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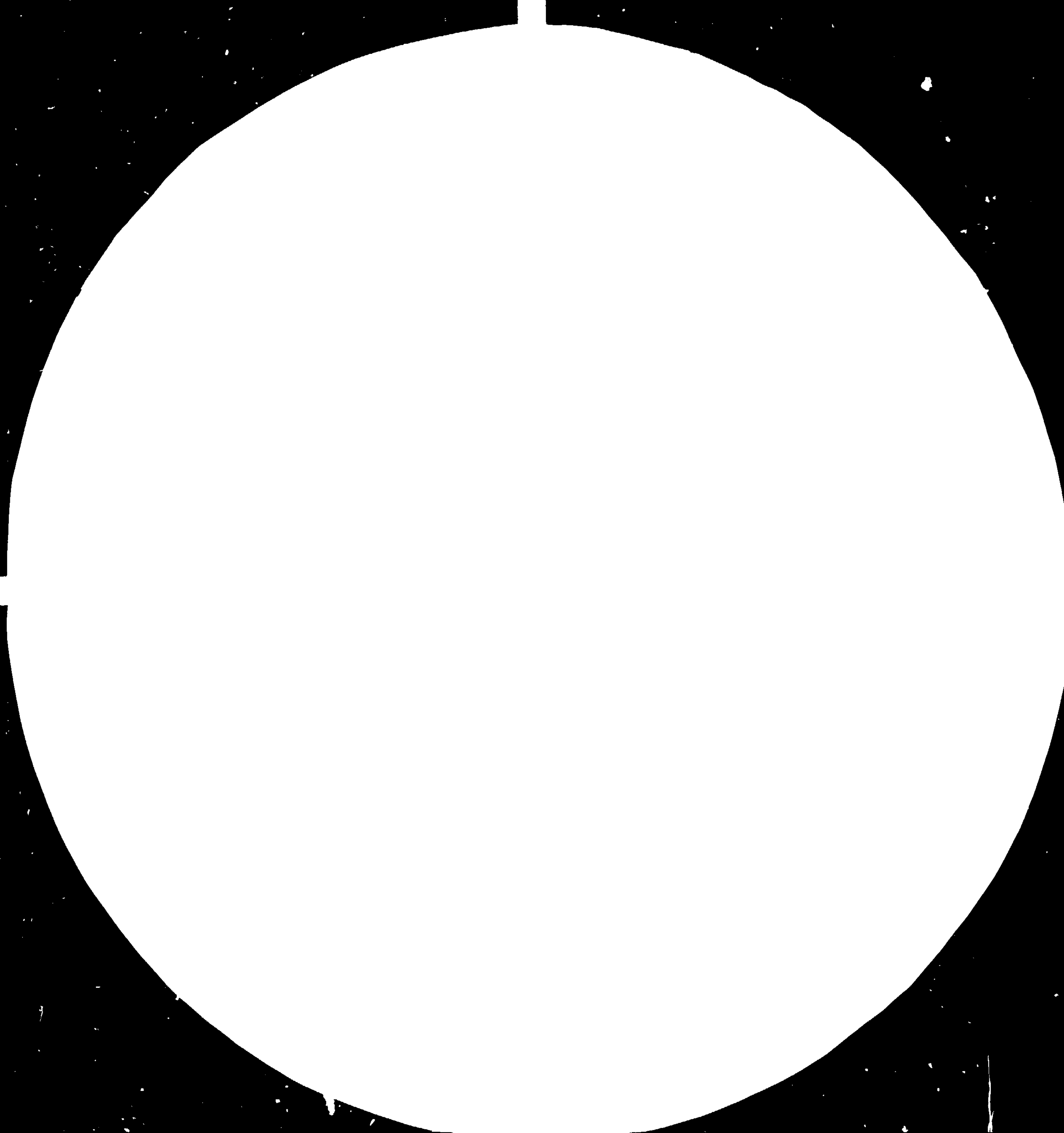

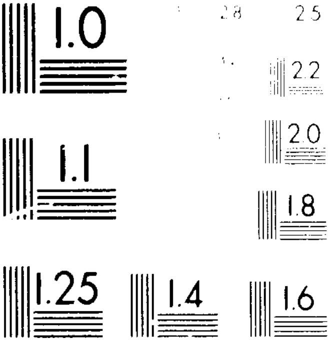

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14569

Consultant Report: Eli M. Pearce
Director, Polymer Research Institute
Polytechnic Institute of New York
333 Jay Street
Brooklyn, New York 11201

India.

