sklitzkova et. al., FIFTH SYMPOSIUM , p. 367). From my own point of view it is regrettable that I could not get samples of these coatings as the internal friction measurement apparatus I had used to take the data in figure 3 had the sensitivity to measure the internal friction



of coatings down to the monolayer level<sup>10</sup>. It would have been interesting to see the effect of extreme coating thickness on the internal friction behavior of the material.

### **Novel characterization methods**

The fifth symposium also saw the application of the methods of nuclear physics methods to the characterization of polyimide interfaces with a paper on the use of Rutherford back scattering to investigate the polyimide/metal interface in a paper by Gujrathi and Sacher ("Nuclear Scattering Profiles of Metallized Polyimides", S. C. Gujrathi and E. Sacher, FIFTH SYMPOSIUM, p. 377). The field of nuclear physics effectively got its start when in 1909 the English physicist Ernst Rutherford and his student Ernst Marsden watched alpha particles being back scattered off very thin gold foils in what has come to be known as the Rutherford Backscattering experiment. Thus it is both amusing and edifying to see this seminal experiment being employed some 87 years later to elucidate the nature of the polyimide/metal interface. In essence by scattering the alpha particles off the interfacial region one can get at the profile of metal diffusion into the polyimide.

Finally, in regard to my own interests in coming to grips with the destructive nature of the residual stress being built up in polyamide films coated on silicon and ceramic substrates, there are several papers by Prof. Richard Farris and his students on measuring the elastic constants and residual stress in polyimide films. Through a clever use of holographic interferometry, Farris and his students were able to get accurate measurements of both the elastic constants and the residual stress in thin polyimide coatings.

("Characterization of Elastic Constants and Stress in Low Thermal Expansion Polyimides", K. C. Seth, M. Chen, and R. Farris (FIFTH SYMPOSIUM, p.303)

### **Closing of the Old Testament. Last of the Ellenville symposia, November 1994.**

The fifth symposium which was held in November 1994 marked the end of the series of polyimide symposia organized by the Mid Hudson Section of the Society of Plastics Engineers. The end came not from a decreased interest in the polyimides but rather from the economic downsizing of the

computer industry in the mid Hudson Valley which also brought about a downsizing in the local section of the Society of Plastic Engineers that was staging the symposia.

### **Opening of the New Testament, MST CONFERENCES, November 1999.**

The Conference Director Dr. Mittal and myself were also caught up in the above mentioned economic adjustment and were therefore obliged to apply our talents elsewhere. During the subsequent years following the last Ellenville Conference I was working at a small startup firm doing consulting and contract work for the U. S. government and the State of New York. Dr. Mittal essentially continued the work he was doing previously by organizing symposia, giving short courses and the odd stint of professional consulting. In 1999 our paths crossed again quite by coincidence and, after reminiscing about the old days we decided that we could continue doing on our own much the same type of professional work we were accustomed to before the downsizing. Since we were basically materials scientists it was quite natural to call our new organization Materials Science and Technology Conferences or MST Conferences for short. As in the past we would interact closely with universities and research laboratories world wide and thus resume our pre downsizing activities albeit on a significantly reduced scale. One thing I have come to notice after many years in both industry and academia is that, whereas the economic conditions that affect the technology development efforts of any given company tend to wax and wane in a largely unpredictable manner, the scientific challenges which stand in the way of the successful development of any given technology remain unshakably constant. Nowhere is this more poignantly apparent than when dealing with materials related problems. The person who in my opinion best stated the situation is Prof. J. E. Gordon<sup>11</sup>:

*"A deep, intuitive appreciation of the inherent cursedness of materials is one of the most valuable accomplishments an engineer can have. No purely intellectual quality is really a substitute for this."*

My own struggles with the self destructive nature of the high residual stresses in the polyimide materials fully supports Prof. Gordon's statement. Thus Dr. Mittal and I felt that by resuming the

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<sup>10</sup> Details of this work was published in "Thermal-Mechanical Properties of a Monomolecular Film Detected by a Vibrating Reed," R. H. Lacombe and B. M. J. Kellner, *Nature*, 289, 661 (1981).

