

Future Trends in Polymer Science and Technology

Polymers: Commodities or Specialties?

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Achievements of the "Finalized Project on Fine Chemistry" in the Sector of Polymer Chemistry: University-Industry Research Relationships

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INTRODUCTION

The present conference "Future Trends in Polymer Science and Technology; Polymers: Commodities or Specialties?" is taking place almost a year before the termination of the Finalized Project on Fine Chemistry (FPFC) of the CNR in which the sub-project Polymeric Materials (SPC) operates. (FPFC started in July 1980 and will officially stop operating halfway through 1985.)

Meanwhile this Conference undertakes a very important role insofar as it contributes to identifying current research and future trends in the field of the science and technology of polymers. Furthermore it gives us the opportunity of discussing the actual status of the research programmes sponsored by the FPFC in the polymeric materials field. Interesting comparisons may therefore be made with international trends, which will emerge during the course of the lectures presented here.

These comparisons will, I hope, lead to suggestions useful for the identification of the most important research lines to be jointly pursued by both academic and industrial groups, in the framework of organizing a second FPFC.

For the attainment of these objectives it is useful to remember the reasons which have led to the organization (within the FPFC) of research activities in the polymeric material sector, the type of articulation and researches activated, as well as the national industrial context in which they are framed.

1) Characteristics of the Italian Polymeric Material Industry and Future Prospects of Development in an International Competitive Context

The sector of polymeric materials (including plastics, elastomers and fibers) represents about 20% of the turnover of the overall Italian chemical industry (see Figure 1).

In this sector Italy holds one of the first places as far as world classifications of production volumes are concerned. Notwithstanding this fact, the sector is characterized by a large presence of foreign companies and this underscores the fact that Italian companies are unable to satisfy the large consumer demand on the home market (see Figures 2 and

COMPOSIZIONE % DELLA CIFRA D'AFFARI
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BREAKDOWN OF SALES ACCORDING TO MAJOR
SECTORS OF ACTIVITY AS A PERCENTAGE OF
TOTAL SALES IN 1983

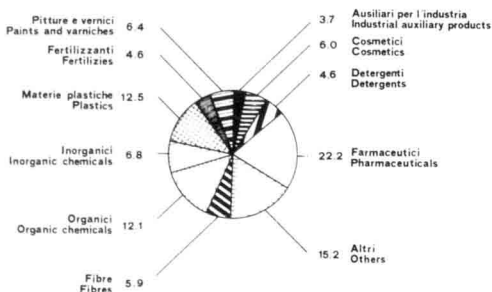


Figure 1. Breakdown of sales of Italian chemistry industry according to major sectors of activity as percentage of total sales in 1983.

3) and by an overall balance of payments which was nearly always negative during 1979 - 1983 (see Figures 4a through c).

The production of polymeric materials in Italian industry is disproportionately weighted to "commodity" or "bulk" plastics and penalizes special polymers (see Figure 5). The latter consideration applies to the whole national chemical sector as illustrated in Figure 6 where the production mix between commodities and specialities of Montedison is compared with that of some worldwide chemical industries.

Halfway through the 70's the European plastic material industry (Italy included) went through the heaviest crisis it had ever known. The extrapolation of early 1970 data for

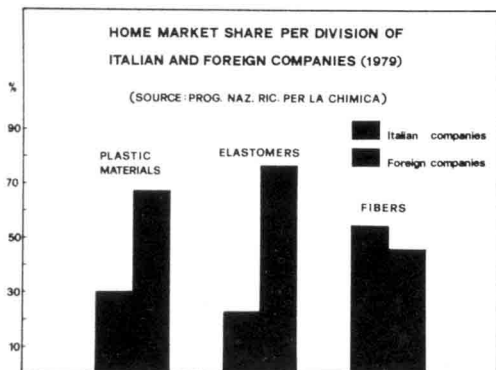


Figure 2. Home market share per division of Italian and foreign companies (1979).

