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The characteristics of high-temperature resistant organic polymers and the feasibility of their use as glass coating materials

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It is desirable to protect pristine glass surfaces from frictive damage by applied coatings and thereby maintain large proportions of the inherently high tensile strength of such glass surfaces. These protective coatings should ideally be applied to glass surfaces immediately after they are formed into their desired configuration. This ideal concept requires that lubricous coatings be able to withstand elevated temperatures with minimal degradation of their protective properties. The majority of aliphatic polymers thermally degrade at temperatures less than 250° C and thus are not useful in the present desired application. The factors which increase the thermal stability of organic polymers beyond this temperature are discussed. The thermal stabilities of two classes of high-temperature resistant polymers, namely polyimides and polybenzimidazoles (PBIs), are reviewed. Finally, results are reported of laboratory experiments to determine the feasibility of using PBIs as a coating material when applied to glass substrates heated to elevated temperatures.

1. Introduction

Pristine glass surfaces can exhibit extremely high tensile strengths [1]. However, if glass surfaces become damaged, the tensile strengths decrease as functions of the depth of the damage cracks and the radius of curvature of the crack tips [1–6]. To protect glass objects from such strength-degrading effects when caused by frictive loads, glass surfaces are coated with both metal oxide and organic coatings [2, 5, 7]. Metal oxide coatings are typically applied at glass temperatures of approximately 550° C. These coatings do not exhibit any scratch-protective properties, but serve as a primer or anchor for lubricous organic coatings [5, 8–12]. Organic coatings are applied after the annealing process at glass temperatures of approximately 100° C. The combination of properly applied metal oxide and organic coatings provides the scratch resistance and lubricity necessary to protect glass surfaces from frictive damage [2–5, 9, 10, 13, 14].

Since metal oxide coatings possess no protective properties, glass surfaces are susceptible to frictive damage until organic coatings are applied [5]. It is therefore desirable to provide glass surfaces with lubricous, damage-protective organic coatings as soon as possible after the forming operation. It is anticipated that polymers which can survive 550° C, the approximate temperature of glass surfaces immediately after formation and the approximate maximum temperature encountered in annealing lehrs, may accomplish the desired objective. In addition, successful application of high-temperature resistant polymer coatings would eliminate current metal oxide coating processes with their attendant acidic reaction effluents.

The thermal degradation characteristics and intramolecular forces of two specific classes of high-temperature resistant polymers (polyimides and polybenzimidazoles) are discussed in detail. A series of laboratory experiments are also sum-

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marized in which the feasibility of using polybenzimidazole as a glass coating material was studied.

2. Thermal stability of organic polymers

When heated, linear or branched polymers such as polyethylene, polyvinyl chloride, polystyrene and polymethylmethacrylates, decompose at temperatures up to 250° C [15]. The thermal properties of these polymers can be attributed to their intramolecular forces, mainly the strength of covalent carbon–carbon bonds. The thermal stability of such polymers can be improved slightly by substituting for carbon atoms in the chain other atoms, whose bond energy with carbon or with themselves is higher than the bond energy of carbon–carbon bonds.

Another polymer, polytetrafluoroethylene (PTFE), has a decomposition temperature of approximately 315° C, which is higher than that of the other polymers listed above even though its chain consists of carbon–carbon bonds. Its higher thermal stability is due in part to a higher potential barrier to free rotation of the polymer. This effect is due to the presence of fluorine atoms attached to the polymer chain.

The most significant means of increasing the thermal stability of polymer molecules is by increasing the intramolecular structural rigidity of the polymer, by incorporating aromatic or heterocyclic rings into the polymer chain. These rings hold the polymer molecule in a planar conformation and inhibit random orientation due to rotation. Aromatic rings also are more resistant to oxidative decomposition than aliphatic chains.

Aromatic rings and heterocyclic rings which contain double bonds also provide a degree of resonance stabilization which improves the thermal properties of polymers. In the covalent carbon–carbon bonding scheme of aliphatic polymers, two electrons are shared by two carbon atoms. Within an aromatic ring, four electrons are shared by six carbon atoms. A heterocyclic ring containing double bonds also behaves in a similar manner as aromatic rings. Thus, more energy is required to break aromatic or heterocyclic carbon–carbon double bonds in the polymer chain than that required to break aliphatic carbon–carbon bonds.