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<sup>11</sup> Structures or Why things Don't Fall Down, J. E. Gordon (Harmondsworth: Penguin Books, London, 1978).

polyimide symposium series we could provide a valuable service to the academic and industrial technical community that has to try to understand and make useful products from these materials. These would be symposia that would address both the purely scientific as well as the applied aspects of these materials and thereby hopefully achieve a rapprochement between the two areas of interest and thereby also mitigate somewhat the sting that can arise from material cussedness. So starting in November 1999 the polyimide symposium series was initiated giving rise to the following string of symposia:

**International Symposium on Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications**, held Nov. 29

- Dec 1, 1999 in Newark, New Jersey.

Documented in: Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications, Vol.I , Ed. K. L. Mittal, (VSP, Utrecht, The Netherlands, 2001) .

**Second International Symposium on POLYIMIDES AND OTHER HIGH TEMPERATURE POLYMERS: Synthesis, Characterization and Applications**, held in Newark, New Jersey, December 3-5, 2001.

Documented in: Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications, Vol.2 , Ed. K. L. Mittal, (VSP, Utrecht, The Netherlands, 2003).

**Third International Symposium on POLYIMIDES AND OTHER HIGH TEMPERATURE POLYMERS: Synthesis, Characterization and Applications**, held in Orlando, Florida, December 17-19, 2003.

Documented in: Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications, Vol.3 , Ed. K. L. Mittal, (VSP, Utrecht, The Netherlands, 2005).

**Fourth International Symposium on POLYIMIDES AND OTHER HIGH TEMPERATURE POLYMERS: Synthesis, Characterization and Applications**, held in Savannah, GA, November 7-9, 2005. Documented

in: Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications, Vol.4 , Ed. K. L. Mittal, (Brill/VSP, Utrecht, The Netherlands, 2007).

**Fifth International Symposium on POLYIMIDES AND OTHER HIGH TEMPERATURE POLYMERS: Synthesis, Characterization and Applications** , held in Orlando, Florida November 5-7, 2007. Documented

in: Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications, Vol.5 , Ed. K. L. Mittal, (Brill/VSP, Utrecht, The Netherlands, in press).

The new symposium series essentially resumes where the "Old Testament" series left off in 1994. Again there is no space here to treat the contents of the above volumes in any level of detail but we can comment briefly on some of the newer topics that have arisen in the field. By far the most prominent new topic has been the introduction of the nanotechnology aspects of polyimide films and composites. I suppose this should not be surprising given that nanotechnology has become a "sine qua non" for much of the newer materials technology work since the start of the new millenium. The main thrust of this branch of materials technology is to see what new properties can be derived from otherwise common materials by carefully controlling their atomic and molecular structure at the scale of roughly 10 to 100 nanometers. An example of this is the work of Schmidt et. al. who fabricated layered structures of polyimide with silica nanoparticles to form lubricating films with a very low coefficient of friction and high wear resistance. ("Polyimide Nanocomposite Coating Materials with Special Functions", H. Schmidt et. al., (Documented in volume 4 mentioned above, p. 195).

It is also interesting to see a furthering of interest in polyimide films being put down by the Langmuir-Blodgett monolayer method. Much of the work involves trying to characterize the properties of these ultra thin structures as typified by the work of Taguchi et. al. ("Characterization of Orientational Ordering of Liquid Crystalline Molecules Deposited on Polyimide Langmuir-Blodgett films by Optical Polarized Absorption and Optical Second-harmonic Generation Measurements", Dai Taguchi et. al., volume 4 mentioned above, p. 347).

Finally, we see a number of relatively new application areas for the polyimides being introduced. Among these are:

1. Application to newer fuel cell membranes which can operate at higher temperatures and thus achieve greater energy conversion efficiency than the current membrane technology
2. Polyimide dielectrics for capacitive energy storage.

3. Polyimide foams as ultra light, highly rigid, high temperature structural materials for aerospace applications.

These and I'm sure many new application areas will be covered in the upcoming 6<sup>th</sup> symposium in the series to be held at the Florida Institute of Technology in Melbourne Florida this coming November which brings us to the end of this brief history of the polyimide symposia which began in Ellenville, New York nearly 30 years ago. Dr. Mittal and I would like to cordially invite all readers of the newsletter that have an interest in the polyimides to join us at that time for what should be an engaging symposium on this most fascinating and useful class of materials.

