

Polyimides—A Review

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NO uptodate review appears to be available in literature on polyimides. Among many known aromatic heterocyclics, imide derivatives are characterized by high melting points and stability towards drastic treatments with acids, bases and oxidizing agents¹⁻⁴. A polymer possessing a recurring cyclic imide unit is also expected to exhibit high heat stability. It is possible to build up polyimides in which each of the atoms present in the molecule is part of aromatic or heterocyclic rings or at least stabilized by resonance. As this type of structure affords high thermal stability, extensive studies have been made to develop these polymers for commercial exploitation.

Polymers based on recurring imide nuclei are of recent origin. Though intensive work in this field has been in progress for the past two to three decades, the majority of the available data on the developments in this field are far from complete⁵⁻⁸. Particularly, the vast amount of work conducted by Russian workers, subsequent to Bogert and Renshaw's⁹ first paper, has not received due attention and hence this review. Some of the salient points like mechanism of formation and dependence of properties on molecular structure have yet to be completely understood. In view of the vastness of the literature on imide polymers, attention would be confined to specific areas in which substantial advances have been made.

Preparation of Imide Polymers

Generally, polyimides are synthesized in two stages. First a diamine (I) is reacted with a dianhydride (II) at relatively low temperatures to obtain a soluble polyamic acid (III). This is then cast into a film, heated to 300°C to eliminate water and cyclized into a polyimide (IV) (Chart 1). The latter process, imidation, is carried out mostly by heating or sometimes through the use of suitable catalysts and water acceptors to yield high molecular weight linear polyimides.

These polyimides can be broadly classified into two types: (i) an all-out aliphatic chain, and (ii) a structure containing aromatic and/or heterocyclic units along the chain.

Solution Polycondensation¹⁰⁻²⁷

This method is extensively used to prepare polyimides based on dianhydrides of tetracarboxylic acids of different classes and aromatic diamines^{10,12}. These are generally prepared by combining the reactants in a medium of a suitable solvent which is sufficiently active to propagate the reaction between these two reactants. If the ratio of the reactants becomes nearly equimolar, there is a sharp increase in the viscosity of the solution. In all solution polycondensations, the temperature is maintained in the range -20 to +70°C. If the temperature is above 70°C, the molecular weight of the polyamic

acid decreases. Almost in all cases, 15-20°C is the optimum reaction temperature at which a high molecular weight polyamic acid is obtained. For example, polycondensation^{22,23} of isophthaloyl chloride and/or terephthaloyldichloride with 4,4'-dihydroxy-3,3'-diaminodiphenylsulphone in *N*-methyl-2-pyrrolidone solution at the temperature of liquid nitrogen gave polyamic acid, which on further heating at 330-50°C in vacuum gave a high melting polyimide. This method gave polymers of molecular weight ranging from 25,000 to 2,66,000.

Zakoshchikov *et al.*¹⁵ reported that all attempts to condense *p*-diaminodiphenylsulphone and dianhydrides in the solvent dimethylsulphoxide failed to yield a polymer, whereas sulphone ether diamine (SED) gave a high melting polyimide with dianhydrides. Following this success, Zakoshchikov *et al.*^{15,16} and other workers^{26,27} synthesized several new polyimides using various solvents.

Recently, attempts have been made to modify aromatic polyimide chains by introducing different links, such as amide and ester links into the main chain. Thus, polyester imides²⁸⁻³⁶ and polyamide imides³⁶⁻⁴⁷ were synthesized using appropriate solvents.

Melt Polycondensation

Edwards and Robinson⁴⁸ were the first to report the preparation of aliphatic polyimides by melting a diamine with tetracarboxylic acid. In general, this method consists in heating equimolar amounts of the reactants in nitrogen atmosphere and when the melt has changed to a more or less solid mass, subjecting the reactants to high vacuum at the reaction temperature. Nikolayev and Zhelobaeva²⁴ synthesized the copolymer β -hydroxyethylphthalimidemethacrylate, in the presence of various catalysts like azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), cumene peroxide, *t*-butylperoxide and cumenhydroperoxide.

X-ray analysis showed that the amorphous product obtained had a structure identical with that of the product obtained by the solution method in the solvent dichloromethane using peroxide initiators²⁴. This method did not find much use in the preparation of imide polymers, since it requires the use of high temperatures which are not conducive to the formation of high molecular weight polyamic acid.