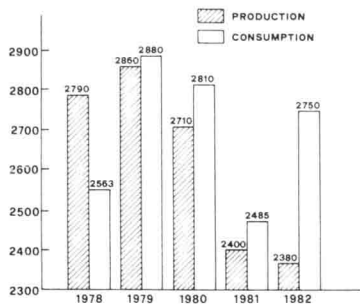


Figure 3. Trend of production and consumption of plastics in Italy over the years (thousands of tons).

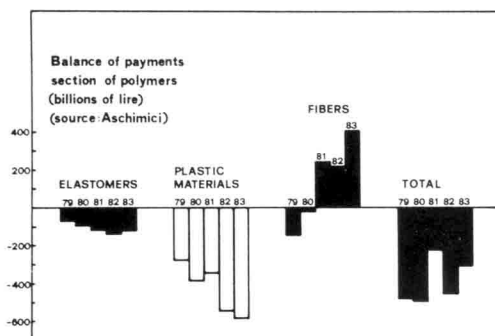


Figure 4a. Balance of payments of polymeric materials sector.

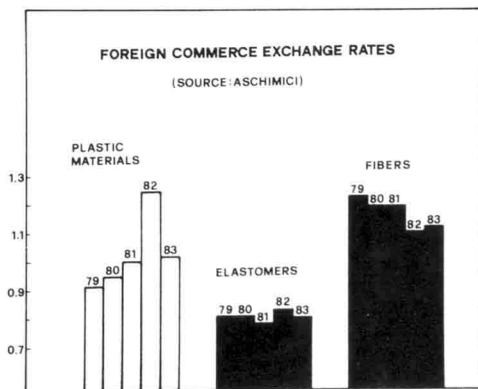


Figure 4b. Foreign commerce exchange rates.

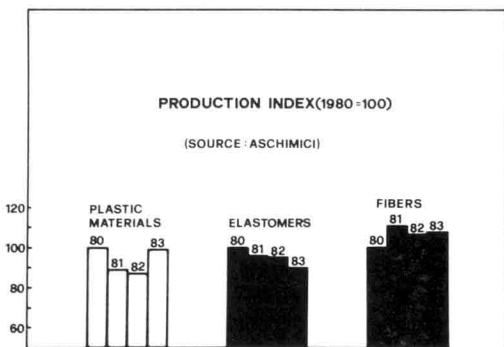


Figure 4c. Production index.

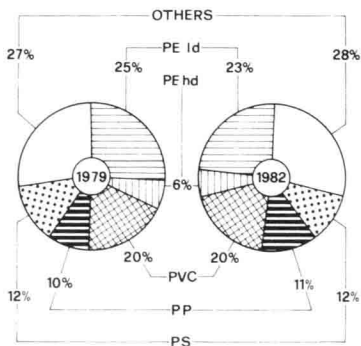


Figure 5. Breakdown of sales according to different thermoplastics, in Italy, over the years 1979 - 1982.

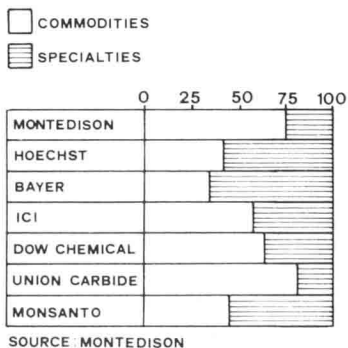


Figure 6. Between commodities and specialties in some chemical industries (1981).

the definition of objectives and strategies was the basic cause of this crisis, as this approach led to a far too optimistic forecast regarding market growth.

Consequently enormous new production plants for plastics (mainly bulk and commodities) were built, but unfortunately forecasts were proved completely wrong. The reasons may be found in the following facts:

- i) The general economic crisis all over Europe in relation to the first energy crisis.
- ii) Concentration of demand after the recession in some important sectors.

Another reason is that many important sectors for the application of commodity-type plastics had been completely opened and as a result the demand could only grow if respective industries expanded their actual market. This indicates that the turnover of commodity plastics is strictly dependent on the general economic trend. Signs of recovery have been observed since 1983. In fact this upward inclination in the European Plastic Material and Chemical Industry in general has reached a peak with a record in production of almost 13.3 million tons. However, this tendency must not be considered a turnabout but an interlude, of which advantage must be taken to improve the efficiency of plants and to eliminate excess capacity.