**CALL FOR PAPERS: SIXTH INTERNATIONAL SYMPOSIUM ON POLYIMIDES AND HIGH TEMPERATURE/HIGH PERFORMANCE POLYMERS : SYNTHESIS, CHARACTERIZATION AND APPLICATIONS; to be held November 9-11, at the Florida Institute of Technology, Melbourne, Florida, USA**

This symposium will be the sixth in a series the first of which was held in Newark, NJ in 1999. In a relatively small but significant departure from the previous symposia, this symposium will be concerned not only with the well established polyimides but also the entire range of high temperature/high performance polymers. As a loose definition this would include all polymeric materials which exhibit thermal stability above 200 C and in addition have outstanding mechanical, electrical, optical, surface and rheological properties. An example would be the Poly(p-phenylene benzobisoxazole) materials and Carbon Nanotube composites. These materials exhibit exceptional thermal, mechanical and electrical properties. Other examples would include the entire range of rigid rod polymers as well as fluorinated hydrocarbon chains that can exhibit extraordinary surface properties.

Of all these materials the polyimides have found the widest range of application in such diverse areas as the aerospace industry and microelectronic components. The unique combination of physical and chemical properties make these materials highly attractive for demanding applications where chemical inertness, high temperature stability, low dielectric constant, mechanical toughness and processability are primary concerns. In addition, their ability to adhere to a range of inorganic materials including metals, ceramics, glasses and semiconductors have made these materials predominant in coating

and composite applications. In this regard the issue of adhesion and interaction with other materials will be one of the major focal points of this symposium.

It is also our pleasure to announce that this symposium will be held in collaboration with Prof. Gordon Nelson of the Florida Institute of Technology and Dr. Martha Williams and Trent Smith of the NASA Kennedy Space Center. These individuals have been active in the area of high temperature polymers especially in regard to aerospace applications.

The invited speakers have been selected so as to represent widely differing disciplines and interests, and they hail from academic, governmental and industrial research laboratories. This meeting is planned to be a truly international event both in geographic coverage as well as in spirit. The technical program will contain both invited overviews and contributed original research papers

#### **TOPICS OF INTEREST INCLUDE:**

- ▶ Chemistry, synthesis and characterization
- ▶ Surface chemistry and surface modification

#### **OTHER HIGH TEMP./HIGH PERFORMANCE MATERIALS**

- ▶ Examples include
- ▶ Aramids
- ▶ Carbon nanotubes
- ▶ Poly phenylenes
- ▶ High. temp. epoxies
- ▶ Fluorinated materials

#### **PHYSICO-CHEMICAL PROPERTIES**

- ▶ Thermal-mechanical properties
- ▶ Electrical properties
- ▶ Adhesion properties and adhesion improvement
- ▶ Surface treatment
- ▶ Use of coupling agents
- ▶ Controlling stress level
- ▶ Encapsulation and barrier properties
- ▶ Effects of aging and environment on long term stability, reliability and durability

#### **APPLICATIONS**

- ▶ Polyimides as adhesives and insulators.
- ▶ Polyimides as dielectrics, photoresists and encapsulants in microelectronic and biomedical structures
- ▶ Metallization of polyimide and investigation of interfaces.
- ▶ Composite applications

## CHARACTERIZATION

- ▶ Chain architecture
- ▶ Bulk morphology
- ▶ Surface morphology
- ▶ Surface chemistry

## NOVEL AND ADVANCED FORMULATIONS

- ▶ Ultralow dielectric materials, low thermal expansion liquid crystals, polyimide blends, nanocomposites, copolymers, foams,... etc.

This symposium is being organized by MST Conferences under the direction of Dr. K. L. Mittal, Editor, Journal of Adhesion Science and Technology. Please notify the conference chairman of your intentions to present a paper or simply attend the meeting as early as possible. To submit a paper an abstract of about 200 words should be sent by **June 15, 2009** to the

conference chairman by any of the following methods:

E-mail: [rhlacombe@compuserve.com](mailto:rhlacombe@compuserve.com)

FAX: 212-656-1016

Regular mail:

Dr. Robert H. Lacombe  
Conference Chairman  
3 Hammer Drive  
Hopewell Junction, NY 12533

Contact by phone: 845-897-1654; 845-227-7026.  
Full conference details, abstract submission and registration via the Internet will be maintained on our web site:

<http://mstconf.com/polyimd6.htm>