

DEVELOPMENT OF THERMOPLASTIC POLYIMIDE "AURUM™" AND PROCESSED PRODUCTS

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ABSTRACT

Aromatic polyimides have outstanding thermal, mechanical, electrical and solvent resistance properties. However, their poor processability is one of drawbacks of these polymers. We focused on the improvement of melt processability of polyimide with retaining the excellent properties by making clear the relationship between structure and thermoplasticity. Then AURUM™ and the other several kinds of unique melt-processable polyimides were developed, and properties of these polymers were characterized. These polyimides are highly processable, therefore many kinds of processed products such as injection molded products, extruded film (REGULUS™), carbon-fiber based prepregs for composites, spun fibers, flexible metal clad (FLEX-MID™) were produced. We also developed some high performance applications such as automobile and aircraft engine parts and electronic components, etc.

INTRODUCTION

Aromatic polyimides¹ have marked thermal stability, excellent mechanical and solvent resistance properties, therefore, they are being used in such applications as automobile and aircraft parts and electric packaging for printed circuit. Aromatic polyimides synthesized from aromatic monomers generally possess excellent thermal stability and mechanical properties. However, many of these polymers are insoluble and infusible,

rendering it impossible to possess them by conventional method, that is, their processability was one of drawbacks of aromatic polyimides. Therefore, much effort has been spent on synthesizing tractable polyimides that maintain reasonable high strength and thermal stability². Mainly, there are two methods to improve the processability of polyimides. One is the improvement of its solubility, on by F.W.Harris et al.³ and the other scientists, they successfully produced several organo-soluble polyimides by using aromatic monomers having bulky side groups. The other is the improvement of its thermoplasticity. This method was chosen by the National Aeronautics and Space Administration (NASA) and Mitsui Toatsu Chemicals, INC., and then melt processable polyimide, LARC #1500⁴⁻⁵ was produced. In order to improve thermoplasticity of polyimide, A.Yamaguchi et al.⁶ investigated the relationship between chemical structures of polyimides and their Tg values by using bis(aminophenoxy)benzene (APB) isomers and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) as aromatic monomers, and reported that Tg values of obtained polyimides strongly depended on the amino substituted position of used diamine monomers. However, systematic study for the relationship between chemical structure of polyimide and its thermoplasticity was not carried out. Therefore, we focused on the improvement of melt processability of polyimide with retaining the excellent properties by making clear the relationship between structure and thermoplasticity. Then AURUMTM and the other several kinds of unique melt-processable polyimides were developed⁷. And we also developed some high performance applications of these unique melt-processable polyimides.

EXPERIMENTAL

First of all, in order to make clear the relationship between chemical structure of polyimide and its thermoplasticity, various kinds of diamine monomers having different amino substituted position, different chain length and different moiety were synthesized. Polyimides were synthesized with obtained various kinds of diamine monomers by polycondensation of tetracarboxylic dianhydrides. And then, thermoplasticity of obtained polyimide was studied by characterizing its Tg value and melt flowability.

Basically, meta amino substituted diamines are synthesized from 1,3-dinitrobenzene and corresponding dihydroxy compounds by nitro- displacement reaction⁸ followed by reduction. Para amino substituted diamines are synthesized from 4-aminophenol and corresponding dichloro compounds, or 4-chloronitrobenzene and corresponding dihydroxy compounds followed by reduction. Polyimides were synthesized from obtained diamines and tetracarboxylic dianhydrides. Inherent viscosities(η' s) of synthesized polyimide powders were controlled to around 0.5 dl/g by selecting the optimum mole ratio between diamine and tetracarboxylic dianhydride. And polymer chain ends were terminated by using phthalic anhydride as an end capper.

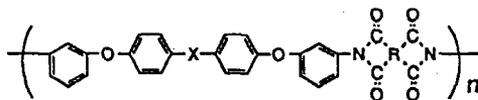
Melt flowability of polyimide was estimated by melt flow start temperature. Melt flow start temperature was determined by using a FLOW-TESTER (Shimadzu Flowtester CFT-500).

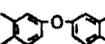
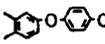
RESULTS

Effects of chain length of diamine monomer and amino substituted position of diamine monomer on Tg's of obtained polyimides were investigated. And then it was found that Tg value of polyimide decreased with increasing of chain length of diamine monomer and it was also decreasing according to increase of meta linkage contents in diamine monomer. This trend is also observed in the case of polyimides synthesized from diamines having more than two benzene rings. Tg's of various kinds of polyimides from meta amino substituted diamines having four benzene rings and tetracarboxylic dianhydrides received from commercial sources were summarized in Table 1. η' s of all polyimides summarized in this table were controlled to around 0.5 dl/g. This result indicated that Tg's of polyimides could be controlled from 169 to 254°C by selecting suitable monomer combination. It was also found that Tg values of polyimides were decreasing according to the increase of structural flexibility of selected monomers.

Table 2 shows the melt flowability of polyimides. This result indicates that it's possible to synthesize melt flowable polyimide from PMDA and meta amino substituted diamine having more than three benzene rings.