DEVELOPMENT OF RESINS - UNIDO SUPPORTED
UNDP, DELHI, INDIA

Visited:

Dr. R. G. Kumble, Director, Dept. of Science and Technology
Government of India, Technology Bhavan
New Mehrauli Road

and the following institutions -

India Institute of Technology, New Delhi
SASMIRA, Bombay
Sardar Patel University, Vallagh, Vidyanagar
Vikram Sarabhai Space Center, Trivandrum

Dates: December 22, 1984 - January 5, 1985

I. INTRODUCTION

The program developed with Dr. R. G. Kumble evolved about the "Development of Resins" and in most cases for composite uses. Based on this, visits to three institutions plus SASMIRA were scheduled.

1. "Indian Institute of Technology, Delhi, which has the responsibility of development of specific polymide resins, would like to consult you on polymer structure and modification vs. flame retardance and brittleness related to bismaleimides;
2. Sardar Patel University, Vallabh Vidyanagar (near Bombay), which has the responsibility of development of furane resins, to consult on polymer structure and modification related to flame retardancy in phenolics;
3. Vikram Sarabhai Space Centre, Trivandrum, which has the responsibility of development of specific polyimide resins, ...to consult on polymer structure and modification in relation to brittleness in bisitaconimides.
4. SASMIRA, Bombay - to visit in regard to the development on the institution on a broader polymer plan base planned with possible UN involvement.

II. VISITS

Indian Institute of Technology, Center for Materials Science and Technology

This visit was with Prof. I. K. Varma, Head of the Center for Materials Science and Technology and Prof. D. S. Varma, Department of Textiles Technology and Dean. Discussions here revolved about addition polyimides from 3,3' diaminodiphenyl sulfone, curing behavior of bis(maleimidophenyl)methyl phosphine oxide the thermal behavior of bismaleimideamine/vinyl ester styrene blends, the synthesis and properties of vinyl ester resins and silane coupling agents.

Work on polyimide resins were to develop low cost resins with good processing characteristcs. The particular diamine diphenylsulfone used here was available at relatively low cost in India from the 3,3'-dinitrodiphenyl sulfone. Included in these studies was the curing behavior of phosphorus containing imide resins. Interest in all of these resins were as matrix resins for fiber reinforced composites. This is related to their thermal stability and resistance to hot/wet environments as well as reduced flammability. A major disadvantage of bismaleimides is their brittleness due to their high crosslink density and the aromatic nature of the bismalemides. By using the meta substituted aromatic diamine, flexibility was introduced into the system and a modest increase in elongation at break was obtained. We discussed the synthesis and curing of the systems. A very fine job has been done in the synthesis and development of a variety of these maleimides as well as studying their reactions by determination of exothermic transitions. Some of the more interesting species that have been evaluated are the phosphorus containing systems in which expected improvements in flammability reduction were obtained. I had the opportunity to also study the project report written by this group entitled "Newer Fibers and Composites." This carefully developed program shows significant possibilities for new resin systems and their use in composites. Much of this was based on previous work done by them at NASA-Ames Research Center but that group has now been disbanded and probably this program in India is one of the few in the world. Among the items that we discussed were further improvement in the elongation. We have been doing work with modified fluorine containing elastomers with some modest success in that direction. Some of this work has been published and the article describing this has been send to Dr. I. Varma. I recommend that approaches of this sort also be considered for improving the impact strength of these systems.

A clever idea was to consider curing these systems the bismaleimides, with vinyl ester resins. These vinyl ester resins are thermesetting resins produced by the addition reaction of the epoxy resin (diglycidyl ether of bisphenol A with methacrylic acid). This is a known commercial monomer and has found utility in the dental repair field as well as a number of other areas. Because the maleimdes are 1,2-disubstituted monomers they do not homopolymerize by radical reactions but readily will form copolymers with other monomer systems. This then was the purpose of the studies to prepare low temperature processable bismaleimide resin formulations by blending these vinyl ester resins containing 40% styrene as a reactive diluent. Cures were obtained and good thermal properties also were obtained when a low weight percent of the vinyl ester resin-styrene was used in the blend. My suggestion here was to also consider the use of monomers like vinylstyrylpyridine in the systems. The difficulties associated with the previous systems is that we are using two difunctional monomers so that the crosslink densities will remain extremely high. We could loosen the structure up by using a monomer like vinylstyrylpyridine. In addition. the polymerization will occur in a more controlled manner since the vinystyrylpyridine will form a donor-acceptor complex with the bismaleimide resin and as such will give a one to one alternating copolymer in those sections of the copolymer when the vinylstyrylpyridine is present. There is published work on the use of styrylpyridine polymers in other systems by the groups at the NASA-Ames Research Center and also in a series of my publications with Dr. Yan.

