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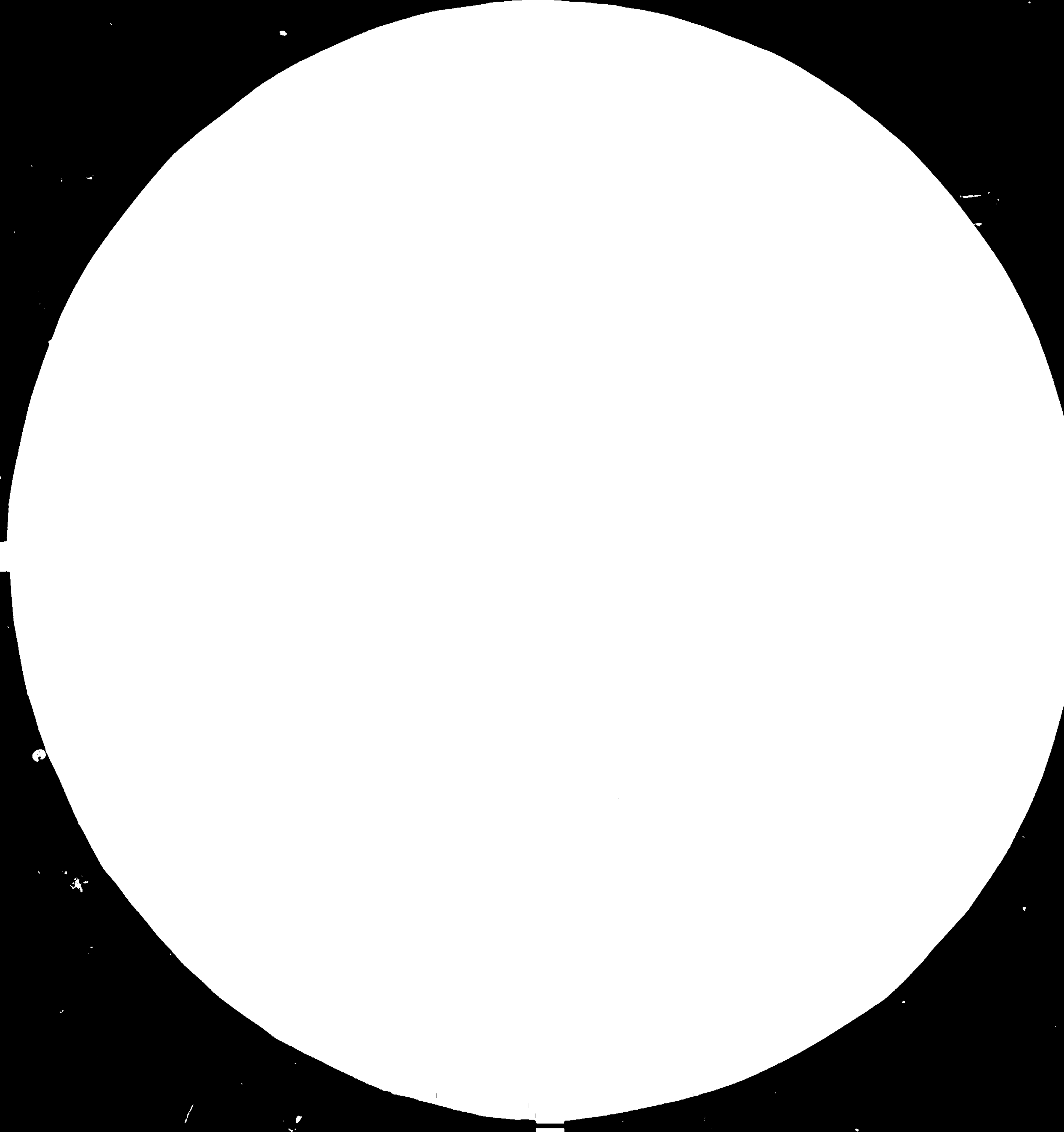

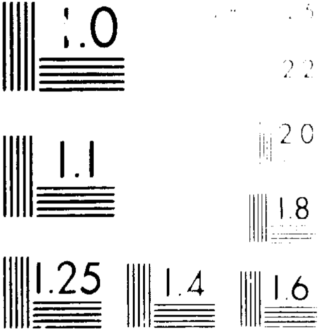
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PROF. DR. ERICH FITZER
Ordinarius und Leiter
des Instituts für Chem. Technik
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Karlsruhe, January 3, 1983
PF/ep

12805

REPORT
on my mission to India (resins programme)
from 15 to 22 December 1982

(This report includes also those of the experts Prof. Dr. R.J. DIEFENDORF, Dr. U. GRUBER, Dr. R. ZIMMERMANN).

1. Schedule:

My personal schedule between 15 and 22 December was realized according to the previous planning.

The schedule of the expert Prof. Dr. DIEFENDORF, between 13 and 22 December 1982 was modified because of difficulties in getting airplane reservations.

Also the schedule of the expert Dr. ZIMMERMANN was changed because of difficulties in obtaining the visa in time. He was in India between 15 and 21 December.

The expert Dr. GRUBER followed the programme and stayed in India between 16 and 23 December.

All experts arrived in Delhi and travelled together with me to Bombay and left from there. All experts attended the Indian Carbon Conference in Delhi and the IIT Seminar in Bombay, and participated in the DST meeting in Delhi on 17th of Dec., as well as in the meeting of the Technical Advisory Committee on 19th of December in Bombay. The experts visited the institutions in Delhi but not in Madras, Bangalore, Trivandrum and Baroda because of shortage in time and especially because of the impossibility to get air reservation during the pre-Christmas time.

Detailed Schedule:

13 Dec.	Arrival expert Prof. DIEFENDORF
14/15 Dec.	Prof. DIEFENDORF's visits to NPL and IIT Delhi, attending Indian Carbon Conference
15/16 Dec. night	My arrival together with Dr. ZIMMERMANN at Delhi
16/17 Dec.	Participation of all experts with me at the Indian Carbon Society meeting at NPL Delhi [redacted]. Simultaneously visits of University of Delhi with expert Prof. DIEFENDORF and visits of IIT and SHRI RAM Institute by the experts GRUBER and ZIMMERMANN. Discussions with Professor VERMA, IIT Delhi, Dr. SETH and Dr. BAHL, NPL Delhi and programme discussions with Dr. KUMBLE, DST and Prof. BHIDE, University of POONA at DST.
18 Dec.	Departure for Bombay together with Prof. BHIDE, Dr. KUMBLE and with the three experts Prof. DIEFENDORF, Dr. GRUBER and Dr. ZIMMERMANN, briefing of the experts by Prof. BHIDE.
19 Dec.	Participation in the meeting of the Technical Advisory Committee at Bombay together with the three experts DIEFENDORF, GRUBER and ZIMMERMANN.
20/21 Dec.	Participation in the IIT Bombay Seminar on Recent Advances in Materials (chairing sessions and presenting papers by all of us [redacted]. Demonstration of a movie on CFRP fabrication produced by DORNIER, Germany. Intensive programme conferences with Dr. KUMBLE, DST, Prof. BHIDE, Indian Programme Coordinator, and all participants of the resin programme, present at Bombay.
21 Dec.	Departure of expert Dr. ZIMMERMANN
21/22 Dec. night	Departure together with Prof. DIEFENDORF
22/23 Dec. night	Departure of expert Dr. GRUBER

2. The state of the resin programme, as demonstrated during the first meeting of the Technical Advisory Committee

The members of the Technical Advisory Committee and the three UNIDO experts were in December 1983 for the first time confronted together with the programme points, the progress in solving the problems and the philosophy of the participating institutions.

The presentations of the participants during the meeting of the Technical Advisory Committee covered therefore the whole activities of the laboratories during the last two years, because the Indian research programmes started two years ago basing on the programme formulated three years ago. A special abstract on the state of the programme as reported by the laboratories and discussed by the experts can be seen from [redacted]
The general impression was, however, disappointment;

firstly, because the members of the Technical Advisory Committee have expected more progress during a nearly two years long research and development work;

secondly, because the economic criteria have not been considered strongly enough for most programme points, and

thirdly, because it is hardly to see how after another two years a useful application of such resins in composites in India can be expected.

Furthermore, the very active and critical contributions of the experts present during the meeting of the Programme Committee fortified the mostly infavourable impression, that most participants have worked isolated on their special programmes which were selected by themselves, but a strong cooperation to a common effort is missing.

As to me personally as General Technical Advisor of the UNIDO contribution I have had the same disappointing impression as I started my activity for this resin programme in september 1982. The UNIDO support and therefore the UNIDO programme started officially in April 1982, but practically only with my visit in September 1982 when we had reformulated together with the Indian project coordinator, Professor BHIDE, the special tasks for the cooperating institutions. There were only 2 1/2 months between that time and the meeting of the Technical Advisory Committee in December, not enough time to report on decisive progress during this short period.

I was, however, very happy to see now in December 1982 that the decisions made in September turned out to become successful:

1.) All participants have tried to follow our advise to start a better cooperation.