Another modification which reduces the thermal vibrations of polymer molecules and thus increases their thermal stability is polymer crosslinking. This provides greater rigidity to the polymer molecule which in turn significantly inhibits molecular rotation.

New high-temperature resistant polymers have been developed which incorporate the features discussed in the previous paragraphs. Two such classes of high-temperature polymers, polyimides and polybenzimidazoles, were chosen for further detailed study based on their commercial availability.

2.1. Polyimides

According to Sullo [16], polyimides are among the most heat-resistant polymers known. These polymers are synthesized by the condensation reaction of aromatic dianhydrides and aromatic diamines, as shown in Fig. 1 [17, 18].

The resultant polymer is capable of withstand-

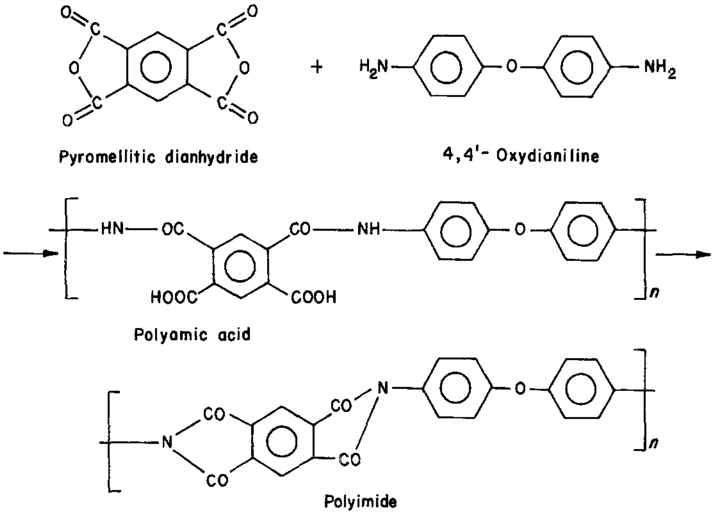

Figure 1 Synthesis of polyimides [17, 18].

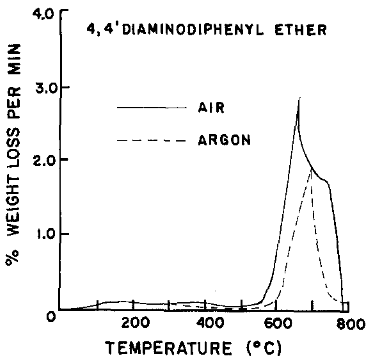

Figure 2 TGA of polypyromellitimides (heating rate, 4° C min^{-1}) (from Frazer [19]).

ing a temperature of approximately 600° C in an inert environment. Unfortunately, the polymer is insoluble in most organic solvents and dilute acids. Therefore, in order to utilize the polymer the reaction intermediate, polyamic acid, must be isolated. This intermediate is soluble in solvents such as dimethyl formamide or N-methyl pyrrolidone (NMP). The polyimide polymer is then obtained *in situ* by applying the polyamic acid solution to the desired location or object, evaporating the solvent, and causing an imidization condensation reaction to occur.

It should be noted that the imidization process must occur at an elevated temperature and that water is released as a by-product. Unfortunately, the presence of water can produce undesirable pinholing in the resultant polyimide polymer, creating strength-weakening voids. Other means of avoiding the production of water and its subsequent deleterious effects have involved alternative polyimide polymerization processes. An addition polymerization process using *bis*-maleimide is a typical example.

The excellent thermal stability of polyimides are shown by the thermogravimetric analysis (TGA) curves in Fig. 2 for pyrolysis in air and argon, and in Fig. 3 for pyrolysis in helium [19]. It can be seen in Fig. 2 that polyimides decompose at a lower temperature and at a faster rate in air than in an inert environment. This is due to oxygen attack of the polymer chain, most probably at the nitrogen intersections. In addition, Fig. 3 shows that the thermal stability of polyimides can vary depending on the specific composition of the diamine used in the polymerization process.

