

EMPOWERING POLYIMIDES

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ABSTRACT

Processing of aromatic polyimides synthesized from traditional diamines and dianhydrides has always been a limiting factor in their widespread use. Decreasing the molecular weight of these polyimides facilitates processing due to higher solubility and lower viscosity which, in turn, improves wetting characteristics. Higher molecular weight polyimides, on the other hand, are usually characterized by better thermomechanical properties compared to their lower molecular weight analogues. The introduction of reactive functional end-cappers allows for a controlled degree of polymerization where the resultant oligomeric polyimides can be easily processed and the properties associated with high molecular weight structures can be reclaimed upon a subsequent curing process. This elegant way of combining processability and performance, with special emphasis on the use of acetylenic groups in varnish and coating manufacturing, will be described. Case studies featuring various polyimide formulations will be presented to further illustrate these improvements.

1. INTRODUCTION

The high performance properties of aromatic polyimides (PIs), such as thermal stability, chemical resistance, good electrical properties and excellent mechanical properties, have facilitated their use in different areas, including electronic components, optical films, aircraft engines, aerospace and automobiles.

It is well known that the outstanding properties of aromatic PIs are based not only on their rigid planar structure, but also on the formation of highly ordered structures due to chain-chain interactions. As a result, high molecular mobility is limited even above the glass transition temperature (T_g), thus requiring severe processing conditions for molding materials. Since the commercialization of the first PIs, it was clear that the poor processability profile hampered their extensive applications.

The improvement of processability has been one of the main driving forces behind PI research. A landmark that led to the use and commercialization of the first aromatic PIs was a two-stage synthetic protocol that allowed for these materials to be processed in the precursor form, i.e. poly(amic acid) (PAA). Dehydration of this intermediate produces the final imide form, with the material becoming intractable after the imidization. These PIs are referred to as pseudo-thermoplastics. The enhanced solubility of this PAA precursor opened the possibility for solution processing techniques and these materials were successfully applied in the form of films and coatings. They have also been formed by hot compression molding but their lack of meltability hampers melt processing.

Thermoplastic PIs: Other strategies were envisioned as a mean to decrease intramolecular interactions and, therefore, to improve processability. Introduction of flexible linkages in the backbone, incorporation of bulky groups in the polymer chain or disruption of regularity through copolymerization are classical approaches that are behind a group of melt-processable PIs known as thermoplastic polyimides. Even though thermoplastic PIs can generally be processed as fully imidized materials, this improvement is achieved at the price of lower thermal and thermo-oxidative stability. In addition, chemical resistance can be problematic, especially if insufficient crystallinity is achieved upon processing.

Table 1 – PI Variants

| Chemistry | Processability | Degree of crosslinking | examples | Remarks |
|--------------|----------------------|------------------------|-----------------|----------------|
| Condensation | Pseudo-thermoplastic | | Kapton, Upilex | PAA processing |
| | Thermoplastic | | Aurum, Ultem | Remelttable |
| Addition | | Bismaleimides | | Brittle |
| | | Thermocurable | AFR-PE, LARC-13 | |

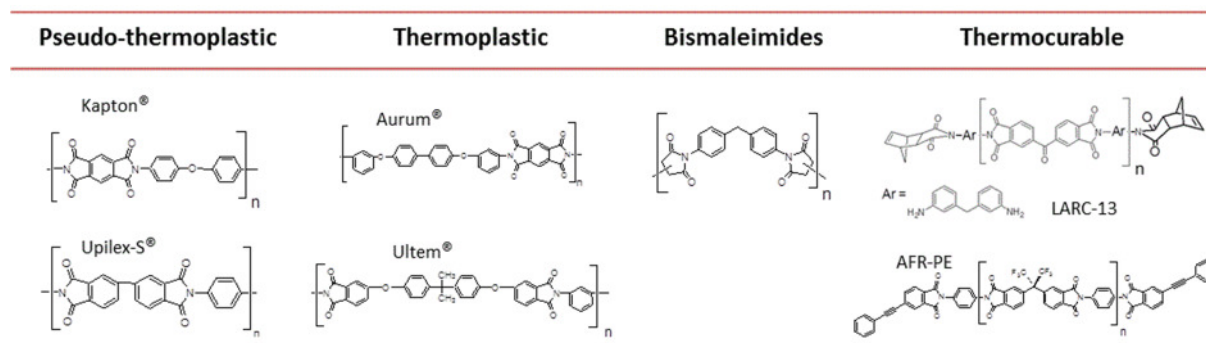
A different strategy lies behind addition type PIs. Low molecular weight (MW) intermediates are functionalized with reactive groups. The processing of these intermediates is facilitated due to the limited MW and, once they have been processed, the properties associated with high