2.) The experts which were selected according to the need after the September presentation of the results, and which were invited to this December meeting for giving criticism on the usefulness of the problems treated by the various institutions were exactly the right persons namely:

Dr. ZIMMERMANN as years long expert in polyesters and phenolics and active director in research laboratories of Farbwerke HOECHST, Germany;

Dr. GRUBER as experienced scientist in development of epoxy-, polyimide- and now vinylester-resins in research laboratories of CIBA-GEIGY, Switzerland, and

Prof.Dr. DIEFENDORF as well known expert in carbon fibre and composite application in the United States.

All these three experts gave also clear criticisms on mode and intensity of the work done in the laboratories which have been visited by them (Delhi area) (see also encl. 3).

3.) The equipments requested by the participants and mostly ordered already by UNIDO will improve the intensity and efficiency of the laboratory work.

4.) The study tours, performed so far, were extremely successful, and their outcome will certainly be reflected in the future results.

All of us had to recognize again how difficult it is to coordinate a successful cooperation of nine individual laboratories, spread over the large territories of India. It seems to me, however, that more critical than the distance is the variety of very specialized items for research and development, performed by these laboratories, favourizing more divergency instead of co-operation.

In order to improve this given situation it seems useful to me to distinguish between:

Main participants, - laboratories which contributions are of decisive importance for the outcome of the whole project, and

a second category of participants, which contributions are helpful but not decisive for the success of the whole programme. Participants of the second category should cooperate with the main participants in scientific research either on the preparation methods of resins or in testing of the resinsand of model composites made from it. The justification for accepting this second category of institutions within the national programme must be seen from the viewpoints of scientific education in the universities on one hand, and on the other of the desire to start a better coordination between university research and the industrial need for applicability of such research results.

3. The responsibilities of the main participants of the resin programme

For the first category, the main participants, let us remind of the immediate objection of this resin programme, as formulated in the project document namely

> "to develop special types of resins used in large quantities for application in composite industry"

In industrialized Western countries, mainly two resin groups fall under this objective:

The polyesters for glass fibre reinforced composites, and

the epoxy resins for advanced, these are mainly carbon fibre reinforced composites.

All evaluations of the research results on more specialized resins must be based on a comparison with such standard qualities used in the industrialized countries. As a consequence, the first step within the cooperative programme must be a critical evaluation of availability of basic resins in India and the information on their qualities and costs, and whether parts of these resins must still be imported.

ONly on the basis of such a critical evaluation of the state of availability and suitability of resins in India one can decide on the need of development of special grades and especially on the usefulness of scaling up of products developed within the present programme.

It should be mentioned , that in case of polyesters available in India, there exists a status report compiled by SHRI RAM some years ago. This report does not satisfy the need for the above mentioned critical evaluation, but can be used as basis for it. There do not exist similar compilations concerning epoxy resins, phenolics or other specialities.

Main participants can only be those, who are able and willing to contribute to this first step within the cooperative programme. According to my judgement these are:

SHRI RAM as specialist for polyesters

VSSC as most experienced manufacturer of epoxy based composites, and

NAL as selected institution for testing resins and composites.

The list of main participants can be extended by CLRI as specialist in phenolics, although phenolics are less important as matrix for FRPs if compared with polyesters and epoxies.

The cooperation between these four main participants should work as following:

The three laboratories working on resin evaluation and resin development (SHRI RAM, VSSC, CLRI) should advise NAL in the selection of most typical polyesters, epoxies and phenolics, and in preparation of most representative samples.

NAL should be responsible for measuring the properties of such standard resins and for preparing a critical data compilation. This compilation will be the basis for comparison with the resin types developed by the participants.

The three laboratories preparing new types of matrix resins must concentrate their efforts to resin systems only,which can be considered as candidate materials for economic application in India.

IPCL Baroda, although working more in the periphery of the whole programme, is asked to advise the participating laboratories on the economic aspects from viewpoint of chemical industry. It is hoped that also other specialists from industry will contribute to such economic considerations.

4. The contributions, expected from the participants of the second category.

Besides of the above mentioned special task for IPCL Baroda, this laboratory as well as PATEL University, IIT Delhi, NPL Delhi, act more in the periphery of this cooperative programme. However, as mentioned above, stronger links with the main institutions of this cooperative programme are absolutely necessary.

IPCL Baroda is asked to support the participating laboratories in scaling up of the resin development as soon as such development work has been decided as worthwhile for further studies. Especially the direct cooperation with PATEL University is strongly recommended. This responsibility should not reduce the own initiative of IPCL on their studies for reinforcement of thermoplastics.

PATEL University is advised to cooperate strongly with CLRI Madras with the objective to compare furane based resins with the phenolic resins and to select economic application for it in India.

For IIT Delhi it is recommended to cooperate strongly with VSSC Trivandrum and to advise them in the development of their new polyimides and the curing agents for epoxies on a more scientific basis. This responsibility does not exclude the own initiative of IIT on adhesion agents for glass fibres, new polyimides and vinyl ester resins.

University of Delhi is advised to cooperate strongly with NAL and to support them in measuring the physical and mechanical properties. University of Delhi should also support NPL, SHRI RAM and IIT Delhi in their preparative chemical studies by thermochemical measurements with the excellent equipment available at the University.

NPL has his own programme on carbon/carbon composites using pitches as matrix precursor. However, alle evaluation of this special research results must also be based on a comparison with standard qualities used in the industrialized countries.

The following graph should explain the intended strong cooperation between the participants. (see page 9).

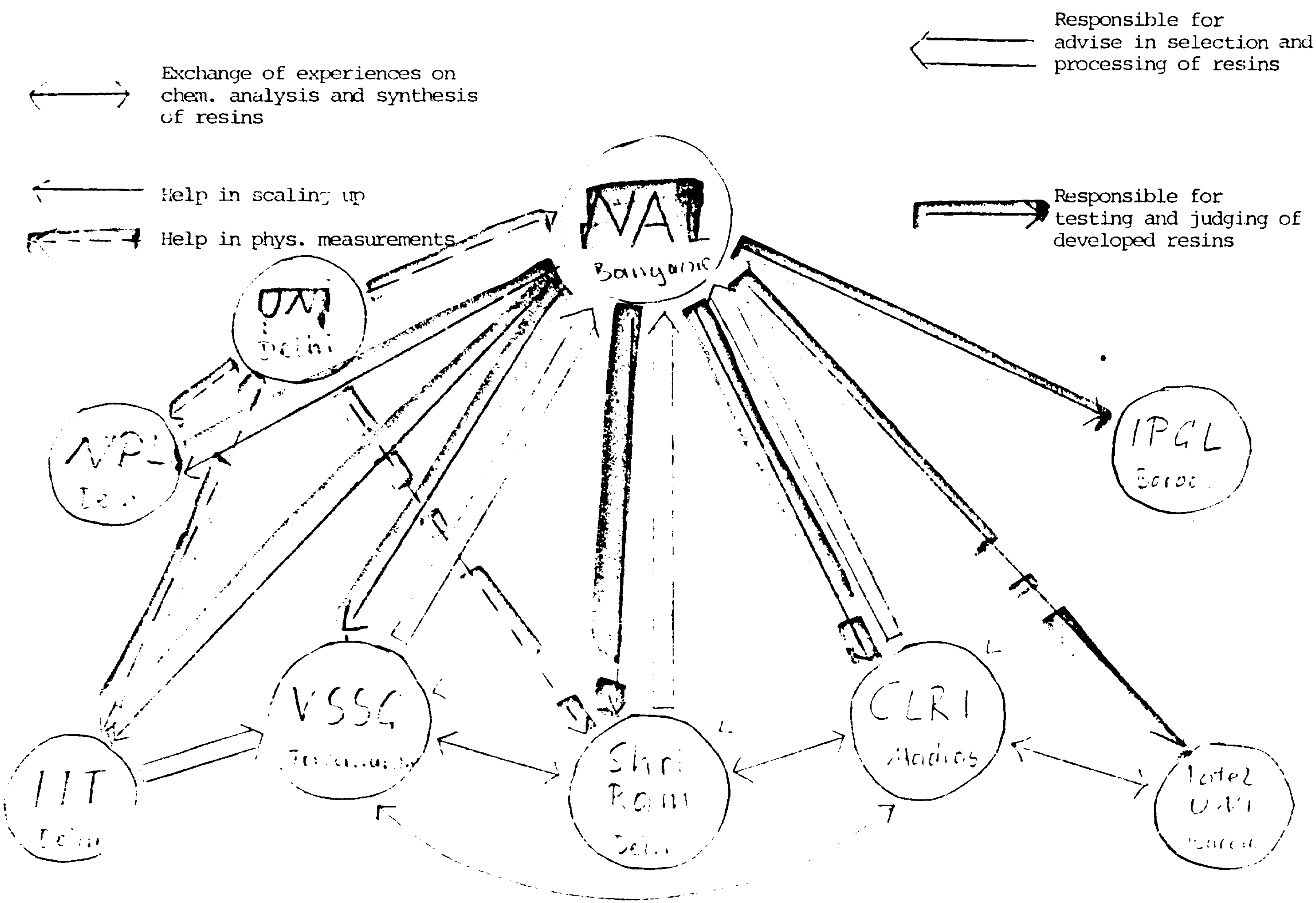
5. Limited tasks for all participants until end of March 1983