Mechanism of Formation

Studies on the mechanism of formation of imide polymers were made by several workers^{13,49-51}. However, more detailed investigations are necessary to understand the influence of heat, vacuum and reaction components on the mechanism of polymer formation.

Leuchteux and Bondert⁵⁰, who first investigated the mechanism of formation of polyimides,

opined that the synthesis of polyamic acid through bimolecular acylation of amines involves nucleophilic attack on the amino group followed by the opening up of the anhydride ring and the formation of the polymer. The mechanism of aminolysis of carboxylic acid anhydrides by monofunctional amines was studied by UV spectroscopy.⁵⁰

Bower and Frost⁵¹ studied the effect of different factors on the mechanism of formation of polyamic acid. At low concentration of the dianhydride, the viscosity of the polymer was very low and did not change even on keeping at constant temperature for a longer time. But increase in the concentration of dianhydride increased the viscosity up to a critical level beyond which it decreased; the maximum viscosity was noted in all cases when the dianhydride ratio was slightly higher than equimolar ratio. The formation of a polyamic acid taking the reactants in equimolar ratio is shown in Chart 1.

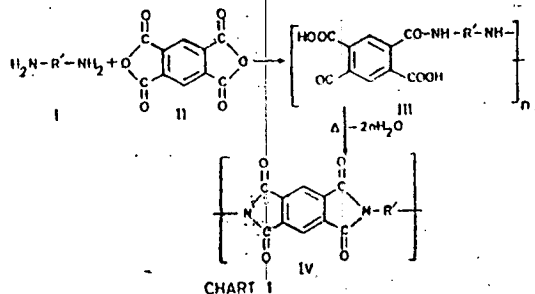


CHART 1

Wrasidlo *et al.*⁵² studied the mechanism and kinetics of the reaction between pyromellitic dianhydride and *m*-phenylenediamine by IR spectroscopy. It was found that the initial reaction occurred in the temperature range -20° to $+70^{\circ}\text{C}$ by the nucleophilic attack of the amino group to give the polyamic acid.

Equilibrium in the reaction system was attained when the concentration of the dianhydride had reached 78 mole %. The remaining free amine reacted to form a 'nylon' type salt through the available carboxylic acid groups (Chart 2).

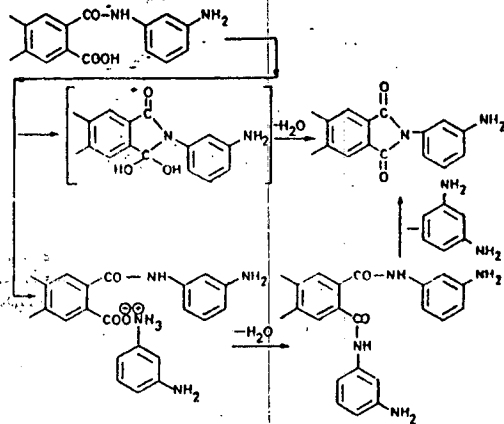


CHART 2

If the reactants were present in equimolar proportions, the reaction between pyromellitic dianhydride and the diamine was more rapid. As the concentrations of the anhydride and amino group decreased, the reaction rate tended to zero rate. In the absence of all other reactions, the polyamic acid would approach a certain limiting value, determined by the ratio of the initial components. However, as the rate of the main reaction decreased, side reactions assumed a major role, forming isoimides⁵³. The various steps involved are shown in Chart 3.

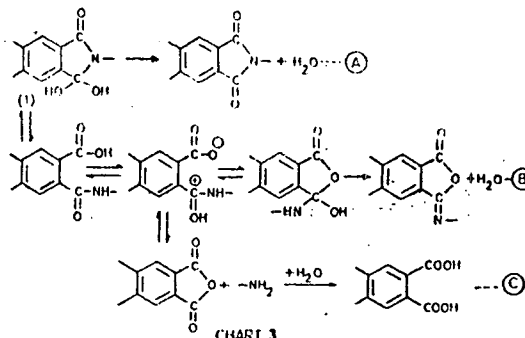


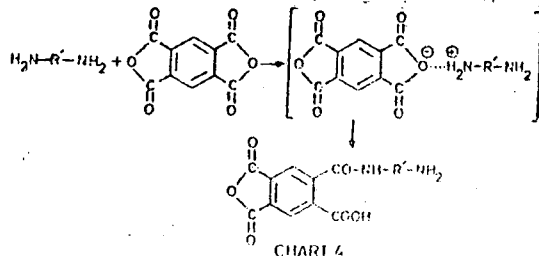
CHART 3

According to Chart 3, structure (I) is intermediate in the main imidization reaction (A), which at room temperature is slow and irreversible and becomes the main reaction after a long interval. The other process, a second irreversible reaction (isoimide formation), which takes place in the system is represented by Eq. (B). Structure (2) evolves water, isoimide and an amino group with the formation of the anhydride, which in the presence of water forms a dicarboxylic acid according to reaction (C).