In regard to problems associated with the use of dimethyforamide, this possibly generating some monofunctional species which then will cut down the ability to obtain high molecular weight polymer in the presence of a monofunctional compound. I suggest considering the possibility of a solvent such as N-methylpyrrolidone. I do not know about its availabiity in India, however, it is becoming a much more important solvent because it is used in the production of aramide fibers both in the United States and in Europe. At least it would be worthwhile to use this solvent in a variety of experiments just to see if improvements in molecular weight are obtained and whether indeed problems thought to be associated with solvent impurities are really due to that. This solvent also has to be purified before use. However, once the impurities are removed they will not have the tendency to reform by hydrolysis as would be the case with dimethylformamide.

In regard to the silane coupling agents, I was asked to comment on possibilities for improving the yields on these coupling agents. The synthesis of 3-(trimethoxysilyl) propyl methacrylate is done by the reaction of allyl methacrylate with $HSiCl_3$ in the presence of chloroplatinic acid, The yield of the 3-(trichlorosilyl) propyl methacrylate was 60% or less. A number of synthetic steps have to be made in this preparation because of the non-availability of several of these materials in India. An approach that I would consider and put more emphasis on would be the preparation of (3-trimethoxysilyl) propanol and its subsequent reaction with methacryloyl choride going via this route and making the propanol first. I think overall this will give a higher yield. The syntheses may be difficult, however, it seems to me that this is the synththetic approach that should be emphasized. The approaches in which allyl methacrylate is made through trans esterifcation of MMA with allyl alcohol should show improved yields. The reported difficulty in regard to fractionation by vacuum distillation could be removed by using some chromatgraphic techniques rather than thermal techniques which might also cause some premature polymerization.

B. Sardar Patel University, Department of Chemistry, Vallabh, Vidyanagar

I was pleased to meet the faculty in this department, to have the opportunity to see the University, to be welcomed into the culture, and to obtain insights into the research program. As part of this effort, Prof. V. Patel will be visiting the Polytechnic during the course of this year to continue his studies on various parts of the programs that we discussed during my visit.

We discussed phenol furfural resins which were prepared in the presence of alkalinecatalysis. There were three types that varied in ratio 1/1, 1/0.85, and 1/1.15. These resins are soluble in many common solvents. The infrared still shows the presence of furfural and also indicates 2,4-substitution of the phenol. These resins were used with glass to form laminates. The percentage of glass was about 70% and it was an E-glass plain weave, 10 mil glass cloth. Curing conditions were usually using a curing agent which was 12% hexa with a curing temperature of about 135° for one half hour and 182° for an additional two hours. After this studies were done on mechanical, electrical, and chemical properties. We reviewed in detail their programs and I will not include all this information as part of this report. Some general comments, however, relate to their studies which in general I think were very commendable. One of the things that we have to be concerned with, however, is as we change the ratios of phenol and furfural even though we keep everything else constant, we are changing the extent of reaction or cure. A number of the studies they have done also compare the phenol furfural resins to commercial phenol formaldehyde resins and again the same questions arise are we dealing with the same extent of cure even though everything else was the same? This will have bearing later on in regard to Dr. Patel's program when he comes to the Polytechnic. Another issue in regard to all of this is the type of substitution that is occurring. In the systems one can get orthosubstitution and parasubstitution and one should understand how much of each of these are occurring. Now again these have not been studied for their resins nor for the resins that they are comparing them with. Another significant problem may be occurring in regard to the preparation of the cured samples. There is a serious question about whether these samples are void free. If they are not doing vacuum bag molding to remove residual amounts of trapped gases, there is a very good chance that they will have voids which will affect properties. In regard to controlling the situation, for example, when they are comparing the different resins, they always use 12% hexa. This should be done on a mole for mole basis for all of the resins involved here in order to obtain equivalency of reaction conditions. The rates of reaction should also be studied as should be a number of other studies related to the cure exotherms. This becomes apparent also in looking at the data of ordinary phenolic resins with cure times, for example of 1 minute, and the properties obtained. One can ask whether these are sufficient for cure really to have occurred throughout the sample in a uniform manner. Nevertheless, there are studies to date which show that these furane systems are quite interesting in a number of composite areas. These include wood flour based and carbon fiber reinforced systems. (See Appendix I for their research summary).