Using the above basic ideas which are derived from the programme objective and the critical remarks and suggestions of the experts, the Indian coordinator, Professor BHIDE, has prepared some very limited tasks for the participating laboratories and asked them to report until end of March on it :

5.1 Immediate limited tasks for NAL, Bangalore

The central institute for evaluation of the results within this cooperative programme is NAL, Bangalore. The special task for NAL on which NAL should report end of March 1983 comprises the following three points :

a) Setting up a data compilation of a few representative matrix resins, world wide used as well as indegenious ones, basing on own measurements with model composites, prepared at NAL (responsible for selection of the resins and advise


Exchange of experiences on chem. analysis and synthesis of resins
Help in scaling up
Help in phys. measurements
Responsible for advise in selection and processing of resins
Responsible for testing and judging of developed resins
NAL
NPL
IPGL
IIT
VSSC
Shri Ram
CLRI
Madras

for composite preparations are the three institutions: SHRI RAM for glass fibre reinforced polyesters, VSSC for carbon fibre reinforced epoxies and CLRI for filled or fibre reinforced phenolics).

b) Testing of resins developed by the various institutions, preparation of model composites from these special resins and measuring of the physical and especially mechanical properties of the composites made from these special grade resins.

c) Report on the establishment of sophisticated testing methods for composites at NAL Bangalore with the help of UNIDO, including simultaneous tensile, compressive and torsional strength testing, ultrasonic testing and fatigue testing and accustic emission.

5.2 Immediate limited task for SHRI RAM Institute, Delhi

a) Selection of some few typical polyester resins for glass fibre reinforcement especially produced in India and advise of NAL for preparation and testing of such model composites.

b) Concentration on the synthesis of larger quantities of the flame resistant polyester resin based on HET anhydrid (hexachloroendomethylenetetrahydrophtalic anhydrid) and DBNPG (dibromoneopenthylglycol). The preparation work should result in enough quantities for testing the properties by NAL. Strong cooperation between SHRI RAM and NAL for the best method of preparation of the samples is precondition for this time limited task. These results are needed for decision on eventual scaling up of this development.

c) The work on the optimization of the synthesis of HET acid itself should not be continued at the moment.

5.3 Immediate limited task for VSSC Trivandrum

a) Selection of few typical epoxy resins for C-fibre reinforcement and advise of NAL for preparation and testing of model composites.

b) Concentration on the development of the curing agents for epoxy.

c) Preparation of enough sample materials of the polyimide based on itaconic acid anhydrid for final testing of the properties. These data are needed for the decision whether this work should be scaled up or stopped.

d) The work on polybenzoxazoles which are very resistant, but difficult to process in fabrication of composites should be stopped.

e) The results of the work on surface treatment of jute must be evaluated and should not be continued until the economic justification will be confirmed.

5.4 Immediate limited task for CLRI, Madras

a) Selection of a few typical phenolics world wide used and indegenious ones for reinforcement with fillers and fibres. Advise of NAL for preparation and testing of model composite made from it.

b) The preparation work should be concentrated on evaluation of the properties of the resins based on cashew nut shell liquids. This work should be performed at CLRI as well as at NAL. Evaluating of the economy of such products from non petroleum sources for application in composites.

c) Proposals for special economic applications of resins based on cashew nut shell liquids in non composite industry.

5.5 Immediate limited tasks for the other participants

a) PATEL University. This institution must concentrate on evaluation of the properties of their furan based resins and on getting some information on the economy of these resins. Without such an economic justification the work on matrix resins should not be continued within this programme, but more economic applications of these special resins should be proposed.

b) IIT Delhi . This participant should concentrate on the polyimides which do not consist of extremely toxid raw materials and which can be easily processed. This University Institute should consult VSSC on the further improvement or optimization of preparation methods for the promising itaconic acid anhydrid based polyimide. This institution should also think on the possibility to start some scientific studies on vinylesters. The work on coupling agents for glass fibres should be continued.

c) IPCL Baroda . This industrial laboratory should not continue systematic work on filling of polymers with different fillers within this programme. They should select some special polymer products from the large list of commercially available products in the Western world. They should try to reproduce these typical qualities. Development, however, should b directed to fibre reinforced thermoplastics.

d) NPL Delhi. This national institute should continue its work on carbon/carbon composites based on the liquid pitch impregnation process. The team should improve the impregnation pitch. They should try to improve the strength properties of model composites. They should prepare composites with various fibre arrangement and they should compile the mechanical data of composites with varied fibre arrangement and contact some eventual users for such composites in orthopedic hospitals.

e) University of Delhi. This University Institute, not yet practically included in the cooperative work, should measure thermochemical properties of resins and curing agents prepared by IIT Delhi, NPL Delhi or SHRI RAM Delhi. They should evaluate possibilities to join NAL in measuring of some basic physical data on composite materials

6. Tentative Schedule for further activities

a) The next meeting of the Technical Advisory Committee is scheduled for 7, 8 April 1983, most probably at Delhi.

b) I was asked to visit the participating laboratories before this meeting, that means end of March and beginning of April. It is hoped that all reports on the limited tasks will be available at the time of my visit for preparing discussions of the presentations during the meeting of the Technical Advisory Committee. It is furthermore planned that I should visit University of Poona (Prof. BHIDE) at the end of this visiting tour and before the meeting of the Technical Advisory Committee for discussions with the coordinat

c) No study tours, no training and no new requests of apparatus will be accepted until the next meeting of the Technical Advisory Committee in the beginning of April 1983.

d) Immediately after this next meeting of the Technical Advisory Committee the first study tour group (under the guidance of Prof. BHIDE with two or three colleagues) should start beginning with Japan and ending with Germany and UNIDO Vienna. The list of the participants with complete personal data must be in hand of the Chief Technical Advisor at least end of January 1983 in order to prepare carefully the visits.

The second cooperative study tour under the guidance of Dr. KUMBLE and with Prof. VERMA will obviously start only end of May because of the University programme of Professor (Mrs.) VERMA. The complete list of participants should be in hand of the Chief Technical Advisor before his departure for India in the last week of March 1983.

The study tour of Mr. SINGH should be performed together with the training fellow Mr. SRINASAR. These both colleagues will start immediately after the next meeting of the Technical Advisory Committee. Again, the personal data and written confirmation of their availability (because of the problems last time) should be in hand of the Chief Technical Advisor end of January 1983 already).

7. Performed study tours

7.1 The study tour of Dr. SETH and Dr. BAHL in November 1982 to Japan was very successful. Their report is enclosed [redacted].

7.2 Also the study tour of Dr. BHARDWAJ was according to his oral report successful. A written report is not yet available.

7.3 Professor NANDA has performed his study tour as a single. Unfortunately, Mr. SINGH, the specialist in testing of composites, was not able to join at that time. Professor NANDA, howver, had a very good impression and had collected much information on properties and testing of composite materials. It is hoped that he can apply these informations during the cooperative programme.

7.4 General conclusions from these visits:

The visit in Japan was well organized and satisfying in any case.

The visiting programme for Professor NANDA was too tight. Especially the long travelling distances within the United States need a longer stay at one place and a smaller number of places to be visited in one week.

The visited institutions were very hospital but also extremely disappointed if the announced visits were cancelled only a few days in advance, or even only afterwards.

8. Future experts

The Indian coordinator expressed the need for the Indian Institutions to have some experts who can stay within the laboratory at least 2 weeks and train the Indian people more basically in handling the daily work with modern technology in more rationalized way.

This is not only important for the polyester synthesis in SHRI RAM Institute and for the epoxy and polyimide development in Trivandrum, but especially for the composite testing in Bangalore, that means for preparation of highly reproducible model composites and testing them with sophisticated methods.

During the April meeting the request for future experts will be discussed, if not earlier decissions are achieved by mail.

Prof. Dr. E. FITZER

- 4 enclosures -

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ENCLOSURES

No 1, 2, 3, 4

to the REPORT

on my mission to India

15-22. Dec. 82

FIRST INDIAN CARBON CONFERENCE

TECHNICAL PROGRAMME

DECEMBER—15-17, 1982

VENUE: NATIONAL PHYSICAL LABORATORY AUDITORIUM

Enclosure 1

December 16, Thursday

Chairman	*R.J. Diefendorf*
1400 hrs	Plenary lecture Carbon-Carbon Composites *E. Fitzer* University of Karlsruhe, West Germany

SESSION F

Chairman	~~*M. Inagaki*~~
1445 hrs	Carbon Fibre Polyimides Composites—(F-1) Stenzenberger University Heidelberg, West Germany
1505 hrs	Development of Carbon-Composites—(F-2) *L.M. Manocha, G. Bhatia and O.P. Bahl* National Physical Laboratory, New Delhi
1520 hrs	Transverse Thermal Expansion of Carbon Fibre/Epoxy Matrix Composites—(F-3) *J.F. Helmer and R.J. Diefendorf* Rensselaer Polytechnic Institute, U.S.A.
1540 hrs	————TEA————

SESSION G

Chairman	*J.W. Stadelhofer*
1550 hrs	Technical requirements for engineering carbons and graphites—(G-1) *A.A. R. Wood* Morganite Special Carbons Limited, U K

December 17, Friday

Chairman :	*E Fitzer*
0900 hrs	Plenary lecture Mesophase formation in pitches *R.J. Diefendorf* Rensselaer Polytechnic Institute, U.S.A.