molecular weight structures can be achieved upon curing. In the context of addition PIs, curing refers to the thermal treatment needed to polymerize the functional intermediates via addition reactions. Even though the functionalization usually relies on the use of reactive end cappers to produce intermediates with reactive terminal positions, these reactive groups can also be intercalated in the back bone (NEXIMID® 400, Figure 3) or incorporated as pendant groups. It should be clarified that these intermediates are also derived from condensation reactions, but polymer formation stems from the addition reaction achieved upon thermal activation. Addition PIs comprises two types of materials, bismaleimides and thermocurable PIs. The low MW of bismaleimide intermediates, together with the addition chemistry of the maleimide functionality, results in brittle structures and, even though they are an important class of PIs, they will not be covered here.

2. THERMOCURABLE POLYIMIDES: UNDERLYING CONCEPTS

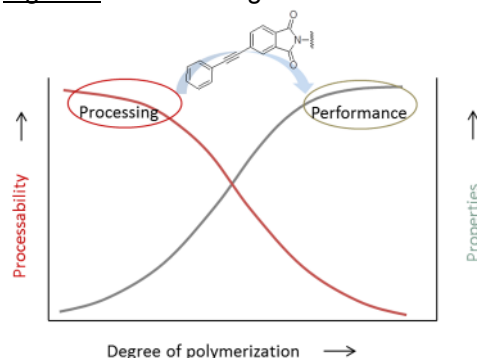
As illustrated in Figure 2, for a given polymer, increasing its degree of polymerization has a detrimental effect on processability, both in terms of solubility and meltability. Often, the lower MW required for easy processing conflicts with the higher MW required for end-use performance. The processing of functionalized oligomers prior to building MW through a curing step represents an elegant way to bring together the easy processing of low MW entities with the performance of high MW polymers.

Figure 1 – Examples of Different PIs



For linear thermoplastic materials, modulus, strength, extensibility, creep resistance, abrasion resistance and thermal stability generally increase with increasing MW. The situation is slightly different when processes others than linear chain extension, e.g. crosslinking, are responsible for building MW. The MW of thermoset addition PIs can be considered infinite and the properties of these materials would tend to approach high-level value, which would then become a function of cross-linking density rather than of MW itself. Also, the crosslinked morphology is revealed as diminished elasticity, and precautions should be taken in order not to compromise the elongation to break and toughness values.

Figure 2 – Processing/Performance Balance



It is clear from this description that (the oligomer formation) should be done at a temperature lower than the activation temperature, which will define the upper limit of the processing window. The MW of these intermediates can range from the one of monomeric or oligomeric spices to the one of polymeric spices with a lower MW than classical condensation PIs. Apart from the MW, the processability of these intermediates will also be dictated by their chemical composition.






Processability can be further improved by working with low MW addition intermediates in the PAA form instead of processing the fully imidized form. The use of reactive low MW poly(amic acids) exemplifies how any other strategy aiming to improve processability can be boosted by the use of addition PIs.