I have recommended that a number of studies be done which will involve extensive efforts using advanced thermal analytical techniques, Fourier Transform infrared techniques and NMR techniques. Among the things that we will be studying will be an exact definition of the cure. We have systems available for defining the cured reactions by infrared studies using difference spectra. We have developed these for other systems and believe that these will be applicable here. The ortho ortho versus ortho para substitution will be also studied by NMR. Blends with a variety of other polymers will also be of interest here. We presently are doing studies on phenol formaldehyde condensates blended with a variety of polymers. We also will be doing a variety of cure studies both isothermally and by dynamic thermoanalytical techniques using differential scanning calorimetry. If we have the opportunity we will also make some void free cured samples using vacuum bag molding. These studies will all be attempted while Prof. Patel is visiting with us.

C. Vikram Sarabhi Space Center Trivandrum

I was tremendously impressed by my visit to this center, not only by the quality and number of staff but also by the facilities available to carry out their research. My visit here discussed in detail their studies on the bismaleimides and bisitaconamides. Attached as Appendix II is a brief summary of my visit prepared kindly by Dr. K. V. C. Rao and his staff. This covers most of the points of discussion and number of suggestions that I made in this regard. As shown in this report, I also had the opportunity to discuss their polyurethane adhesives and epoxy curing systems and make some contributions to this program. My discussions with the director and his staff suggested the possibility for a number of opportunities for collaborative research and I am looking forward to some suggestions from them in this regard. I also had the opportunity of reviewing various sections of a textbook presently being prepared by the Director which will be very useful for the teaching of polymer chemistry to scientists in India. My review was forwarded upon my return to the director.

D. SASMIRA - Bombay

My visit was with Mr. Schroff and his staff and gave me the opportunity to visit this institution which is well known in the textile area and is being considered for further development as a polymer science research center. I had the opportunity to visit the facilities and also meet with a number of the staff. The facilities themselves have much of the standard equipment associated with a textile research center. These also include a whole variety of standarized test equipment They also have a pilot plant facility which can be used for spinning thermplastic fibers such as nylon and polyester. This little facility is a very impressive one and not usually found at too many places. Obviously they now have capabilities for making condensation polymers, polymerizing them and converting them into fiber. Previous background has given them experience in regard to weaving them into various kinds of textile. I was very impressed by their program in which they will attempt to teach the making of hand loom fabrics to Indian citizens throughout the country using synthetic fibers. At present this facility lacks the kind of equipment that one would use for more sophisticated polymer studies and characterization. This includes the state-of-the-art equipment and various analytical areas such as infrared, gel permeation chromatography, light scattering, nuclear magnetic resonance and so forth. They would also require the faculty skilled in these areas. I did not have the opportunity to meet any individual that would appear to be knowledgeable in regard to the basic polymer sciences and this might be another area where we will need resources. I believe that with the proper financial incentives that these are obtainable in India. India is fortunate in that they have some very fine technical people being produced at their universities that could help staff such an institution in its development as a central polymer institute. I look forward to its development with interest.

III. Summary

I regard the programs that I visited which were being developed for resins and composite systems as one which had a good degree of organization. They were an unusual group of people at the three centers, all having unique capabilities for the different aspects associated with these problems. I personally was pleased to have the opportunity to participate in some small way and I hope to move these projects forward. I look forward to the opportunity of working with each of these groups at some point in the future.

APPENDIX I

UNDP RESIN PROJECT

Sardar Patel University
(Dept. of Chem)
Vallabh Vidyanagar, 388 120.
INDIA

Prof. Pea

- Phenol-Furfural resins : alkali catalysed
  Three types : 1:1, 1:0.85 and 1: 1.15 >
- Soluble in Common solvents
- IR shows presence of furfural and indicates 2,4-substitution of phenol.
- Laminates - using E. glass plain weave 10 mil glass cloth

(a) Percentage of glass ~ 70 %

(b) Curing conditions :

Curing agent : 12 % Hexa
Curing temp. : 135°, 1/2 hr.
180 , 2 hr.

(c) Properties studies :

Mechanical, Electrical and Chemical resistance.