The process of conversion of polyamic acid to polyimides (second stage of the synthesis) is the imidization reaction (cyclodehydration) and involves intramolecular evolution of water from the polyamic acid with the formation of a cyclic polyimide. The imidization reaction may be conducted in two ways—thermal^{11,12,14} and chemical^{12,13,62}.

The mechanism of formation of the polyamic acid by the reaction between pyromellitic dianhydride and tetramethyl *p*-phenylenediamine was studied by EPR⁶¹. Since pyromellitic dianhydride is an electron acceptor, and aromatic diamines has a low ionization potential, complexes may be formed with charge transfer between the reacting compounds. A typical indication of the complex formation was the intense coloration which appeared when pyromellitic dianhydride was added to the diamine solution. However, the colour rapidly disappeared, since the complex formation was accompanied by rapid proton transfer from the amine to the anhydride group (Chart 4), indicative of the formation of amide bond between the dianhydride and the diamine, as expected from the reactions depicted in Chart 1.

Recently, Gordina *et al.*⁶³ and other workers⁶⁴⁻⁶⁶ confirmed the formation of charge transfer complexes of some aromatic polyimides based on electron



spectroscopy. It may be inferred from the above that the first intermediate in the formation of polyamic acid is an amide.

Effect of Structure on Polymer Properties

To prepare high molecular weight imide polymers with the desired properties in respect of solubility, thermal stability, toughness, retention of tensile strength at higher temperature, etc., different modifications in the skeleton structure of polyimides were made with a view to studying the relationship between the structure and the properties of the polymer. The above properties of imide polymers seem to depend primarily on the rigidity of the polymer chain/backbone. The fundamental skeletal structure (Fig. 1) of imide polymers offers wide scope for effecting several modifications.

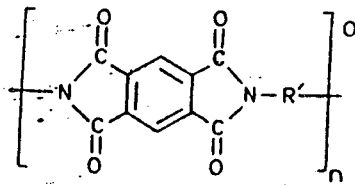


Fig. 1

$R' = (CH_2)_n$, where $n = 6, 7, 8, 9, 10$, etc., diphenylmethane, isopropylidiphenylene sulphide, oxide, sulphoxide, etc.

Considering the different types of modifications of imide polymers that have been achieved so far, they could be conveniently classified as follows:

- (1) The diamine component can either be diaminobenzene or diaminodiphenylmethane or even an ether or sulphone group containing diaminobenzene.
- (2) The tetramine component can be tetraminobenzene, tetraminodiphenyl methane (TADM), or even an ether or sulphone group containing tetraminobenzidine, where these groups are inserted in between the phenyl groups of the tetramine.
- (3) The acid dianhydride component can be varied over a wide range: aliphatic, aromatic and heterocyclics.

Based on the above possibilities, several novel polyimides have been prepared and their properties evaluated to establish relationship between the properties and structures of the polymers. Polyimides derived from different diamines and tetramines have been evaluated extensively. The superior thermal stabilities of DAB polymers have made them commercially acceptable.

As could be expected, the introduction of recurring aromatic units in the main chain of the polyimides

increases their rigidity at the cost of solubility. However, imide polymers from the condensed aromatic units like naphthalene and benzophenone also give linear high molecular weight products. The nature of substitution had a pronounced effect on the ultimate physical properties of the polymer. The polyimides from aromatic diamines decompose between 400° and 510°C . For those which are connected only with the benzene nucleus, the *para* position gave higher decomposition temperature and better thermal stability than *meta* substitution. The order of thermal stabilities is shown in Fig. 2⁵⁷.