3. FACTORS DICTATING PROCESSABILITY AND PERFORMANCE

3.1. Reactive end-caps

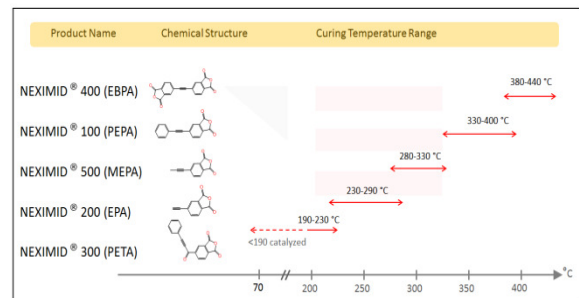
Even though there are different reactive groups that have been successfully applied when working with thermocurable PIs (Table 2), ethynilic end-cappers are recognized as one of the most promising.¹ This is due to a very attractive combination of properties affecting the processing/curing, e.g. processing window, lack of volatile evolution; and the properties of the cured material, e.g. thermo-oxidative stability, mechanical properties and micro-crack resistance.

Table 2 – Reactive End-Caps

| Reactive Group | Curing Temp (°C) | Observations |
|---|------------------|--|
|  Cyanate | 200-300 | Poor thermal stability |
|  Maleimide | 230-250 | Poor thermal stability |
|  Ethynyl | 250 | Small processing window |
|  Phenylethynyl | 350-370 | High cure temperature Excellent stability 177°C |
|  Nadimide | 350-370 | Volatile evolution Low toughness |

The physical properties of the precursor and the characteristics of the processing technique define an optimal curing temperature that can dramatically vary from case to case. These products can be used to set the curing temperature at the desired level, and thus, address

Figure 3 – Heat-Activated Crosslinkers

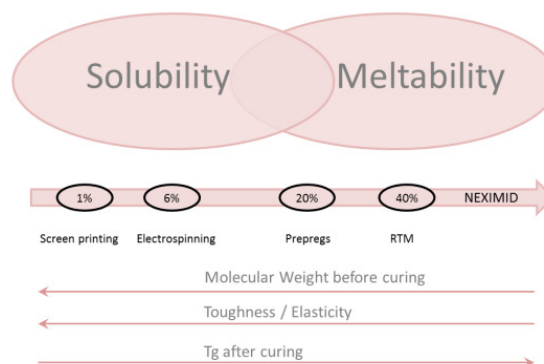


an urgent request expressed by industry. The activation temperature of heat-activated crosslinkers (e.g. NEXIMID® 300, Figure 3) can be as low as 70 °C in the presence of catalyst. These low activation temperatures, even though they are not suitable for melt processing, find application in solution processing techniques.

3.2. Degree of oligomerization

High molecular weight PIs are obtained when using stoichiometric amounts of difunctional comonomers, i.e. diamines and dianhydrides. When working with monoanhydride end-cappers, an excess of diamino component is used to decrease the resulting MW of the oligomers and to provide an anchoring point for the reactive end-cappers. These are dosed in a concentration so that the final ratio of amino and anhydride functionalities is balanced. The higher the offset of one of the difunctional comonomers, or the higher the concentration of reactive end-cappers in the formulation, the lower the MW of the obtained reactive oligomer.

Figure 4 – Degree of Oligomerization, Properties and Use



The targeted MW of the starting thermocurable intermediate will be defined by the processing technique and by the desired final properties of the cured material. Improvements in solution processing can be attained readily with low concentrations of reactive end-cappers (Figure 4). Under these conditions, and for the final cured material, a small decrease in elasticity is expected. The situation is different when trying to affect meltability. Quite low MWs are needed in order to improve meltability and, therefore, higher

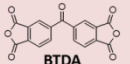

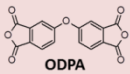
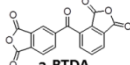
loadings of reactive end-cappers are typical for these kinds of formulations. Resin transfer molding (RTM) and other out of autoclave techniques take the extreme position, where processing melts require the use of very low molecular weight intermediates.

3.3. Selection of difunctional comonomers

Even though improvement in processability is a consequence of the low MW of the oligoimides, the nature of the dianhydride and diamine used in the condensation of oligoimides always impacts processability and final properties. Thus, even compositions with a low degree of polymerization can suffer from poor processability if these compositions are based on planar rigid components.

In the synthesis of PIs, dianhydrides are critical comonomers influencing dielectric, thermal and oxidative behavior of the material. Symmetric and asymmetric ultrapure dianhydrides (e.g. JAYHAWK BTDA®) are available to meet the expanding requirements of industry. Examples are provided in Figure 5.