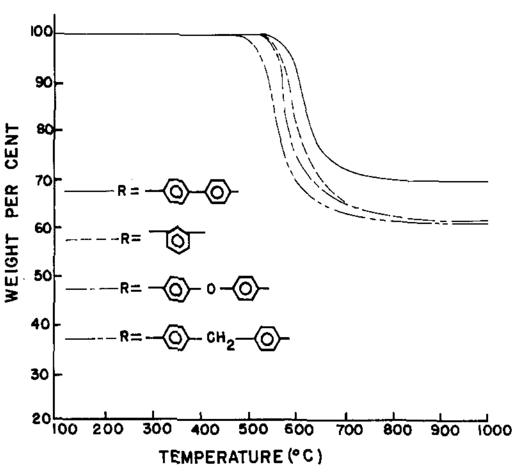

Figure 3 TGA of polypyromellitimides in dry helium (heating rate, 3° C min^{-1}) (from Frazer [19]).

The major problem with polyimides is the insolubility of the fully imidized polyimide. As discussed by Bateman *et al.* [20], a recent adaptation of the polymerization reaction has resulted in the formation of a co-polyimide which is soluble in various organic solvents while retaining excellent thermal stability characteristics, as shown in Table I [20]. The co-polyimides are formed by the reaction of 5(6)-amino-1-(4'-aminophenyl)-1,3,3-trimethylindane (DAPI) and

TABLE I Data on DAPI/BTDA polyimides from Bateman *et al.* [20]

Diamine component		Inherent viscosity*	T_g (TBA) (° C)	TGA (N_2)† (° C)		TGA (air)† (° C)	
% DAPI	% MDA			2%	10%	2%	10%
100	0	0.55	320	472	492	420	285
90	10	0.45	310	465	495	400	455
80	20	0.55	310–15	450	482	430	490
75	25	0.33	320	452	495	400	460
70	30	0.52	307	465	492	428	500
60	40	0.61	305	465	495	440	500
50	50	0.64	300	470	500	445	504
40	60	Insoluble	–	–	–	–	–

*0.5% in NMP at 25° C.
†Temperature at which the indicated weight loss was observed; heating rate 5° C min^{-1}.

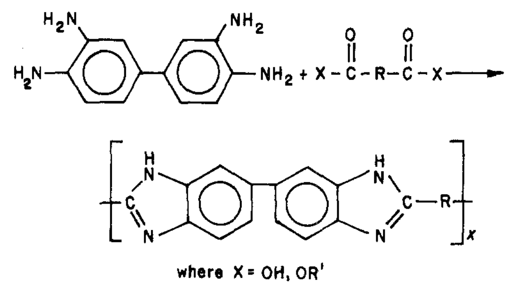

Figure 4 Synthesis of a polybenzimidazole [19].

methylene dianiline (MDA) with benzophenone tetracarboxylic dianhydride (BTDA).

Bateman *et al.* [20] attribute the thermal stability of this copolymer to its predominantly aromatic structure, and to the absence of oxidative-susceptible benzylic hydrogens in the cycloaliphatic portion of the molecule. They add that there are no adjacent atoms bearing hydrogen, thus depriving the system of low-energy oxidative degeneration pathways.

2.2. Polybenzimidazoles

Polybenzimidazoles (PBIs) have been developed to provide high-temperature resistant polymers which, in their fully polymerized form, are soluble in common polar solvents, overcoming the main historical objection concerning the use of polyimides. PBI is formed by the condensation reaction of *bis-o*-diamine and aliphatic dioic acids or their derivatives. One specific example is given in Fig. 4 for the condensation reaction between 3,3'-diaminobenzidine and diphenyl isophthalate [19].

The thermal stability of PBI is attributed to the presence of aromatic and heterocyclic rings found in the polymer chain, providing rigidity and resonance stabilization through extended conjugations. The crystallinity and solubility properties of the polymer are found in Table II [19].

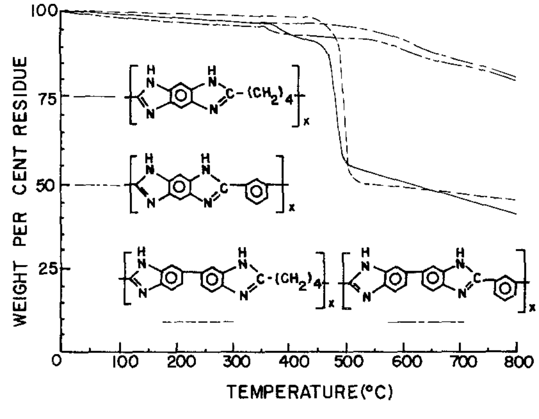

Figure 5 TGA plot for polybenzimidazoles under nitrogen (from Frazer [19]).