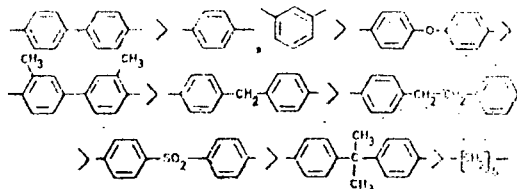


Fig. 2

The order of solubilities is the reverse of this. The introduction of heterocyclics like pyridine rings and *o*-, *m*- and *p*-phenylenedioxy linkages^{58,59} into the diamine component resulted in fairly high molecular weight polyimides. This substitution improved the solubility of the imide in a wide range of solvents.

The introduction of simple chains like $-CH_2$ groups between the two benzene rings in the diamine can improve the solubility of polyimides markedly without causing notable reduction in the molecular weight. A number of imide polymers have been prepared based on diaminodiphenylmethane (DADPM)^{12,13,60-61}.

When polyamide³⁶⁻⁴⁷ or polyester²⁸⁻³⁵ units are introduced in the main chain of the imide polymer, the mixed polymers so formed are of intermediate molecular weights and possess the usual disadvantages of polyamides and polyesters.

It may be concluded that imide polymers derived from aliphatic units are less rigid than those having aromatic units. By a combination of rigid aromatic, heterocyclic or methylene groups, imide polymers with the desired properties can perhaps be tailor-made. In many cases, the effort has centred around the modification of the anhydride portion of the molecule through the introduction of a flexible segment, such as carbonyl, sulphone, phenylene, etc. The location of such a flexibilizing segment relative to the imide ring is important in determining the ultimate performance of the polymer system. The various groups can be arranged in the decreasing order of thermostabilities shown in Fig. 3.

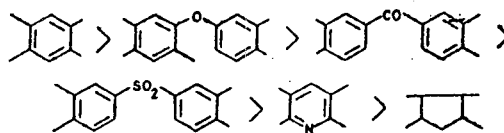


Fig. 3

Reaction Conditions

The stoichiometry and reaction conditions play an important role in the synthesis of imide polymers.

(1) Frost *et al.*⁵ and Brown *et al.*⁶ studied the effect of the ratio of the starting reactants on the variation in the viscosity of the solutions of polyamic acids during their formation and on prolonged standing in the case of pyromellitic dianhydride and 4,4'-methyl-diamine. They concluded that the optimum dianhydride-diamine ratio is 1:0.15:1:0.20 for obtaining high molecular weight polyamic acid. If the reagents are not in equimolar ratio or if the dianhydride is in large excess, the viscosity and hence the molecular weight of the polyamic acid is low.

(2) The selection of the solvent also plays an important role in the reaction. It is observed that dimethylsulphoxide, which is the most highly viscous solvent, yields a polyamic acid with a higher molecular weight than the *N,N*-dimethylformamide and *N,N*-dimethylacetamide.^{5,6} Kobelnikov *et al.*⁶⁶ prepared polyimides based on 2,3,5,6-diphenyltetracarboxylic acid dianhydride and benzidine or 4,4'-diaminodiphenylmethane. When this reaction was conducted in dimethylformamide at 30-100°C, polyamic acids of very low molecular weights were obtained ($\eta_{sp}/c < 0.074$), which may be due to the poor stability of the complex of the dianhydride with the solvent. High molecular weight polymers could be obtained in dimethylsulphoxide, a more highly polar solvent than dimethyl formamide and dimethylacetamide; these results are in agreement with those of Frost *et al.*⁵ The above-mentioned polar solvents are used both alone and in combination with benzene, benzonitrile, dioxane, xylene, toluene, cyclohexane, etc.

(3) The reaction for the preparation of polyamic acid is generally conducted between -20°C and +70°C. If the temperature is above 70°C, the molecular weight of the polyamic acid decreases. Almost in all cases, 15-20°C is the optimum reaction temperature at which a high molecular weight polyamic acid is obtained.

(4) It is suggested that dianhydride should be added slowly and steadily to the diamine in order to get high molecular weight polymers. If, for instance, the addition sequence of the reagents is changed, say, slowly adding the solution of diamine to the dianhydride, or if the reagents are mixed together in equimolar proportions, the viscosity of the solution will be very low.

(5) Zikoshchikov *et al.*^{15,16} studied the specific viscosities of the polyamic acids and their dependence on the concentrations of the reagents in the solvent. There is an optimum concentration at which the resulting high polymer has maximum viscosity. Hence, it is suggested that the reaction be run in a particular amount of the solvent.