SESSION H

Chairman :	*B. P. Singh*
0945 hrs.	Relation between the softening point and the glass transition point of pitches—(H-1) *M Sakai and M. Inagaki* Toyohashi University of Technology, Japan
1005 hrs.	Characterization of Indian coal-tar pitch for use in Carbon-Carbon Composites—(H-2) *M.K. Sridhar, P. Kanakalata and B.C. Pai* National Aeronautical Laboratory, Bangalore
1020 hrs.	Use of petroleum coke in Aluminium industry—(H-3) *M P. Whitakar* Great Lakes Carbon Corporation, U.S.A.
1040 hrs.	Coal char and purification of Mine effluents—(H-4) *J. Joga Rao, S R. Das and H.C. Nandi* Central Fuel Research Institute, Dhanbad
1055 hrs.	Structural changes of the Carbon and Graphite Industry in the Eighties *Karl Maier* Voest Alpine AG (Linz), Austria
1115 hrs.	————TEA————

Carbon—Carbon Composites

E. Fitzer

University of Karlsruhe, West Germany

Carbon fibre reinforced carbon composites are "all carbon" materials. Similar to classical carbon ceramic materials (such as graphite electrodes) they consist of a filler t, that is the fibre network, and of the binder carbon. Only endless fibres are used and stly in two-or three-dimensional arrangement, thus reprepresenting two continuous ctural phases for the binder as well as for the filler part.

CFRC-materials combine the outstanding high temperature properties of ygranular graphite materials with those of carbon fibre reinforced composites. erefore, they became the unique material for heatshields and nose cones in the space hnology and as nozzle material in solid fuel engines. The reliability was repeatedly nonstrated during the spectacular space shuttle landings. The literature on this terial, however, is limited because of its military importance.

The paper describes the two methods for fabrication of such materials, the CVD and liquid impregnation techniques. Results of systematic studies on the process ameters for fabrication of UD (unidirectionally reinforced) model composites according the liquid impregnation technique will be discussed in detail. Most important is the ction of suitable fibres as well as binder coke precursors. The effect of adhesion ween fibre and matrix precursor is different from that in fibre reinforced polymers ause of the stresses built up by the carbonization shrinkage of the matrix.

As final densities of the bulk material are achieved by multiple liquid impregnation recarbonization treatments, the pore structure of the primary binder coke controls the mechanical and thermal properties of the composites.

Pitches are superior as matrix precursor as compared with thermosetting resins, but d high pressure carbonization in order to get high carbon yields. Several resins as

well as additives to the binder and impregnation pitch for crosslinkage will be reported in comparison. Finally, the effect of graphitization as intermediate and final process step will be discussed.

For re-entry application, impregnation with oxidation resistant substances is applied, as will be shown. On the other hand, final resin impregnation leads to composites with hybrid matrix, which are a completely new material group with mechanical properties, similar to those of CFRPs.

Present and future application possibilities of both, carbon carbon as well as carbon polymer hybrid materials as in automobiles and as biomaterial will be discussed.

Enclosure 1

Transverse Thermal Expansion of Carbon Fiber/Epoxy Matrix Composites

J.F. Helmer and R.J. Diefendorf

Materials Engineering Department, Rensselaer Polytechnic Institute Troy, New York 12181

The prediction of laminate properties from those of constituents is an important aspect of better understanding overall composite behaviour. In order to achieve this goal utilizing micromechanical analysis, composite constituent properties must be modelled in a more detailed manner. The transverse properties of laminates, specifically coefficient of thermal expansion, are critical in a variety of applications. While the axial properties of fibres alone and in composites are both predictable from theory and are easily measured, transverse properties, particularly of anisotropic fibres, are almost impossible to generally predict and difficulties arise in experimental measurements. Physical properties of several anisotropic fibre types were studied to obtain property data and to clarify the effect of structural anisotropy has on fibre properties. Composites of various filament volume percents were measured for thermal expansion by a push-rod dilatometer and a plot of coefficient of thermal expansion versus corresponding volume for each fibre type was constructed. From this a value for the transverse coefficient of thermal expansion can be extrapolated.

Mesophase Formation in Pitches

R.J. Diefendorf

Rensselaer Polytechnic Institute Troy, New York 12181

The fundamentals of mesophase formation in model compounds will be described. The concepts developed to describe model compound mesomorph/non-mesomorph binary systems will be generalized to pitches. The critical average molecular weight for mesophase formation and the effect of molecular weight distribution will be presented.

Indian Institute of Technology,.Bombay

Jubilee Commemoration Seminar

Recent Advances in Material Research

December 20-22, 1982

I. I. T. Bombay
Organised by

Sponsored by

Board of Research in Nuclear Science
Defence Research and Development Organisation
Department of Electronics
Department of Science and Technology
Indian Institute of Technology, Kanpur
Indian Space Research Organisation
Indian National Science Academy

Monday
December 20, 1982

11.00 to 13.00 hrs.
(IDC)

SESSION A1

SPECIAL STEELS AND SUPERALLOYS
Invited Talks

A1-1 V. RAMASWAMY AND N.S. DATAR, SAIL, Ranchi
New developments in high strength low allow steels.

A1-2 S.K. GUPTA, MIDHANI, Hyderabad
Status of special steel production for nuclear, space and aeronautical applications in India.

A1-3 RAJENDRA KUMAR, NML, Jamshedpur
Development of creep resistant materials.

Monday
December 20, 1982

14.00 to 15.30 hrs.
(IDC)

SESSION A2

COMPOSITE MATERIALS-I
Invited Talks

A2-1 H. STENZENBERGER, West Germany
Carbon fibre-reinforced composites with polyimide matrix.

A2-2 K.A.V. PANDALAI AND N.G. NAIR, IIT Madras
R and D activity at FRP Research Centre, IIT Madras.

A2-3 R. ZIMMERMANN, Hoecnst AG, West Germany
Polyesters, phenolics and melamine resins.

Monday
December 20, 1982

16.00 to 17.30 hrs.
(IDC)

SESSION A3

COMPOSITE MATERIALS-II
Invited Talks

A3-1 (MRS) I.K. VARMA, IIT, Delhi
Advanced fibre-reinforced organic matrix resin composites.

A3-2 B.J. DIEFENDORF, RPI, New York
Carbon-fibres, present properties and future applications.

A3-3 S. BANDYOPADHYAY, MRL, Victoria, Australia
Characterisation and application of composite materials.

Monday
December 20, 1982

16.30 to 17.30 hrs.
(MB)

SESSION A4

CONTRIBUTED PAPERS
Poster

A4-1 D.S. VARMA AND R.G. RAJ, IIT, Delhi
Amine cured epoxy/glass fibre composites.

A4-2 P.R. PRASAD, S.RAY, J.L.GAINDHAR AND M.L.KAPOOR, University of Roorkee, Roorkee
A modified mixture law for particulate composites.

A4-3 L.M. MANOCHA, O.P. BAHL, R.K.JAIN AND V.P.WASAN, NPL, Delhi
Thermal behaviour of carbon fibre reinforced plastics.

A4-4 K.SREENIVAS, T.SUDERSENA RAO, AJAY DHAR AND ABHAI MANSINGH, University of Delhi, Delhi
Dielectric and pyroelectric studies on triglycine sulphate - polymer composites.

A4-5 R.L. SETH, NPL, NEW DELHI
Use of pitch for carbon-carbon composites.

Tuesday
December 21, 1982

9.00 to 10.30 hrs.
(IDC)

SESSION A5
COMPOSITE MATERIALS-III
Invited Talks

A5-1 E.FITZER, Karlsruhe University, West Germany
High temperature materials.

A5-2 V.M. NADKARNI, NCL, Poona
Developments in high performance fibres and matrices.

A5-3 U.GRUBER, Ciba-Geigy, Switzerland
Vinylester and epoxy resins for advanced composites.

Tuesday
December 21, 1982

11.00 to 13.00 hrs.
(IDC)

SESSION A6

HIGH TEMPERATURE CERAMICS
Invited Talks

A6-1 (Mme) A.M. ANTHONY, CNRS, Orleans, France
High temperature refractory applications of Zirconia.

A6-2 T. SATA, Kumamoto Institute of Technology, Japan
High temperature vaporizations of ceramics materials.

A6-3 B.V.S. SUBBA RAO, DMRL, Hyderabad
Grain boundary engineering in ceramics.