A steady recovery in the sector and the increased competitiveness of Italian industries on an international scale has provoked the start of vigorous innovation in both processing and products. This intervention cannot be further postponed and must foreshadow a change in the type of production whereby the predominating factors will be quality, suitability and performance.

The development of basic polymers should still be pursued, but above all great attention must be given to those special products having high mechanical, thermal and conducting characteristics.

In a country like Italy, advanced in technology but deficient in raw materials, the polymer chemistry industry should prevalently direct its steps toward the development of special polymers so as to reduce ever increasing competitiveness from developing oil producing countries. The low profitability in the commodity plastics business and the increasing threat of exports from the developing world means that companies in the sector (especially those belonging to non oil-producing countries) would look even more towards high performance plastics as a means of reducing the threat to their business.

In accordance with the principles of the international breakdown of labour it won't be long before the Italian Industry of Polymeric Materials mainly imports bulk plastics instead of actually producing them (with some exceptions due to the high degree of technology reached in some processes, for instance, in the case of polypropylene). It should concentrate on manufacturing specialities. Forecasts regarding the development of the Polymeric Materials Industry all conclude that the growing use of speciality polymers and their modified compounds as structural replacements for metals in the automotive, aerospace and construction industries will stimulate demand for these products at a very rapid rate over the next years. World producers of polymeric materials are preparing producers for a fundamental transformation; after an uncontrollable post-war quantitative expansion the sector must switch to a qualitative evolution, constantly concentrating production on high performance products for specialized and sophisticated applications.

The general trend for relaunching the sector is to pursue a strategical and technological innovation policy, particularly in the field of special polymers. Because the production of commodity plastics cannot be abandoned in the immediate future, the strategical and technological innovation policy for such materials should be aimed at the individualization of new models by using the instruments of Joint Ventures (see the

agreement between Hercules and Montedison in the case of polypropylene), with the objective of achieving a geographical presence on a worldwide scale. At the same time an effort should be made to reduce production costs.

The development of a competitive industry for special polymers at an international level must necessarily foresee the conversion of industries from "consumer" of technological innovations to "producer" of technological innovations.

This type of conversion can only be reached through enormous investments in research and development, which must have as an objective not only "know-how" but "know-why."* Public Research Institutes such as the CNR must actively participate in this enormous need for research in agreement with the fact that the main task of the CNR should be the development of a fundamental scientific culture contributing to technological innovation in priority sectors vital for the socio-economic progress of the nation.

It was this philosophy in the early 70's which led to the organization of "National Finalized Research Programmes" under which the FPFC and the sub-project polymeric materials have operated since 1980.

STRUCTURE AND EVOLUTION OF THE SUB-PROJECT "POLYMERIC MATERIALS": EVALUATION AFTER FOUR YEARS

The overall structure of the FPFC is schematically shown in Figure 8. The sub-project "Polymeric Materials" was born with the aim of contributing to the formation and development of a fundamental background, with the purpose of giving support to research activities having applicative interest.

Large research efforts, never attempted before, were undertaken in fields where the

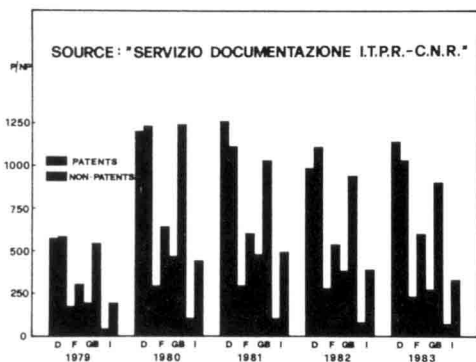


Figure 7. Number of scientific papers and patents of major West European countries over the years 1979 - 1983.

*The fact that in Italy there is the necessity to develop further research efforts in the sector of polymeric materials clearly emerges from the data shown in Figure 7 where the number of scientific papers and patents of major Western European countries is compared over the years 1979 - 1983.