(6) It is a common observation that the degree of purity of monomers to a large extent determines the molecular weight and the molecular weight distribution of the products. Wallach⁶⁷ studied 13 samples of polyamic acids obtained by homogeneous and heterogeneous polycondensation of different samples of the dianhydride and the diamine in a solvent

(*N,N*-dimethylacetamide) of different degrees of purity. The maximum number of average molecular weight ($M_n = 55,000$) and the narrowest molecular weight distribution ($M_w/M_n = 2.39$) were obtained in the case of heterogeneous polycondensation of reagents of particularly high purity. On the contrary, a wide molecular weight range ($M_w/M_n > 3$) is obtained, if the solvent has not been purified and when a solution of the diamine is added to the solution of the dianhydride.

(7) Polyamic acids are generally converted to polyimides in two ways: thermal and chemical. The thermal method^{68,69} usually consists in heating the dried polyamic acid, the rise in temperature being gradual or stepwise. Imidization at temperatures above 200°C is conducted in vacuum or in an inert medium. The chemical method^{70,71} of imidization consists in treating the polyamic acid powder or film with dehydrating agents. Such agents are acetic anhydride or anhydrides of other lower fatty acids, such as propionic, valeric, etc. Tertiary amines are generally employed as catalysts during chemical imidization.

Properties

The imide polymers are generally coloured materials ranging from light yellow to dark brown. A few of them exhibit sharp melting point. Generally, when heated to higher temperature (750°C), they become insoluble in all solvents, showing that crosslinking precedes melting of the polymer.

Solubility—The ability of the imide polymers to form stable, concentrated solutions is of great practical importance in the fabrication of these materials. These polymers are generally soluble in unconventional solvents, such as conc. sulphuric acid and fuming nitric acid^{66,68}.

Vinogradova *et al.*²⁰ prepared several polyimides soluble in the solvents derived from diamines, such as bis-4-aminophenylphthalide and bis-(4-aminophenyl)-phthalimide. More symmetrically oriented diamines resulted in greater crystallinity and decreased solubility of the polymer. For instance, the imide polymer synthesized from *m*-phenylenediamine, *m*-xylenediamine, etc., (which is amorphous) is more soluble in a wide range of solvents than the *para*-substituted polymer. Polyimides derived from aliphatic diamines are generally soluble in a wide range of solvents.

In an attempt to increase the solubility of imide polymers, Russian workers^{39,68,69,70} studied mixed polyimides derived from a mixture of isomers of aromatic diamines and aliphatic diamines with various dianhydrides. Christian *et al.*⁷¹ synthesized polyimides by condensing aromatic diamines with a tetracarboxylic acid mixture consisting of 10-90% bicyclo-(2,2,2)-oct-7-enetetracarboxylic dianhydride and *p*-diaminodiphenylmethane in cresol at 140-170°C. These imides are soluble in most of the solvents.

Kurita *et al.*^{39,68} and Koton and coworkers^{69,70} prepared soluble polyimides from diamines having pyridine rings (*o*-, *m*- and *p*-phenylenedioxy linkages) by condensing them with benzophenonetetracarboxylic acid dianhydride.

Recently, attempts have been made to modify aromatic polyimide chains by introducing different links, mainly amide and ester links, into the main chain; the products have improved solubility properties.^{28,36,37,72,73}

Polyimides having an ether linkage either between the two imide groups or between the phenyl groups of the diamine moiety showed high solubility properties. The imide polymer derived from sulphone ether diamine and benzophenonetetracarboxylic acid dianhydride is partially soluble in DMF, conc. sulphuric acid and fuming nitric acid. Since the introduction of oxygen atom between the imide units increases the solubility of the polymers, attempts were made to study the solubility of polyimides containing aryl sulphone linkages either between the imide nuclei or between the phenyl group of the diamine moiety.^{26,37,71} Such polymers are partially soluble in DMSO, DMF and DMAc.

Thermal stability High temperature polymers are expected to maintain their mechanical properties like rigidity, tensile strength and impact strength and, therefore, it is essential that they do not melt or drastically undergo decomposition in that temperature range. Hence, the relationship between the thermal stability of imide polymers and their structure has been studied in detail. The method principally consists in maintaining the polymer in air or nitrogen atmosphere for a specified time and estimating the percentage loss in weight. Generally, the loss in weight of the polymer in nitrogen atmosphere was comparatively less than in air. Thermogravimetric investigation of these imide polymers showed that the presence and nature of a substituent in the side chain of the macromolecule affect strongly the thermal stability of the polymer. Thus, aliphatic imides completely decompose below 350°C, while the aromatic ones decompose at 500-650°C and, in some cases, even at 1000°C, the decomposition is only about 35%. The high thermal stability of these polyimides is considered to be due to the aromatic nature of the polymer.