A 2-3

RESINS AS MATRIX FOR FIBRE REINFORCED COMPOSITES

R. ZIMMERMANN

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After a general consideration of the economic importance of polyesters as component for reinforced plastics the prefered manufacturing processes and examples of application are described. The applied properties of unsuturated polyesters as a function of the molecule structure are evaluated by means of several diagrams. Finally, the importance of aramide and carbon fibres as reinforcing material is described.

VINYLESTER - AND EPOXY RESINS FOR ADVANCED COMPOSITES

U.GRUBER

CIBA-GEIGY LIMITED, BASLE, SWITZERLAND

Vinylester- and Epoxy Resins for advanced composites

Vinylester resins are the reaction products of epoxy resins with acrylic- or methacrylic acid. The commercial VE resins are solutions in styrene that can be handled and cured like the unsaturated polyester resins. The VE resins are known for their good hydrolytic stability and are used when superior chemical resistance is required.

A very promising new development are UV- or sun light curable formulations. Such formulations combine the advantage of a long pot life with short curing without requiring expensive ovens or other heating equipment.

The epoxy resins are the classical matrices for high performance composites. As a consequence of the oil price shock, the European industry has begun to investigate the replacement of heavy steel parts by light weight high performance composites. Hereby a necessary precondition was that the engineers learned to construct and to calculate composite structures. One of the most important characteristic values for such calculations is the transverse tensile strength of the matrix resin on a given reinforcing fibre. These values can now be determined by routine.

For composite parts of engines high temperature matrices are required. It is shown that some EP-systems did resist 180°C aging in motor oil during the whole life span of a motor.

HIGH TEMPERATURE MATERIALS

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WEST GERMANY

The paper describes research in Karlsruhe on high temperature materials for the temperature range above 1000 °C in oxidizing atmosphere as well as above 1600 °C in non oxidizing atmosphere.

So far as high temperature alloys (super alloys) are concerned, protection against oxidation and hot corrosion in turbine blades are studied.

The aluminizing coating within the cooling channels can be deposited by the subchloride process, the Cr-Al coatings on the outer surface can be replaced by silicon containing ones with increased resistance against attack by sulphur, alcaline and vanadium oxide. The report includes description of a process for fabrication of such very reactive coatings without damaging the substrate alloys.

For higher temperatures application in oxidizing atmosphere silicon ceramic can be applied. The paper describes methods to improve the oxidation resistance especially the resistance against intergranular oxidation and as a consequence against creep by densification of silicon carbide and silicon nitride bulk materials. The possibilities for reinforcement by fibres will be discussed.

A new material with the highest oxidation resistance is $MoSi_2$ improved in its mechanical properties by means of reinforcement with niobium wires. Its strength, fracture and oxidation behaviour will be presented.

Finally, results on and limits for fibre reinforcement of oxide ceramics (Al_2O_3, mullite, SiO_2) will be referred.

[illegible] superior material for application in non- oxidizing atmospheres at highest temperatures, but also for a limited time in oxidizing atmosphere carbon fibre reinforced carbon materials will be presented.

Enclosure 3

The reports of the participating laboratories and the discussions during the meeting of the Technical Advisory Committee 19th of December at Bombay.

1. SHRI RAM Delhi, Dr. DABOLGAR. Dr. Dabolgar reportet that standard polyester resins (UP resins) are already manufactured in India. The SHRI RAM institute itself is experienced in this field and has given some licences to Indian companies. There are approximately 350 small companies which use UP resins. UP production in India is in the order of magnitude of 10.000 to/year.

Dr. DABOLGAR reportet on the development of a special unsaturated polyester resin (UP resin) based on HET acid (hexachloroendomethylenetetrahydrophtalic annydrid) and DBNPG (dibromoneopenthylglycol). The flame resistance apparently was at least equivalent to commercial types as Hytrom and Viapal resins. Also the tensile strength was similar. The experts Dr. ZIMMERMANN and Dr. GRUBER congratulated SHRI RAM Institute for this success.

SHRI RAM has sampled some 100 grams to NAL as well as to University of Delhi for testing. Only first one has tried to make glassfibre reinforced composites from it. However, in spite of personal cooperation with members of SHRI RAM Institute, the sample size was too small for preparation of representative laminates. Dr. DABOLGAR was reporting that chemical resistance tests were planned. Dr. GRUBER explained how such tests were conducted in his laboratories at CIBA-GEIGY. Expert Dr. ZIMMERMANN went into more detail concerning the polycondensation reaction. This expert also stated that this type of flame resistant UP's (with bromium content) have a very limited market in Western countries (only a few percents). He proposed to consider the alternative way to get flame resistance in UP's namely by adding the flame retarding fillers such as red phosphor, antimonpentoxid or others to standard qualities. Dr. GRUBER proposed Al_2O_3 ($H_2O)_3$. Both experts pointed out that when fillers may be used (if there is not a limitation by increased viscosity of the mix) this would be the cheapest way and also has the advantage of low toxitity. Also liquid phosphor containing additions should be considered.

Dr. DABOLGAR reported furthermore on the experiments to synthesize the HET acid itself as well as to start with scaling up in cooperation with other participants, eventually IPCL Baroda.

It was concluded however, that these developments should only be continued if the tests of larger quantities of this special type of UP have shown that an economic product can be expected from these experiments for India.

2. VSSC Trivandrum - Dr. RAO

Dr. RAO and his colleagues reported on several items started within this programme.

a) Polyamides, polyaminoamides :

A medium molecular weight liquid or low melting reactive polyamides based on fatty acids was developed. Dimer esters and aliphatic di and tri amines have been used for the preparation of the polyamides. The dimer esters are prepared from commercially available castor oil.

Expert GRUBER stated that such adducts are widely used in Europe as hardeners for expoy additives (CIBA-GEIGY India offers those also imported from Switzerland).

b) Thermosetting polyimides

The scientist reported on the preparation of additional polyimides, the recent synthetic routes for polyimides synthesis, which used preimidized short molecular segments similar nature to those of condensation polyimides. The cure is achieved by polimerisation of the reactive termini of the prepolymers without loss of volatiles. Therefore, the processing of such polyimides become simple while the thermostability slightly sacrified.

Especially itaconic anhydrid was used in the experiments. It was reacted with p, p-diamino-diphenylether under suitable conditions to get bisimide which is a mixture of approximately 90 % bisitaconic imide and 10% biscitraconimide due to isomerisation. This mixture of bisimides was reacted with p, p-diaminodiphenylmethane in DMF under certain conditions to obtain a solution of low molecular weight polyamino-bisimide of itaconic and citraconic moieties The tentative test on thermostability and processibility are very promising. Especially itaconic acid has the advantage to be locally available to a price comparable to maleicacidanhydrid.The expert Dr. GRUBER was not familiar with this type of polyimides, but he had the impression that these studies are promising (it is intended by UNIDO to bring the polyimide expert Dr. STENZENBERGER to Trivandrum for consulting this work).

c) Polybenzoxazoles

Polybenoxazoles are a relately new class of heterocyclic polymers with excellent thermal stability. VSSC has reported having synthesized such a polymer in laboratory scale. Following the remarks of Dr. GRUBER, that in principle similar work was done in America but was stopped because of the extremely bad processibility of such resins, it was agreed also by VSSC , that this work should not be continued within the UNIDO programme.

d) Liquid anhydrids

Liquid anhydrids are curators for epoxies (hardener). The representatives of VSSC reported on the synthesis of dodecemyl succinic anhydride from lauryl alcohol by dehydration through a heated alumina colomn, giving predominantly 1-dodecene with some quantities of isomerized branched olefins and short chain olefines due to cracking. This mixture of olefins on reacting with maleic anhydride gives liquid anhydride having the boiling range of 182-188 ^{o}C.These anhydride cures with epoxy polymer in presence of amine catalysts. Research and development work on the process is completed. The product gives similar properties as compared to imported material.

The expert Dr. GRUBER made the comment that the commercial product imported from Switzerland by CIBA-GEIGY is the hardener HY 964. This hardener gives a heat destortion temperature of 40 - 45 ^{o}C only with standard epoxy resins. Therefore, it is used preferently as co-hardener. His opinion was one should not vaste time and money on exploring the properties of this commercially available hardener. If it is intended to produce this hardener locally, the main efforts should be directed to his scaling up and production.

e) BF_3 ethylene diamine complex.

Also this complex is a commercially available CIBA-GEIGY-product namely the hardener HT 973. BF_3. MEA complex (monoethylamine) have been prepared by VSSC starting from BF_3-etherase solution and monoethylamine. Since the reaction is highly exothermic, it is carried out at subzero temperature. In view of the hygroscopicitiy of the product, dry atmosphere is maintained.