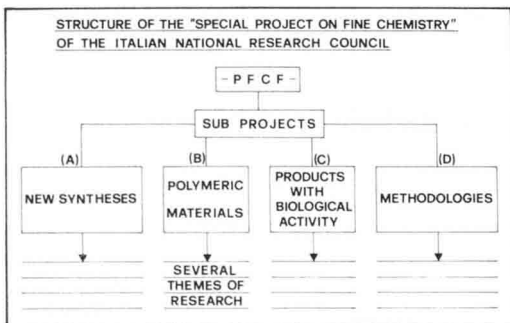


Figure 8. Overall of finalized projects on fine chemistry of Italian CNR.

Italian industry was traditionally present and highly active, in order to enlarge the basis of fundamental knowledge. At the same time research activities in highly innovative fields were started with the aim of constituting the cultural basis for possible interventions of the national industry in new and highly competitive sectors.

Following this philosophy, topics and research-lines were identified and activated, taking mainly into consideration input coming from the world of production. Teams were constituted including researchers belonging both to academy and company laboratories.

The overall structure of the sub-project "Polymeric Materials" and its evolution over the years is illustrated in Figure 9.



Figure 9. The structure of the sub-project "Polymeric Materials" and its evolution over the years.

Details of the research, relative objectives and principal results achieved for each topic will be illustrated during the Conference by the coordinators of the main themes.

On the whole the main effect of the research was aimed, on the one hand, at acquiring basic knowledge for the understanding of fundamental aspects of the chemistry and technology of polymers and, on the other hand, at contributing to the realization of new materials having special performances i.e., Speciality Polymers.

After 4 years work we may affirm that all activities developed have on the whole corresponded to the demands of national research with overall objectives in line with up-to-date international tendencies in the science and technology of polymeric materials.

Funds allotted for research activities of the Polymeric Materials sub-project, have grown over the years, moving from 850 million Lira in 1980 (funds refer to only half-year periods) to about 5.6 billion Lira in 1984. In terms of percentage compared to three other sub-projects the allotments rose in 1980 - 1984 from 19% to about 27% (see Figure 10).

In the period 1980 - 1984 an overall total of about 16.6 billion Lira was spent for research, about 4.8 of which was earmarked for equipment. These appropriations, relative to the investment items, have helped to renovate and improve the Italian "big facilities" park in this sector.

As shown by Figures 11 and 12 the number of researchers (usually expressed in terms of equivalent researchers (ER) and of operating units (OU)) has progressively grown from 1980 to 1984. 1980 ER = 128; OU = 77; 1984 ER = 449; OU = 183). The large participation of private and public company groups in the research activities must be pointed out.

The geographical distribution of the operating units is illustrated according to each institution in Figure 13. It is interesting to note how most of the industrial OU are concentrated in the North of Italy, in particular Lombardia and Piemonte. Even though large companies are present in the South, with large industrial plants, they do not develop any research activity in this part of the country. In the case of the small/medium companies situated in the South their deficiency is due to a low technological level and an insufficient awareness of the importance of research as a source of technical innovation. As shown by the data of Figure 14, where the distribution of the dimension of companies in terms of number of employees, is illustrated, together with the most important firms of

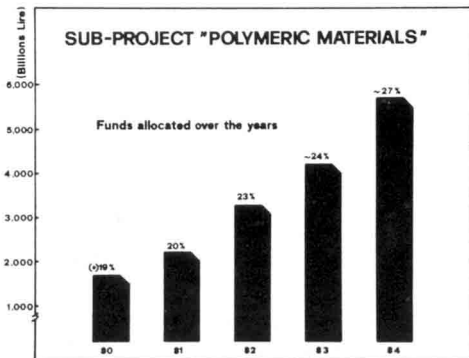


Figure 10. Funds allocated to the sub-project polymeric materials over the years.

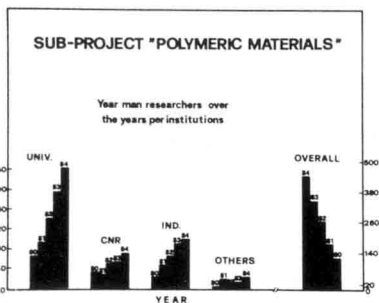


Figure 11. Years mass researchers, over the years, per institutions.