Aromatic polyimides have been studied extensively, with particular emphasis on their thermal behavior.^{75,76,77,78} Polyimides derived from diamines and pyromellitic dianhydride in which the diamine component was *p*-phenylene, *m*-phenylene, benzidine⁷⁵, bis-(4-aminophenyl) ether⁶⁸ and 4,4'-diaminophenyl sulphone⁷⁹ exhibited a sharp increase in the rate of weight loss above 500°C followed by levelling off after 35% of the initial weight had been lost. Beyond this, the residues showed almost no weight loss up to 1000°C. By contrast, on heating in air at these temperatures, these particular aromatic polyimides are slowly but completely oxidized.

The thermal stability of aromatic polyimides has also been studied extensively by differential thermal analysis, both in air and in an inert atmosphere. Nishizaki and Fukami⁸⁷ found that in nitrogen atmosphere, all aromatic polyimides show clear endothermic reactions; these were believed to be due to decomposition. In those cases where the benzene rings of the diamine component were connected with functional groups, such as sulphone and isopropylidene, the decomposition temperature

was as low as 400-420°C. In those cases where the rings were connected with an ether group, a methylene group or an ethylene group, decomposition occurred above 480°C. For polymers containing side chain methyl groups, such as polyimides derived from 2,2-bis(4-aminophenyl)propane, decomposition occurred at 330°C. If the benzene rings in the diamine component were separated by functional groups, the nature of the functional group determined the stability. The polyimide containing a sulphone group as the connecting group in the diamine decomposed at 320°C, whereas those containing an ether as the connecting group were stable up to 400°C. The order of decrease in thermal stability is given in Fig. 4.

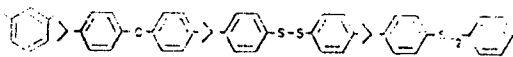


Fig. 4

Copolyimides, such as amide-imides, ester-imides and hydrozide-imides are reported to be markedly inferior to the homopolyimides.^{60,61} The isothermal weight loss at 300°C for the polyamide-imide from diaminobenzanilide and pyromellitic dianhydride⁸² was almost twice that for the polyimide from 4,4'-diaminodiphenylether.⁶⁸

Spectral Studies

The IR spectra of imide polymers agree well with those of model compounds and show characteristic absorption bands for the imide grouping.⁷⁵ For example, the IR spectrum of the polyimide derived from 4,4'-diaminodiphenylether and 4,4'-diaminodiphenylsulphide with pyromellitic dianhydride showed characteristic absorption imide bands at 5.63 and 13.8 μ . The complete conversion of polyamic acid was identified by the disappearance of the characteristic -NH band at 3.08 μ and the appearance of the characteristic imide bands at 5.63 and 13.8 μ .

Corlino *et al.*⁶³ and other workers⁶⁴⁻⁶⁶ used electronic spectroscopy to demonstrate the formation of charge transfer complexes between electron-donating polyimides (Fig. 5D, E) and low molecular weight electron acceptors, like *p*-chloranil (F), 7,7',8,8'-tetracyanoquinodimethane, etc.

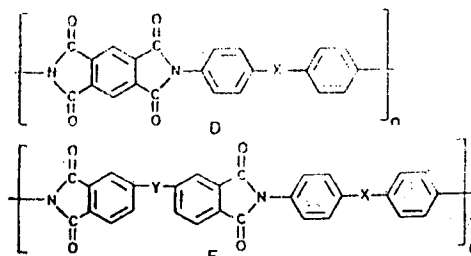


Fig. 5

where X = NH, -NMe, NPh, S, O, CH₂
Y = SO₂, O, Co

The positions of the absorption maxima of the complexes of polymers with (F), and those of the

complexes of the corresponding diphenyl compounds with (F) were linearly related to the ionization of the diphenyls. The slopes in both the graphs were the same, indicating that the introduction of the donors into the polymeric chain lowered their ionization potential by ≈ 0.3 eV. The colour of the polymeric complexes was attributed to the charge transfer interaction between the electron accepting imide chain fragments and the electron donating diphenyl fragments.