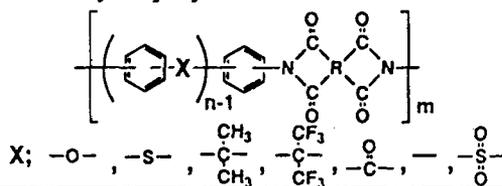
Table 1 T_g 's of polyimides and their chemical structures.

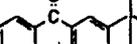
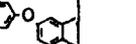


X \ R		T_g (°C) ^a						
								
     		254	237	236	235	224	211	200
	↑	250	232	228	221	216	199	195
	↓	230	222	214	211	205	193	183
		218	215	209	208	201	189	182
		218	212	202	202	195	184	178
		212	208	200	199	192	181	171
		208	207	200	195	186	175	169

a: Differential Scanning Calorimetry at a heating rate of 16°C/min

Table 2 Melt flowability of polyimides and their structures



Diamine		R				
amino substituted position	n					
para	1					
	2					
	3					
	4					
meta	1					
	2					
	3					
	4					

□ Infusible ■ Melt flowable

According to these results as mentioned above, melt processable polyimide AURUM™ having repeating structure as shown in Figure 1 was developed and commercialized. Basic properties of AURUM™ are summarized in Table 3.

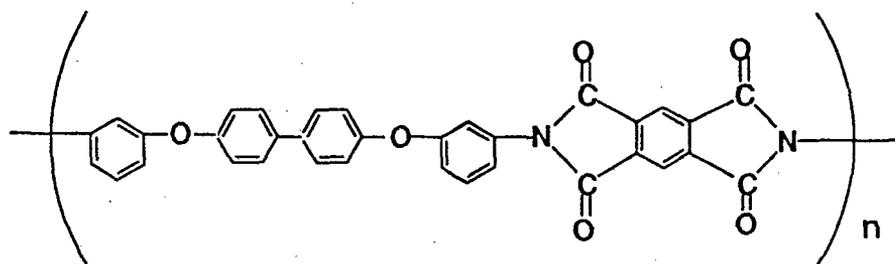


Figure 1

Table 3 Basic Properties of AURUM™

Items	Unit	<AURUM>	PEEK	<ULTEM> 1000	<VESPEL> (SP-1)*
Tg	°C	250	143	215	-----
Tm	°C	388	334	-----	-----
Density	g/cc	1.33	1.30	1.27	1.36
Tensile Strength	kgf/mm ²	9.40	9.90	10.7	7.38
Flexural Strength	kgf/mm ²	14.0	14.5	14.8	9.84
Flexural Modulus	kgf/mm ²	300	380	337	253
Compression Strength	kgf/mm ²	12.2	12.2	14.3	-----
Izod Impact Strength (Notched)	kgfcm/cm	9.0	7.0	5.0	-----

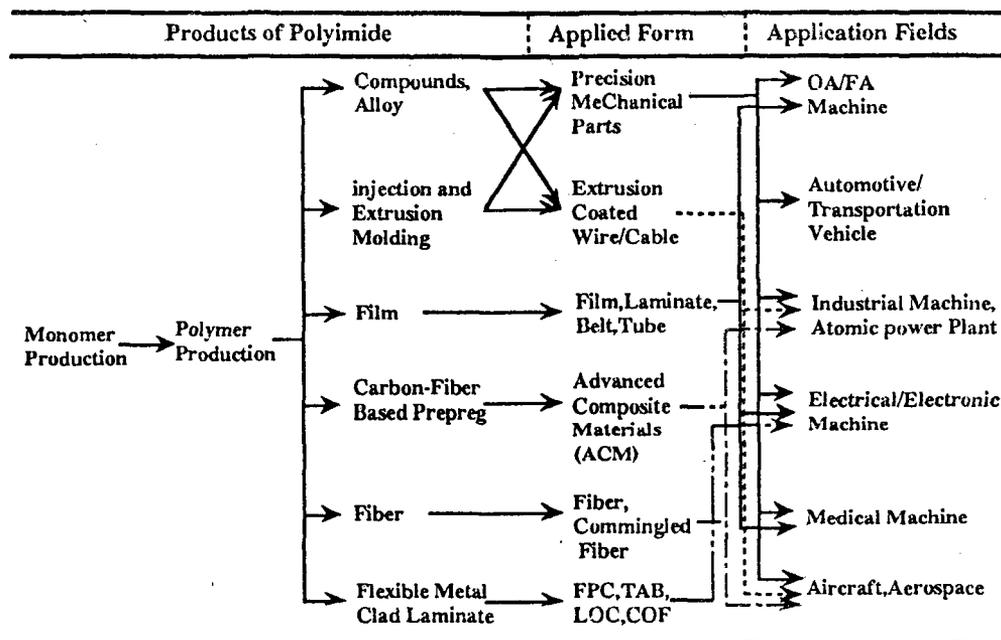
* Cited from "Engineering Plastics". Edited by T.Hirai, Plastic Age Press, p209(1984)

APPLICATIONS

Processed products of AURUM™ family and their application fields are shown in Table 4.

γ-picaline / m-Cresol 150°C 4h.

Table 4 Processed Products of AURUM™ family and Their Application Fields



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