Figure 5 – Dianhydride Co-Monomers

| Dianhydride | Notes |
|---|---|
|  BTDA | 3,3',4,4'-Benzophenone tetracarboxylic dianhydride General purpose |
|  PMDA | Pyromellitic dianhydride For high-temp performance |
|  ODDPA | 4,4'-Oxydiphthalic anhydride For increased solubility and flexibility |
|  a-BTDA | 2,3,3',4'-Benzophenone tetracarboxylic dianhydride Asymmetric version to reduce melt viscosity and increase Tg |

3.4. Performance

PETI-5, Phenyl Ethynyl Terminated Imide oligomer with medium molecular weight of 5000 g/mol, was developed by NASA as a lightly crosslinked thermocurable polyimide. Oligoimides with different molecular weights were prepared by proper adjustment of the reactive end capper concentration. The properties of these oligoimides, before and after curing, can be

used to exemplify the concepts previously presented.

The potential of these intermediates for solution and melt processing can be correlated to the inherent and melt viscosities presented in Table 3.² It is clear from the inherent viscosity that, for a given viscosity value, higher solid content can be achieved when reducing the MW. A more dramatic effect of the degree of oligomerization is observed in the minimum melt viscosity values. Decreasing the MW reduces not just the viscosity value, but also the temperature needed to achieve it. While lowering the MW, the melt viscosity approaches values suitable for the processing of PI composites by non-autoclave techniques, such as RTM, which are quite common in epoxide resins but quite challenging in the case of PIs. Lowering the melt viscosity is also important to improve wetting properties of the resin in the production of composites.

Table 3 – Oligoimides: MW-Properties

| M _n (g·mol ⁻¹) | η _{inh} (dL·g ⁻¹) 0.5% (w/v) NMP 25°C | Minimum Melt Viscosity (Poise@°C) | T _g (°C) | | Unoriented cured film tensile properties | | |
|---------------------------------------|--|---|---------------------|-----------|--|------------------|----------------------------|
| | | | Initial / Cured | Temp (°C) | Strength (MPa) | Modulus (GPa) | Elongation at break (%) |
| | | | 5000 | 0.27 | 10,000@371 | 210 / 270 | 23 |
| 2500 | 0.20 | 900@335 | 210 / 277 | 177 | 84 | 2.3 | 83 |
| | | | | 23 | 152 | 3.5 | 14 |
| 1250 | 0.15 | 50@335 | 170 / 288 | 177 | 77 | 2.2 | 43 |

To evaluate the mechanical properties of the materials obtained from the oligoimides with different MWs, unoriented thin films were cast and cured in flowing air at 350 °C. The measured strength and modulus correspond to values of high MW polymeric materials. Tg values are higher when curing low MW oligoimides, which is expected as this value is usually proportional to the crosslinking density. As it has been mentioned, the elasticity follows the opposite direction, i.e. lower values achieved with increasing crosslinking density. Worth noticing are the relative large values for the elongation to break of the cured samples. The phenylethynyl group undergoes a complex reaction involving chain extension, branching and crosslinking. The observed high elongation to break is more typical of a linear thermoplastic than a thermoset,

suggesting that chain extended structures contribute significantly to the final cured morphology. The film obtained from the smallest oligoimide had variable thickness due to excessive resin flow during oven cure. Even though mechanical characterization could not be obtained, the film was flexible and creasable, indicating reasonable toughness.

4. CASE STUDIES

Addition curable PIs are necessary for meltable resins to be used in structural composite materials. Plenty of information about this topic can be found in scientific literature, with the previously mentioned PETI-5 as one of the main inspirations for this research. It is the purpose of the two following study cases to illustrate how this approach is not restricted to melt processing of structural parts, but has also been used in solution processes.

4.1. Screen printing of PI film as insulator layers

Screen printed PIs can be used as passivation coatings for mechanical and environmental protection of any type of device. The use of this technique in the coating of wafers has demonstrated significant advantages in efficiency and cost over convectional spin-etch.