Fabrication

The commercial methods of preparation of imide polymers and their fabrication are mostly covered by patents⁸³⁻⁸⁶. The processing of polyimides is more complicated than that of standard laminating and adhesive systems like phenolics, polyesters, etc. Since the high molecular weight imide polymers are highly insoluble and infusible, the development of a convenient method for fabricating polyimide material was considered a priority requirement. Narmco Plastic Division of Whittaker Corporation^{83,85,86} and E.I. du Pont de Nemours and Co. Inc.^{87,88}, developed methods for synthesizing polyimide prepolymers having melting points and solubility characteristics suitable for the impregnation of glass cloth and filament type reinforcements. The process for the preparation of the prepolymer consists essentially in interrupting the melt polycondensation reaction at a stage when the product is soluble in moderate solvents like DMF, pyridine, etc. At this stage, the prepolymers are of high molecular weight and are suitable for the conventional laminating and adhesive bonding processes.

Polyimide prepolymers can be fabricated either by hot melt or solution coating techniques⁸⁴. The hot melt technique consists in drawing the glass cloth under a blade heated to a temperature slightly above the prepolymer melt temperature. By controlling the rate of feed of cloth, a predetermined resin loading can be obtained and it is possible to have high resin content in reinforcement by this method. As the prepolymer possesses limited solubility in relatively strong solvents, it is not possible to obtain solutions with high solid contents of this polymer. However, using pyridine as the solvent, useful preimpregnated laminates can be made from these prepolymers⁸³.

Adhesives and Varnishes

Polyimide adhesives exhibited the excellent thermal stability of the parent polymer, but the adhesive bonds prepared had shear strengths lower than those of comparable commercial epoxy-phenolics⁸⁹. However, the polyimide adhesive bonds could be retained at higher temperatures over a long period. In addition, the imide polymer adhesive exhibited outstanding resistance to water, salt spray, jet fuel hydraulic oil⁸⁸. Various varnishes⁹⁰ showed satisfactory adhesion to almost all metals. For the utilization of polyimide varnishes to impregnate windings of electric machines, it is important for the varnish not only to have a high bonding power but also not to soften at elevated temperatures. This is particularly important in dc collector machines which

often breakdown due to the adherence of coal dust to the winding⁹¹.

Coatings

Of all the polymers, the polyimides are the ones which have been most thoroughly studied as coatings, both as wire enamels and as coatings for papers. Polyimides have special features to resist moisture and insensitivity to solvents, greases, lubricants, exotic fluids and acids. A general comparison of the initial properties of wire coated with polyimide against those of other commercial enamels clearly showed superiority of the polyimides⁹².

Glass-Reinforced Laminates

Fibre glass laminates made with polyimide binders exhibited high temperature resistance. These have high flexural strength superior to that of copolyamide imides. In filament wound composite structures, the polyimides exhibited excellent thermal stability and retention of properties at elevated testing temperatures.

Fibre Formulations

Polyimide fibres with excellent mechanical properties, i.e. high strength, have been prepared; they exhibit good long-term stability under air ageing conditions at temperatures above 300°C. Rudakov *et al.*⁹² studied the fibres of polypyromellitimide. The use of polyimides results in fibres which have even better parameters. In its intermediate (polyamic acid) form, this polymer can be readily processed into fibres by the conventional 'dry' or 'wet' methods. It is claimed that using the 'dry' method, polyimide yarns of acceptable properties on commercial type of package can be produced with efficiencies of the order of 80-100%.

Applications

The unique combination of properties which polyimides possess makes them specially suitable for a range of important applications in the aerospace, electrical and nuclear power and such other industries where materials of superior performance are needed. They can be safely used at continuous operating temperatures without any serious deterioration in properties. Although they are still in the development stage, they are now available in solid state film form and as adhesives and laminates. The main applications of imidepolymer reinforced laminate resins are in structural parts of high performance aircrafts where retention of mechanical properties on long-term exposure to heat is required. The applications include high temperature aircraft deicer-ducts, radomes, deflectors, wings, turbine blades, re-entry nose cones, leading edges and surfaces of aircrafts and missiles. In general, polyimides possess all the requisite properties for replacing metals as structural elements in aircraft, space research, and material research.

Summary

Recent advances in the field of imide polymer are reviewed, with particular reference to the work of Soviet scientists. The correlations established between the structures and properties of imide polymers are discussed.

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