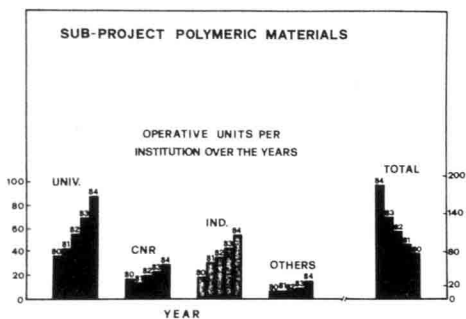


Figure 12. Number of operating units, over the years, per institutions.

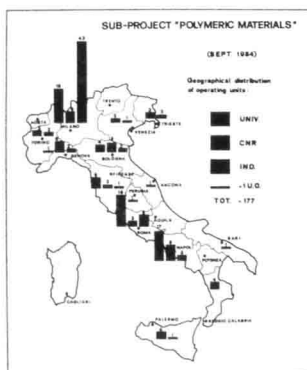


Figure 13. Geographical distribution of the operating units per institution.

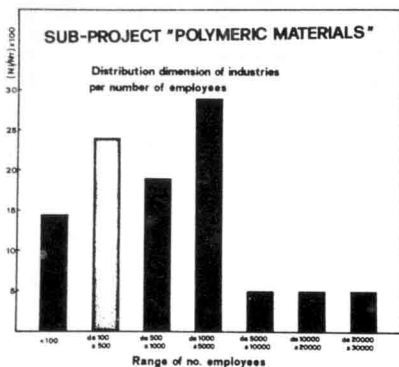


Figure 14. Distribution dimension of industries, operating in the sub-project "Polymeric Materials," per number of employees.

the sector (ENI, Montedison, SNIA etc.) many small and medium companies participate with their groups of research in the sub-project's activities.

An analysis of the quantitative participation of Research Groups for each institution allows us to draw the following conclusions:

- i) As far as the University and CNR are concerned it is possible to note how almost all groups working in Polymer Chemistry and Technology have joined the sub-project since 1980. The number of groups interested in polymer chemistry and technology belonging to CNR and the University is larger when compared to that of 1980.
- ii) Small and Medium Companies seem to have invested more in their research potential, whereas large companies tended to engage only a small part of their overall capacities.

After more than four years of activity it is possible to make a first significant summary and critically analyse the evolution of research and all the problems which have arisen and to express a general evaluation.

As shown in Figure 9, updated in September 1984, more than 260 papers of a good scientific level have been published (mostly in international journals). Most of these works are the result of collaboration between groups from different institutions (CNR, Universities, Industry). More than 30 patents have been registered, and some are being developed in various Italian companies (some also in foreign companies).

During the course of these four years technical know-how has been consolidated in new sectors thanks above all to the development of interactions between operative units working in public research institutes and in the laboratories of industry.

Academic research centers and their groups have often reoriented their research, converging on topics of major applicable interest while receiving part of the input from the industrial world.

The project has favoured, through the activation of new research topics and the purchase of equipment of high technology, the formation of highly specialized centers, where new skills have been developed and old skills consolidated.

In general, the results of the project can be considered satisfactory which leads me to

believe that at the end of the finalized project the knowledge which will have been acquired and consolidated will have certainly re-paid this great financial and organizational effort.

The spirit of collaboration between public and private components has helped to arouse consciousness, especially in the small and medium industries, of the vital importance of research as an essential contribution to technological innovation.

Most of the scientific results are the outcome of a strong collaboration between operating units of the CNR, University and Industry. This has given rise to a very positive evolution in the relationships between public research and industrial research, thus allowing and facilitating the transfer of knowledge, which is often the essential presupposition to develop follow-up interventions of research for technological innovation.

The degree of integration which has been developed over these years between public institutions (University and CNR) and research structures of large, medium, and small industries in the field can still be consolidated. The 5 year duration of the project represents too brief a period of time and does not allow the full development of all the operations, or interventions begun, and a harvest of the fruits.