The expert Dr. GRUBER, CIBA-GEIGY , reported that Ciba-Geigy has found that such accelerates lowers the long term heat stability of anhydride cured epoxies. This accelerator is used in quantities of only 0.5 to 2 % of the mixture. Therefore, according to the opinion of the expert, there is no reason to reinvent such an accelerator.

f) Development of polyurethane adhesives

Polyurethane adhesives were developed for bonding of glass epoxy laminates. The cured laminate has large concentration of hydroxyl groups which will be quite reactive with isocyanat groups present in the adhesive. The system developed is a two-component-system, the first component being a hydroxyl terminated polyester, and the second component toluene diisocyanathe. The research and development work on this polyester synthesis and on the adhesive formulation is completed. Tentative testing gave the following bonding properties: Fibre glass t fibre glass laminate 6.5 N/mm^2, fibre glass laminate to aluminium 5 N/mm^2, fibre glass laminat to mild steel - 6.5 N/m^2 , aluminium to aluminium - 8 N/m^2. The expert Dr. GRUBER reported that tensile shear strength of commercial products range from 14 to 25 N/mm^2. The qualities developed at VSSC are not yet finally optimized therefore. However, he mentioned that the development of adhesives is more "black art" than a scientific problem. He jugded this type of work as a good idea that establishment of adhesion development laboratory in India is advantageous as compared with imports from foreign companies because last ones have very often not the ability to respond quick enough to a low volume demand for special adhesion problem in India.

g) Improvement of jute fibres

The research work at VSSC was concerned with the decrease of the water retention value and of the resin absorption of jute as a filler in polyester composites.

Several methods were studied. It was found that treating of the fibre with organic coupling agents like glycithil-methycrylate (GMA) improved the shear strength of the laminates by 10 to 20 % without effecting the other properties of the fibre.

But it was found to be very difficult to bring down the moisture content and resin absorption of the fibre significantly with simultaneous improvement of the mechanical properties,only some treatments are able to bring down the moisture content and resin absorption without any significant loss in the mechanical properties of the fibre and the laminate. One such treatments is the surface coating of the fibre with reactive polymers like Adiprene HTPB - DTI etc., which brings down the moisture content by 6 - 7 % and a resin absorption by 40 %, also the tensile strength of the yarn is improved by 20 - 25 %, whereas the other mechanical properties of the fibre and of the laminates are not harmed significantly. The experts acknowledged the result of this comprehensive studies on improvement of jute. They pointed out, however, that the costs of such a treatment will perhaps exceed that of glass fibre fabriques. In such a case, replacement of glass fibres by surface treated jute is not justified. Mainly, because jute is not so strong and stiff as glass fibre by far. Perhaps there are some other applications where not high strength but only wall thickness is required. Then, surface treated jute could be advantageous.

It is recommended to continue the work only if the economic situation of such a surface treatment has been proved and found to be tolerable by the various users.

3. CLRI Madras - Dr. REDDI

Dr. REDDI reported on the research on phenolic resins from non petroleum sources. Especially, on the suitability of a phenol (cardanol) from cashew nut shell oil (CNS-oil) for the manufacture of phenolicresins. The best properties were obtained with blends with standard phenol. Also samples filled with wood flour, asbestes, glass fibre mat, cotton, lignin were prepared and demonstrated. The experts Dr. GRUBER, but especially Dr. ZIMMERMANN acknowledged the results. Similar work was done years ago in Germany by Farbwerke HOECHST, especially by ALBRECHT Co. It was found at that time that it is extremely difficult to prepare such filled samples free from pores. Also the samples demonstrated by CLRI representatives were insufficient in quality. There was the surprising discussion between the CLRI people and the experts, that even in India CNS - oil is much more expensive than phenol. Then it is not worthwhile to fabricate standard qualities of phenolics from CNS-oil. It was discussed also that the Dr. BECK Company of India has epoxydized cardanol and diphenol made from cardanol and has submitted samples for testing to CIBA-GEIGY. Dr. ZIMMERMANN promised to submit all reports available at HOECHST on this special development of CNS-oil derived phenolics, and also to give proposals for more advantageous use of this special natural product from India.

4. PATEL University

Dr. S. PATEL reported on furane resins from furfurol and/or furfural. Again, the reason for this development work was the availibility of the raw materials in India, or better, that this raw materials can be made available by new fabrication plants in future. Dr. PATEL reported that laboratory work on resin development is nearly finished , and that they are preparing larger quantities for submitting to NAL for testing. They have already tried to make some materials filled with several fillers. It is well known, that furane resins have excellent chemical resistance.

During the disussion, however, it came out, that furfural costs even in India 20 - 37 Indian rupies/kg, whereas phenol costs only 16 rupies/kg although this price is much higher than that on the world market. Dr. ZIMMERMANN, however, reported that there exist many special applications for this chemical resistant resin. He promised to submit a report and list with proposals for such special applications (for instance chimney paints).

5. IPCL Baroda , Dr. BARDWAJ

This report on the work on properties of polypropylene filled with different materials was presented by Dr. SHARMA. They used $CaCO_3$, Talc, Mica as filler. It is planned to reinforce PET and PBT and Nylon 6 with shopped glass strands. The expert discussed whether filling of thermoplastics is a subject for a composite programme. They recommended , however, to continue the work because of the increasing importance of filled thermoplastics in the Western world. For reinforcment of PBT, Dr. GRUBER reported on the difficulties at CIBA-GEIGY to get pure enough starting material. He recommends filling with chopped glass strands , 6 mm length.

The expert Dr. GRUBER also warned the Indian colleagues to produce plastic bottles. The Western world is polluted with them.

6. IIT Delhi, - Professor (Mrs.) VERMA

Prof. Verma gave a very short report because of shortage of time for a longer presentation. She also treated several project items.

a) Sizing for glass fibres.

This is a new item in the research work of IIT, Delhi, taken from NPL Delhi. Professor Mrs. VERMA has problems with the synthesis of suitable silanes. Expert Dr. GRUBER proposed as specialist Prof. Dr. G. GREBER, Institut für Chemische Technologie Organischer Stoffe in Technical University of Vienna. Prof. GREBER was leading researcher in CIBA-GEIGY and has developed there such coupling agents. There exist no chance to get a Know How or licence for fabricating of such coupling agents. It is strongly recommended to continue this work.

b) Synthesis of high temperature resistant polyimides.

Professor VERMA is internationally known on this work. She reported on three types of polyimides, namely

i) Synthesis of aromatic di- and triamines as componenents for corresponding polyimides . Expert GRUBER pointed out that any work with benzidine must be stopped immediately, as this is one of the most powerful cancerogenic substances. He proposed that some of the bulky or higher molecular weight amines should be tested as hardener for epoxy prepregs. He offered that also CIBA-GEIGY of India in Bombay could perform some type of testing.

ii) Polycondensation - polyimides based on reaction of a diamine with dianhydrids (PMDA or BTDA)(PMDA = pyromellitic-dianhydrid). The results of this laboratory were well appreciated by the expert Dr. GRUBER. He recommended to develop varnishes for wires for electrical motors and to make temperature resistant films within the UNIDO programme from this polyimides. The development of the polyimides as a bulk material is obviously supported by the Indian space programme and should not be supported by UNIDO simultaneously.

iii) Thermosetting polyimides based on bismaleinimides (BMI). The basic idea is to combine this with amines in order to reduce the brittleness of the bismaleinimide polymers. Such combinations are available commercially under the trade mark KEREMID 601 from RHONE-POULENC.

The expert Dr. GRUBER mentioned that thermosetting polyimides based on BMI and the amines mentioned above in i) could be independent of Rhône POULENC Patents .
First step , however, should be the production of the triple amines. He again proposed to use this combination mainly for electrical industry and for applications where low thermal expansion coefficient is needed. The expert Prof. DIEFENDORF acknowledged the excellent work done by Prof. VERMA in chemical synthesis of special resins. He pointed out, however, that the development of the matrix materials for composites .emphasis should be placed on these resins which would have the greatest impact on the Indian economy. In general, these materials would be large volume general use resins, but not speciality resins.

He agreed with Dr. GRUBER that although the primary goal is the development of resins for composite laminates, it should be realized that some resins may have greater application to other areas, and which may be found to be of no values for laminates. The research therefore should be extended for these other applications as well.

7. NPL Delhi - Dr. SETH

Dr. Seth reported on the work of his team on development of special pitches from coal tars available in India. These pitches should have high carbon yield, but low quinoline insoluble parts. Unidirectionally reinforced carbon/carbon composites were made with these pitches. The density after first carbonization and after several impregnation and recarbonization steps, however, have reached only 1.6. In the Western world carbon/carbon composites are applied with bulk density between 1.8 and 1.9.

In agreement with Professor DIEFENDORF I pointed out the need of optimization of the impregnation pitches and the fabrication processes. We both also proposed to fabricate sample materials with several arrangement of fibres (UD, 2D and 3-dimensional reinforced). Finally, especially Professor DIEFENDORF made the comments that in the United States such carbon/carbon composites were mainly produced for military purposes with the goal of maximum heat transport properties. This development in India is directed to biomaterial, the mechanical properties and especially the modulus should be improved and very precisely controlled.