Liquid Phenol-Furfural resin

- Alkali catalysed reaction at 115 - 120°
  Molar ratio varied from 1:1 to 1:2

- Properties :
  Dark coloured thick liquid with cup flow decrease with increase in phenol to furfural ratio

- Resins cured under ambient conditions in presence of acid catalysts.

Acetone-Furfural Resin

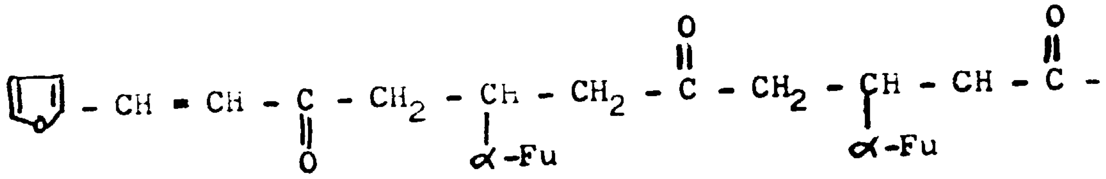
- Two modes of preparation using alkali as catalysts
  - (a) direct condensation Ac-F
  - (b) condensation of monofurfurilidine acetone PMFA

- Characteristics

  Yellow powders,

  melting range depends upon reaction condition,

- Possible structure



$$-CH=CH-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{\alpha\text{-Fu}}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{\alpha\text{-Fu}}{|}}{CH}-CH-\overset{\overset{O}{\|}}{C}-$$

- Curing study :

  Cured by PTS at 180°C

  Cured by Hexa at 200°C

  Proper curing not achieved

- Liquid acetone-furfural resin

  Prepared under basic (comparatively milder) conditions, cured by PTS, Hexa and $ZnCl_2$. proper curing conditionsto be established.

APPENDIX II

Visit of Prof. Eli M. Pearce to VSSC, Trivandrum during 31st Dec. '84 - 3rd Jan. '85

31-12-1984

Prof. Eli M. Pearce visited VSSC, Trivandrum and had discussions with Director, VSSC.

1-1-1985

Prof. Eli M. Pearce called on Shri M. R. Kurup, Director, PCM Group. The possibilities of collaborative efforts between VSSC and Polytechnic Institute of Brooklyn were discussed.

After a brief introduction by Dr. K. V. C. Rao and Dr. M. M. Singh Bisht, the work on polyimides was presented by the working team. During presentation extensive interaction took place. Some of the salient points discussed are given below:

(1) Purity of the starting material - Some of the starting materials like diamino-diphenyl methane are likely to contain impurities like isomers, trimer, tetramer etc. This can be identified by HPLC technique. Elimination of the impurities will ensure better reproducibility and possibly help in reducing the weight loss observed below decomposition temperature.

(2) While making laminates, complete removal of the solvent should be ascertained as the residual solvent may lead to voids and could affect thermal stability. This could be ensured by FTIR or TGA.

(3) The mechanism of curing of bis itaconamide and bis maleimide and also the part played by solvent DMF and amines were discussed exhaustively. Although no clear-cut conclusions emerged, it was thought worthwhile to study the curing

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behaviour in the absence of oxygen to eliminate undesirable reactions. FTIR could be a useful tool for studying the mechanism.

(4) The possibilities of using low boiling solvents were discussed and it was suggested that low boiling solvents can be used subject to having better polar-polar interactions. No specific conclusions emerged.

(5) Discussions regarding possibilities of reducing cure temperature took place and Prof. Pearce suggested that styryl vinyl pyridine could be tried for this.

(6) For reducing brittle character of the polyimide systems, Prof. Pearce agreed that copolymerisation could be one of the ways to tackle the problem. Other suggestions included incorporation of fluorine containing polymers capable of hydrogen bonding and functionalised perfludro compounds.

The discussions in general were very useful.

Prof. Pearce was later taken round the facilities in PFC and the work on polyamides and scale up studies were explained to him.

<u>2-1-1985</u>

Prof. Pearce was shown round Polymer Complex and the work done on various aspects of polymer research including polyurethane adhesives and epoxy curators were explained to him. Various methods of toughening of epoxy resins were also discussed. Prof. Pearce is currently interested in this area.

Prof. Pearce also gave a talk on 'Thermal Stability and Non-inflammability', which was highly informative.

... 3

3-1-1985

Prof. Pearce met the Director, VSSC and gave his appreciation of the work carried out in the polymer field with special reference to DST Project.