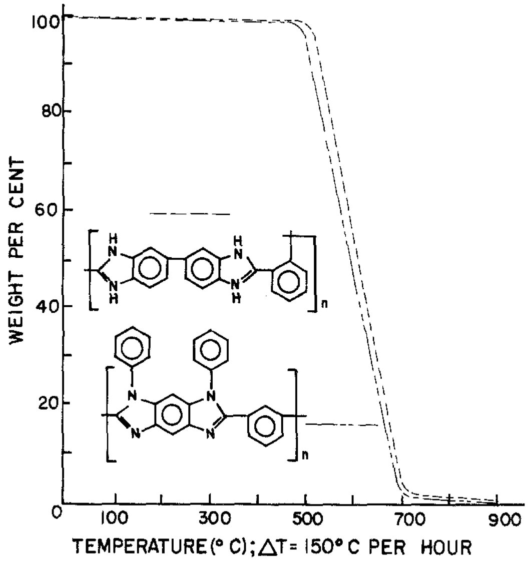

Figure 6 TGA curves of polybenzimidazoles in air (from Frazer [19]).

The weight losses upon heating in nitrogen and air as determined by TGA analyses are summarized in Figs. 5 and 6 respectively [19]. It is evident that specific PBI compositions are stable in inert environments to extremely high temperatures of approximately 800° C with minimal decomposition. However, in an oxidizing environment the polymer begins to decompose at approximately 500° C, and total disintegration occurs at 700° C.

Chatfield and Einhorn [21] also have recently investigated the thermal decomposition of PBIs under inert environments. They have attributed the decomposition of PBI at temperatures up to 570° C to the selective loss of ammonia and methane. Ammonia initiates from heterocyclic rings and methane orginates from the initial decomposition of aromatic rings. The detection of hydrogen, methane, propene and benzene between 570° C and 700° C was attributed to further decomposition of the aromatic rings. The detection of HCN, benzene and propene was interpreted to indicate that sufficient temperatures had been reached to cleave the polymer chain. The authors indicate that the cleavage sites are between the aromatic rings and/or at the imide rings. At temperatures above 700° C the authors observed complete polymer pyrolysis.

TABLE II Properties of polybenzimidazoles from Frazer [19]

Polymer	Reactants		Properties			
	Tetraamine	Acid	Crystallinity*	Solubility (wt %)		
				Formic acid	Dimethylsulphoxide	N,N-dimethylacetamide
5	3,3′-diaminobenzidine	Terephthalic	+	2 to 3	0.5 to 1	Insoluble
6	3,3′-diaminobenzidine	Isophthalic	0	5 to 6	> 20	Partially insoluble
10	3,3′-diaminobenzidine	Biphenyl-4,4′-dicarboxylic	+	Partially soluble	Insoluble	Insoluble
11	3,3′-diaminobenzidine	Biphenyl-2,2′-dicarboxylic	0	20	> 20	> 20
7	3,3′-diaminobenzidine	Pyridine-3,5-dicarboxylic	+	10 to 15	> 20	Partially soluble
8	3,3′-diaminobenzidine	Furan-2,5-dicarboxylic	+	3 to 4	> 20	> 20
13	1,2,4,5-tetraaminobenzene	Terephthalic	+	2 to 3	Insoluble	Insoluble
14	1,2,4,5-tetraaminobenzene	Isophthalic	+	5 to 6	Insoluble	Insoluble
12	1,2,4,5-tetraaminobenzene	Adipic	+	20	Partially insoluble	Insoluble

*Crystallinity: +, detected; 0, undetected.