8. NAL Bangalore

Mr. SRINAGAR reported, that some resins obtained from VSSC as well as from SHRI RAM were tried to test. The sample materials, however, were small in quantities (in the order of 100 to 200 g only) and ill defined (for instance high contents of solvents). Therefore, representatives of this laboratory were only in position to report on the programme they understood since last meeting end of September 1982 . According to Professor DIEFENDORF, the overall programme for testing by NAL seems sound, and well through. Also expert Dr. GRUBER supported the opinion that a minimum quantitiy of 200 g are needed from the laboratories to give a tentative judgement of the usefullness of this special resin development. For more detailed testing larger quantities are necessary which only can be obtained after scaling up. A scaling up however can only be decided if tentative data are available which justify just scaling up effort.

9. University of Delhi - Prof. NANDA

Prof. NANDA reported on the equipment he has available at his institute for the characterization of polymers. All participants and especially the experts were impressed by the amount of sophisticated instruments. The experts expressed the hope that this participant will not be subject to the pitfalls of the computerized instruments. What today's first generation computerized instruments produce has to be examined critically and with much better understanding how these results were generated by the computers. Professor NANDA has performed a four weeks study tour just recently. It is hoped that he will understand the main problems of his special task for active contribution.

1o. <u>National Chemical Laboratory, Poona - Dr. NADKAMI</u>

This instution is not yet participant in the resin programme, but was in discussion to be invited to participate. Dr. NADKAMI referred on polymer alloys. The presentation was very general, and no one was able to find out, what special combination Dr. NADKAMI was planning to develop. The expert, Dr.GRUBER, mentioned, that years ago the leading polymer research laboratories in the United States were asked where the most progress to be expected in polymer science. The result was: not with new polymers but with modificiations,blends(alloys) of existing polymers. So promising these statements were at that time, so little was the success during the following years. Only a very few blends are inpractical application. The expert Dr. ZIMMERMANN mentioned his experiences in HOECHST. 10 chemists worked six years long on the blending and alloying of polymers and produced only two new products based on polymer alloys.

Also in my opinion , this task of blending of polymers (polymer alloys) can be excepted within the resin programme only , if the participants will identify an intended end-product, then establish a product profile and after that try to match it with polymer alloys. The other way, to start a basic research on all possible alloys would be completely wrong because of infinite dimensions and no hope for a practical application of the results.

(2)

Enclosure 4

REPORT ON STUDY TOUR OF DR. R.L. SETH AND DR. O.P. BAHL, SCIENTISTS, NATIONAL PHYSICAL LABORATORY IN CONNECTION WITH WORK RELATING TO RESIN PROJECT ON COMPOSITES.

PLACE: CARBON CONFERENCE AT TOYOHASHI AND VARIOUS RESEARCH AND INDUSTRIAL ORGANISATIONS IN JAPAN.

PERIOD: NOVEMBER 1-13, 1982 PLUS JOURNEY TIME

1. PARTICIPATION IN INTERNATIONAL SYMPOSIUM AT TOYOHASHI

The carbon symposium was attended by 350 delegates [illegible] from overseas. It comprised 6 plenary lectures, about 140 invited papers and 20 poster presentations by leading industries covering mostly new processes and new applications. The topics broadly covered - (a) carbon composites, (b) mesophase pitches, (c) intercalation compounds, (d) surface [illegible], (e) cokes, and (f) various other carbon materials. Over 60 papers were connected with carbon fibres, carbon carbon composites and pitch processing. Carbon-carbon composites were used as materials for biomedical, space and other applications. Use of carbon fibres and carbon fibres based composites for ligaments, dental implants, hip joints (cups, heads and stems), finger, thumb, ultra shoulder and vascular systems was highlighted. Biomedical applications of carbon materials were highlighted by Dr. Huttinger.

The light weight high strength characteristics of the carbon composites materials have been made use of for saving energy in the field of space engineering as aircraft breaking shoe material having low specific weight, excellent refractoriness and high strength. Friction and wear properties of the composites were determined and microstructure of the material examined. The carbon-carbon composites were made from carbon fibre cloth and phenolic resins giving heat treatment even upto 2600°C.

Carbon (graphite fibre) epoxy composite rings were made for use as retaining ring for generator applications. The metallic rings present several problems namely - (1) size limit in respect of [illegible], (2) stress corrosion cracking, and (3) strength/size ratio. The carbon epoxy rings are advantageous over metallic rings. Data regarding use of the rings have been presented paying particular attention to ring [illegible] to the rotor and electrical flow consideration.

Carbon fiber/glass like carbon composites were made using high modulus PAN based fibre and furfuryl alcohol having high mechanical properties specially strength at elevated temperatures. The structural dependence of the material was examined from measurements of thermal conductivity, electrical resistivity and strength. Suitable methods were adopted to measure the properties.

In a composite, the degree of combination that mixes the carbon fibre and a resin matrix determines definitely the qualities of the composite and effective methods of improving the bonding force and interlaminar shear strength between the fibre and matrix play important role. Five methods of surface treatment namely whiskering, oxidation (dry and wet) anodic, monomolecular layer were discussed and wetting affected by this treatment calculated for the fibre. Since sufficient adhesion between the fibre and matrix is a precondition for complete stress-transfer and efficient translation of fibre properties into the composite, it is important that the surface of the fibre be made suitable for resin wetting. Usually the high modulus (graphite) fibre is used for composite forming and the adhesion becomes more difficult the more graphitic is the fibre. The surface treatment must also not destroy the fibre structure in the sheath. The wet and dry oxidation is normally adopted, however the dry method gives very little acidity due to thermal decomposition of the surface groups but wet oxidation is not economically feasible if done for longer duration. Some results on increase in ILSS and flexural strength have been indicated as a result of dry and wet oxidation, the latter being more effective as far as ILSS is concerned.

Use of carbon fibre and pyrocarbon composites as implant materials was made. Dental implants were made and inserted in monkeys jaws and had borne masticatory load for 2 years. The fine Rehmen surface (FRS) can be used as artificial replacement of the skeletal defect that needs strong attachment with living tissues. Studies on magneto resistance of carbon fibre/CVD composites were made.

Raman microprobe studies on carbon fibre-CVD composites was made to monitor separating the graphitisation of the matrix and the substrate observing any influence or interaction between them.

Another important source of carbon matrix in the carbon-carbon composites is the pitch (coal tar, petroleum or synthetic). Several papers connected with pitch processing, modifications (by chemical or physical means) and resulting structure were presented, Role of mesophase, its nucleation, growth, coalescence and alignment were highlighted in large number of papers and how the microstructure of the matrix is affected, thereby modifying the mechanical properties of the composites. The properties of the mesophase pitch such as its molecular structure, mesophase content, molecular weight distribution and rheological properties play important role in determining the strength of the carbon-carbon linkages in the composite. Use of petroleum pitch/coal tar was made to develop crystallinity to the carbon matrix to impart high modulus to the composite. In the case of coal tar pitch solvent fractionization and separation of QI were done at a fast coagulation rate to assist filtration. Pitches from synthetic materials were made and developed into mesophase pitch. Effect of pressure on carbonization yield of pitches and resins such polyethylene, polypropylene PVC, PVNO studied and the carbon spherules examined by SEM. The role of QI in the case of coal tar pitch was studied in detail.

Q.I. role on coke strength, temperature of mesophase formation, ~~thermosetting~~ were important for carbon-carbon composites. Mesophase formation was studied in polynuclear aromatic compounds. The viscosity of the mesophase controls the orientations of the molecular consistuents on the fibre interface and large optical texture matrix carbon results from low viscosity mesophase. Carbonization under pressure or use of high viscosity mesophase precludes the parallel orientation of the matrix carbon in the composite.

Disclinations are essential features of the micro-structure of carbon matrix composition. They are introduced in the formation and deformation of the carbonaceous mesophase, a discotic liquid crystal. The properties of the composites depend upon the microstructure of the carbon matrix and disclinations are expected to play important role in properties such as fracture, graphitisability and thermal expansion. Usually the crack formation follow the basal planes but some cracks do occur normal to the plane layers. The disclinations present in the microstructure in the mesophase contribute to crack blunting, crack diverting and energy absorption which work in high fracture.

Hot stage microscopy has become a powerful tool in studying mesophase nucleation, growth, coalescence and appearance of bulk mesophase. The decrease of viscosity after passing the temperature of intermediate maximum can be observed in situ. There is formation of halo of small size (in the case of acenaphthalene).

MPW particles surrounding mp spherules of about 50 μm act [illegible] as barriers for further coalescence of big spherules. While hot stage microscopy is useful for study of dynamics of mesophase growth, there are certain experimental difficulties such as surface effect of melts, gas bubble formation, thermal convection, condensation of the vapours and overheating of the microscopic equipment.

Chemical treatment of pyrenes and similar compounds such as hydrogenated derivatives are found to affect various roles of early carbonization improving pitch yield and resulting anisotropic carbon. The behaviour of the anisotropic liquid crystal derived from hydrogenated pyrenes were studied in terms of solubility, fusibility, and reconstruction in the recrystallisation process. Use of Friedel Craft reaction using $AlCl_3$ has been made producing anisotropic carbons. There is effect of catalyst amount, refluxing, fractionization and temperature. The optical texture of the carbon is dependent upon the chemical composition of the parent carbonaceous precursor, heating conditions and so on. Pyrolysis chemistry of pitch is of importance with respect to mesophase formation. Hydrogenation of the pitch and its carbonization is associated with hydrogen transfer reactions (hydrogen Shuttling) involving transfer of hydrogen from pitch to reactive radicals in the carbonization process, the hydrogen transfer occuring at the early stage of carbonization.