The viscosity of the ink in screen printing is desired to be low when being forced through a fine mesh screen but sufficiently high to avoid blot and sagging once it has been printed and left motionless. In other words, inks with high thixotropy are desirable. This is an important parameter to ensure high resolution and repeatable printings. The reliability of the prints can be achieved only when the PI coating exhibits good mechanical properties, thermal stability and adhesion to substrates. The coefficient of thermal expansion (CTE) of the PI film should be as low as possible to reduce the differences in the CTE of the silicon die and the polyimide, thus minimizing the induced detrimental mechanical stresses.

The effect of using functionalized intermediates on the properties of screen printed insulator films is displayed in Table 4.³ In Case 1, addition curable triple bonds were intercalated in the backbone by replacing ODPa from the original formulation with NEXIMID® 400, EBPA. In Case 2 the original formulation was capped with NEXIMID® 100, PEPA. Due to the similar MW, Case 2 has similar processability properties to the reference formulation, with similar viscosity and thixotropy. Case 1 has a different viscosity profile due to its lower MW. The lower apparent viscosity is partially compensated by its higher thixotropy. In all cases, printability, reproducibility and adhesion, both to silicon oxide and silicon nitride substrates, are satisfactory.

Table 4 – Screen Printing: PI Properties

| Properties | Reference: ODPA/BAPP:BM | Case 1: EBPA/BAPP:BM | Case 2: ODPA/PEPA/BAPP:BM |
|-------------------------------|----------------------------|-------------------------|------------------------------|
| Mn (Dalton) | 33650 | 6900 | 36900 |
| Viscosity (Pa·s) ¹ | 24 | 1 | 25 |
| Tg (°C) ² | 185 | 256 | 230 |
| Td 5% (°C) ² | 493 | 520 | 535 |
| Strength (Mpa) ² | 70 | 88 | 83 |
| Elongation (%) ² | 14 | 10 | 9 |
| CTE (ppm/K) ² | 69 | 48 | 56 |
| Modulus (Gpa) ² | 2.2 | 2.7 | 2.5 |

¹ Apparent viscosity of 28% solution at 333 s⁻¹

² Curing done at 300 °C for one hour

After curing the film, a significant improvement of the thermo-mechanical properties is achieved. An exception to this trend is the elongation to break value that, even though it is still acceptable, is decreased compared to the classical formulation.

An important improvement in chemical resistance is also obtained upon curing of the films as shown in Table 5. This was evaluated based on the presence of surface abnormalities or dissolution.

Table 5 – Chemical Resistance Data

| Solvent 25°C, 15 min | BAPP:BM/ODPA | BAPP:BM/ EBPA | BAPP:BM/ ODPA/PEPA |
|-------------------------|--------------|------------------|-----------------------|
| Acetone | xx | Ok | Ok |
| Isopropanol | Ok | Ok | Ok |
| γ-Butyrolactone | xx | Ok | Ok |
| NMP | xx | Ok | Ok |

4.2. Increasing throughput in electrospinning

In this patent from DuPont⁴ the authors present the use of reactive intermediates to increase the poly(amic acid) concentration used in solution spinning of nanofibers. This results in a remarkable increase in production of nanofibers.

It is generally desirable in solution processes to work with high solid concentrations to increase line speed and to minimize solvent problems such as flammability, toxicity, recovery and cost. However, it is quite common that, for a given processing technique, the maximum practical concentration is not limited by the solubility of the substrate but by the optimum solution viscosity suitable for such a process. In solution spinning processes, viscosity is a critical parameter that will affect the resultant fiber size and also the laydown of the nanofiber.

Table 6 shows how the different MWs, defined by the offset between PMDA and ODA and expressed as mole ratio, affect the viscosity value for different concentrations. It can be seen that a 25 weight% solution with 0.93 mole ratio has a lower viscosity than a 20 weight% solution with 0.97 mole ratio (Comparative Example vs Composition 1). This approach enables an increase in solid concentration up to 30% while maintaining the viscosity at suitable processing values.