TABLE III Scratch resistance and lubricity of PBI sprayed from a DMAC solution onto glass at various temperatures

Glass temperature (° C)	Number of revolutions	Dry tests*		Wet tests*	
		$\bar{\mu}_{max}$	SR (kg)	$\bar{\mu}_{max}$	SR (kg)
500	1	0.73	3	0.69	3
	3	0.66	3	0.70	3
400	1	0.70	3	0.69	3
	3	0.67	3	0.71	3
300	1	0.65	3	0.67	3
	3	0.55	3	0.68	3
200	1	0.70	3	0.63	3
	3	0.70	3	0.66	3

*$\bar{\mu}_{max}$ = average maximum kinetic coefficient of friction measured at the scratch resistance load; SR = scratch resistance load, the minimum load at which frictive damage was produced during sliding contact.

The apparent discrepancy for temperatures above 700° C between Chatfield and Einhorn's data [21] and the data published in Frazer [19], as shown in Fig. 5, is unimportant in the context of the intended use of these polymers as glass coating materials. High-temperature glass coatings would be applied at approximately 550° C, which is well below the point where the major deviations in the data occur.

Chatfield and Einhorn [21] have measured significant amounts of nitrogen during thermal oxidative decomposition of PBI between 25° and 900° C in an air environment. The detection of nitrogen indicates that the imide rings are being oxidized. Further oxidation processes could not be specified due to the oxidation of the decomposition reaction products. However, it was postulated that oxygen probably attacked the carbon links in the imide chain as well as the benzene ring at these higher temperatures.

3. Applicability of high-temperature polymers as glass coating agents

Uncoated 350 ml capacity bottles were heated for 15 min in an electric muffle furnace maintained at 580° C. Each bottle was individually removed and placed on a turntable rotating at 1 rev sec^{-1}. When the bottles had cooled to temperatures of either 200, 300, 400 or 500° C, they were subjected to a finely atomized spray of a 33 wt % solution of PBI in dimethylacetamide (DMAC). Each bottle was sprayed for either 1 or 3 revolutions (1 or 3 sec) and then allowed to cool at room temperature. Duplicate bottles were coated for each combination of glass temperature and coating-spray exposure time. The protective properties of the deposited polymer coatings on each pair of bottles were determined under dry and wet surface conditions by use of the crossed member technique [5]. The test load was increased from 3 to 7 kg and then in 7 kg increments to 56 kg, or until frictive damage to the glass was detected in the sliding contact area.

The scratch resistance of the polymer coatings was defined as the minimum load at which frictive damage was created during sliding contact. The lubricity was measured in terms of the average maximum coefficient of kinetic friction measured at the scratch resistance load. The scratch resistance and lubricity results are summarized in Table III.

The dry and wet scratch-resistances of the coatings were less than 3 kg for all combinations of glass temperatures and coating duration. The lubricities for all tests ranged from 0.63 to 0.71. The appearance of all coated ware was brownish in colour. The deposited material had a texture of loosely adhered granular powder.

The scratch-resistance and lubricity data and the appearance of the resultant glass surface indicate that PBI is not feasible as a glass coating material when applied at elevated glass temperatures under the experimental conditions studied. The data in Figs. 3 and 4 indicate that PBI is thermally stable for the glass temperatures studied. However, that data is applicable to PBI in bulk form. It is conceivable that thin films of PBI may exhibit entirely different thermal behaviour, contributed to the unsuccessful application of protective organic coatings. It is also possible that the manner in which the PBI solution was applied to the glass surfaces in this study contribute to the failure of PBI to produce a continuous, lubricous, well-adhered organic coating. The application technique used in this study replicated the manner in which such coatings would be applied under commercial conditions employing current application methods.

4. Conclusions

Advances in polymer science have resulted in polymers which can endure temperatures up to 900° C in an inert environment with a loss of only 15% of the total polymer weight. However, in an oxygen-containing environment the polymers studied in this report begin to decompose at 500° C, and are substantially decomposed at 700° C.

Based on the results of our laboratory trials, current high-temperature resistant polymers are not feasible as protective coatings for glass surfaces, when applied to glass surfaces under the conditions studied. Significant advances in polymer technology will be necessary before polymeric materials will find utility as coatings applied to hot glass surfaces. Specifically, the thermal stability of the polymers must be increased, the visual appearance of the deposited coatings must be improved, and the adhesion of the polymer to glass surfaces must be increased. Alternatively, radical changes in the method of applying protective coatings to glass surfaces from these polymers must be instituted.

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