Strong Lewis Acid promotes hydrogen transfer and results the free radicals stabilization to create the circumstances in which the mesophase development is enhanced.

Pitch fibre has gained momentum in the past 10 years. Mesophase pitch fibre is the formation of structural and preferred orientation carbon fibre from pitch. High performance continuous multifilament fibres from pitch require considerable input and skill and the stage is still far from trivial. Several factors control the success of mesophase based pitch fibres and they are - (1) Use of precursor pitch as capable of forming large domain mesophase, (2) ease of coalescence, (3) speeding up and enhancing uniformity, (4) no ash or infusible solids. The fibres can achieve high strength depending upon various types of structural defects produced during processing. Thus pitch fibres with high modulas and high strength are possible. They are likely to be less costly. Carbon-carbon composites based on pitch have scope in outer space as they have light weight, high stiffness and strength besides high thermal conductivity and low CTE. For possible applications of intercalated wire, high electrical conductivity, low CTE and graphitic character are main considerations which make mesophase pitch based fibres the preferred choice. Thus a rosy picture of pitch fibres in place of PAN fibres for composite materials has been presented. The Union Carbide, USA is making half a million pound pitch fibres/annum.

The Conference was attended by Prof. Otani, Prof. Fitzer, Prof. Marsh, Prof. Bragg, Prof. Mrozowski, Prof. Donnet, Prof. White, Dr. L.S. Singer, Prof. Boehm, Dr. Kelley and several other top carbon scientists.

Another important feature of the carbon symposium was the Poster Session wherein display of several newer carbon artifacts was ~~displaced~~ presented by several research and industrial organizations. Needle coke from coal tar pitch with characteristics superior to that made from petroleum based material was one of the most important items of interest to us. Its density, strength and thermal expansion as well as electrical resistivity values were better and so it could find extensive use in production of high amperage graphite electrodes. The coke was produced commercially from solvent fractionization of coal tar pitch. Other items of interest were continuous silicon fibres activated carbon fibre, newer type of glassy carbons (beads), supreme coke, isotropic graphite, kish graphite, carbon springs and several other items such as related to intercalation, whiskerisation and silicon fibre reinforced composites.

2. VISIT TO TORAY RESEARCH CENTRE

Some new applications of carbon fibres and various characterization techniques for precursor, carbon fibres and composites were discussed in depth. They are interested to collaborate with us to study the compatibility of pitch matrix with their fibres (PAN based). Loudspeaker, special fibre cloth which gives less porosity compared to normal fibre are fascinating. A prepeg more than 1 meter was also shown. So this shows that heavy wt processing of pitch fibre possibility is there and requires engineering endeavour.

Several types of carbon-carbon composites were made for use in fishing, sports and other industrial applications.

3. VISIT TO RESEARCH INSTITUTE OF INDUSTRIAL SCIENCE, [illegible] VERSITY

Prof. Mochida and his group are conducting considerable mount of R & D work on Solvolysis and fractionization of carbonaceous materials including coals, pitches, synthetic pitches and blends. Mesophase development in hydropyrenes was studied using techniques of optical microscopy with hot stage arrangement and Video Recording over a TV screen. Disclinations were visible and their alignment as well as formative was related to conditions of processing and nature of parent compounds. Carbonization techniques using metal bath were simulated to those of delayed coking. Coking was done in a metallic bomb upto 600°C. The pitch fractions were separated from solvents and structural developments in cokes formed studied. Use of catalysts for graphitization of carbon fibres and their influence on mechanical properties was investigated. Most of the work related was done on 5g - 10g scale in

Prof. Mochida laboratory using reactions of hydrogenation and chemical treatment in presence of catalysts which affected hydrogen transfer in the reactions.

4. VISIT TO GOVERNMENT INDUSTRIAL RESEARCH INSTITUTE KYUSHU

Prof. Kobayashi and his research group are engaged in a number of carbon products. The green coke was ground to a few micron size and then compacted into a pellet which was carbonized and graphitised. The effect of quinoline extraction on strength, density and porosity of the compacted pellets indicated improvements. The morphology of the coke powder was also affected by extraction as observed in Scanning microscope. Quinoline extraction removes about 7-10% of low molecular weight fractions. They seem to result in porous structure hindering the direct contact of coke particles. Thus the sintering is affected and densification as well as strength is controlled by quinoline fraction. No binder was used to form the pellets. The effect of boron carbon on graphitisation and densification on pitch coke and glassy carbon was studied below the melting point of boron carbide. Techniques of hot pressing was used. Boron distribution, microstructural change and graphitising degree were determined. Hard carbons containing carbides of boron, silicon and titanium with carbon substrate were also made.

Studies on solvent fractionization and solvolysis of coal and asphaltene fractions were studied for affecting high recovery on a pilot plant scale and structure of the resulting cokes were examined. The solvent fractions (pyridine) of coal tar pitches were used to make mesophase pitch used for drawing the carbon fibre with about 1000 m/minute. Use of wastes such as volcano ash was made to make refractory composites.

5. VISIT TO KOA OIL, OSAKA

There is an active research group at Koa Oil, Osaka. They are working on pitches, cokes and coke based carbon products. Most of the work is related to heavy residues obtained from Arab countries and Indonesia. The formation of needle coke and pitch fibre from the petroleum fraction is governed by several factors such as the viscosity of the mesop [illegible] its asphaltene content, molecular weight fractions and solubility of the mesophase. Their main interest was concentrated in making cokes of lower thermal expansion coefficient and there was a correlation between thermal expansion coefficient of cokes and thermal expansion of graphite rods and their strength and modulus occurs. The laboratory was well equipped for fractionization of pitch extracts from petroleum residues on larger scales including their recovery. Laboratory scale experiments involved coking the residues at 600°C in test tubes. Determination of CTE at higher temperatures was of interest to us.

6. VISIT TO DEPARTMENT OF ENVIRONMENTAL HYGIENE, NATIONAL INSTITUTE OF INDUSTRIAL HEALTH, KAWASAKI, TOKYO

Dr. Y. Matsumura, a student of Prof. H. Takahashi, is conducting studies on activated carbons using electrometric titrations for study of acid-groups on activated carbons and their adsorption behaviour vs surface acidity. The use is mostly for adsorption of organic vapours in higher concentrations. Surface groups were formed by wet and dry methods. Use of carbon fibre was also made for making active carbon but its bulky nature had some drawback prohibiting its wide-spread use for activation but work in this direction is going on. The structural development in carbons affect their activity and this requires further investigations. Some standard activated carbon samples were collected to compare the activity with activated carbon fibres processed at NPL. The investigations of surface groups by automatic titrations is a useful technique with high degree of accuracy and fastness.

7. VISIT TO TOKYO UNIVERSITY

Prof. Takahashi and his group are actively engaged in development of carbon-carbon composites using mesophase beads of coal tar pitch and petroleum pitch. This gives some porosity on processing and in some of applications of biomedical nature, bone plates should have some porosity. Of course, this method may not be of any use for hip joint bones. They are employing adsorption techniques and surface energy measurements including heat of wetting for relating surface activity. Surface studies on activated carbons and carbon fibres are in progress. Work on carbon-carbon composites is of great interest as very little information is reported in literature on this method.

8. VISIT TO GUNNA UNIVERSITY

Prof. S. Otani and his groups are actively engaged in research on varieties of carbon products such as carbons for biomedical applications, carbon diaphragm and electrodes for fuels cells, carbon-carbon composites from pitch fibres and pan fibre including tooth implants, flexible springs, etc. The laboratory is processing synthetic materials such as naphthalene for making carbon fibres by ~~spring which was clearly~~ spinning. The spinning process involves delicate processing requiring strict control of temperature, pressure and viscosity. Fibre spinning was continuous type and the spinnet was of orifice 0.03 mm. Chemical treatment of organic compounds was done to make variety of pitches for varieties of carbons. Carbon implants for dental applications is almost complete, studies on mesophase pitch, catalytic graphitisation and carbon fibre for battery are also in progress.

9. DISCUSSION WITH PROF. YOSHIDA OF TOKYO INSTITUTE OF TECHNOLOGY

They are making composites using phenolic resins as well as pitches including those made from synthetic compounds. The role of the matrix was particularly explained by Dr. Yoshida for ultimate performance of the composite. Use of carbon-carbon composites for biomedical and space applications was discussed. It was pointed out that pitch based composites had tremendous scope owing to high temperature stability, flexibility and perhaps low cost.

Most of the organisations visited were equipped with equipments used for characterising both chemically and physically the raw material, products and composites. Even sophisticated physical tools such FT(IR), Raman spectroscopy and high temperature testing were available.

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