Table 6 – Effect of MW on Viscosity

| Composition | End-capper | Monomer (mole ratio) | | | Polymer w% in DMF | Viscosity (Pa-s) | Mw (Dalton) |
|-------------|------------|----------------------|------|------------|-------------------|------------------|-------------|
| | | ODA | PMDA | End-Capper | | | |
| Comparative | ----- | 1 | 0.97 | 0 | 23 | 8.5 | 34K |
| 1 | EPA | 1 | 0.93 | 0.14 | 25 | 4.2 | 11K |
| 2 | EPA | 1 | 0.97 | 0.06 | 20 | 8.4 | ND |
| 3 | EPA | 1 | 0.89 | 0.11 | 30 | 12 | ND |
| 4 | PEPA | 1 | 0.88 | 0.12 | 29 | 11.2 | ND |
| 5 | PETA | 1 | 0.88 | 0.12 | 29 | 10.9 | ND |

It is claimed that a 50% increase in the production of nanofiber is achieved by processing a 30 weight% solution of the low MW addition intermediate instead of processing a 20 weight% solution of the conventional poly(amic acid). This improvement is based solely on the increased polymer concentration.

The acetylene end-capped poly(amic acid) nanowebs obtained from the lay-down of the nanofibers were imidized at 350 °C for two minutes and annealed at 450 °C for five minutes in a convection oven under air atmosphere. The different materials were tested for break load. The performance of these nanowebs as separators in electrochemical cells was also evaluated by cycling the cells at 1C for 50 cycles with charge and discharge time of one hour each. Results are shown in Table 7.

Table 7 – Cycling Results

| Sample | Stoichiometry & End-capper | Break Stress (Kg/cm ²) | First Cycle Discharge Capacity (mAh) | Third Cycle Discharge Capacity (mAh) | Fiftieth Cycle Discharge Capacity (mAh) |
|-------------------|----------------------------|------------------------------------|--------------------------------------|--------------------------------------|---|
| Comparative-cured | 0.97 ---- | 360 ± 50 | 2.91±0.1 | 2.85±0.1 | 2.45±0.1 |
| 1-cured | 0.93 EPA | 500 ± 25 | 2.94±0.1 | 2.87±0.1 | 2.51±0.1 |
| 2-cured | 0.97 EPA | 425 ± 25 | | | |
| 3-cured | 0.89 EPA | 400 ± 50 | | | |
| 4-cured | 0.89 PEPA | 360 ± 50 | 2.92±0.1 | 2.85±0.1 | 2.47±0.1 |

It can be concluded that the addition PIs result in a significant increase in the production of nanofibers, while retaining or even improving their strength if annealed under optimum conditions. Also, within experimental error, the performance of the electrochemical cells with cross-linked PI nanoweb separators performed equivalently to the control sample.

5. CONCLUSIONS

The use of addition curable PIs allows for better processability while retaining the mechanical and thermal properties typical for high molecular weight polymers. The use of low MW intermediates and the crosslinked morphology of the final structure provide very attractive values for properties such as wetting ability, chemical resistance and Tg. These properties are responsible for the widespread use of addition curable PIs in high temperature composites. On the other hand, elongation to break can be compromised in materials with high crosslink density and this can be fatal in PI films and coatings due to embrittlement.

It is now better understood that, in the curing of ethynilic reactive groups, chain extension processes can make a valuable contribution,

leading to a less detrimental loss of elasticity. This problem can also be alleviated by the use of sufficiently high molecular weight precursors that will result, upon curing, in materials with low crosslink density. Effective structural modifications, such as the use of flexible comonomers or block copolymers, allow for these relatively high MW intermediates not to be exclusively processed in solution and, therefore, creasable materials can also be obtained by melt processing techniques. As a result, the use of addition cured PI is gaining popularity in non-composite processes e.g. films and coatings.

6. ACKNOWLEDGEMENTS

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References

1. Polymer 41 (2000) 5073-5081
2. Polymer 41 (2000) 5073-5081 / NASA, CR-1998-206927
3. PI R&D CO LTD; JP, 2013, 173820 A
4. E. I. DU PONT, WO 2013, 181333 A1

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