However on expiration of the present project we firmly hope that a "Second Finalized Project on Fine Chemistry" will be launched. This will allow us to reach objectives and thereby recompensate such a great organizing and financial effort.

This experience is considered very positive by both the academic and industrial world. To avoid dissipation of their efforts and results, all researchers working on the FPFC generally agree to the activation of a second FPFC. An introductory study has already been undertaken and only just recently approved by the CNR, thanks to the positive action of the Chemistry Committee. We are now waiting for the appointment of an ad-hoc committee for the elaboration of the operating research project. Our particular recommendations therefore to the President of the CNR, to the Minister for Scientific and Technological Research and to the President of Chemistry committee of CNR are that operations may quickly begin.

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Present and Future Trends of Composite Materials with Unsaturated Thermosetting Matrix

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The first composite materials to find industrial application were those with a thermosetting matrix (phenolics, amino and furane resins). In these last years, the highest increase has been in the field of composites based on unsaturated and on epoxy matrices. Epoxy composites have been mainly developed in specific fields (aeronautics, electro technicals), while unsaturated thermosetting composites have found a wide application in many different fields, such as the automotive and building industries, agriculture, electronics and industrial installations. Unsaturated thermosetting matrices can be defined as polymers with carbon-carbon double bonds which can be copolymerized with unsaturated monomers (usually styrene) to give crosslinked tridimensional networks. These polymers, like other thermosetting resins, have relatively low molecular weights, since they are dissolved in styrene: these solutions must have viscosities suitable for a good impregnation of the reinforcing fibres. The range of molecular structures is wide, as it is easy for the chemist to tailor-make them to the processing requests and to the desired final properties of the manufactured piece.

1. MOLECULAR STRUCTURES OF UNSATURATED THERMOSETTING RESINS

The most widely used molecular structures are rather complicated (Fig.1). Structure A is an outline of an unsaturated polyester obtained by reacting phthalic and maleic anhydrides with dialcohols (propylene glycol, ethylene glycol, diethylene glycol, dipropylene glycol, etc.). Many are the possible structural variations. For instance, by increasing the ratio of maleic anhydride to orthophthalic acid, the cross-link density of the polyester-styrene copolymer increases, consequently leading to higher values of heat distortion temperature (HDT) and of stiffness. Using dialcohols with a longer chain, the width of the tridimensional lattice is increased and so is the deformation under load of the cross-linked resin. Structure B represents an isophthalic acid-based unsaturated polyester obtained by a two-stage process: first stage reaction between isophthalic acid and dial-

3. NEW TYPES OF THERMOSETTING MATRICES

Research has been carried out in our labs on the syntheses of new molecular structures in order to improve the performance of the matrices. Some theoretical structures are outlined in Fig.2. The dicyclopentadiene-based polymer (Structure F) has been synthesized in our labs to take advantage of the fact that dicyclopentadiene can add terminal carboxyl groups and, under suitable conditions, decompose into cyclopentadiene.

Under controlled reaction conditions it is possible to produce unsaturated polymers with terminal dicyclopentadiene and cyclic structures in the chain, owing to endomethylenetetrahydrophthalic anhydride obtained by Diels-Alder reaction of cyclopentadiene on maleic anhydride.

When the formation of cyclic structures is promoted, it leads to an increase in the heat distortion temperatures, whereas when the addition reactions are promoted end-type dicyclopentadiene molecules are introduced into the chain which on one hand lower the molecular weight, but on the other hand introduce a highly reactive double bond (easily copolymerizable by UV curing). The resulting structure has a solubility parameter very close to styrene and therefore an increased affinity with it. This fact makes these polymers particularly suitable to dramatically reduce the amount of styrene evaporated during copolymerization in the transformation processes, since a lower amount of styrene is required in comparison with conventional polymers. The lower the amount of styrene used, the lower the amount evaporated.

Structure G shows an epoxyacrylic or vinyl ester resin obtained by reacting the oxirane rings of epoxy resins with unsaturated carboxylic acids (acrylic acid, methacrylic acid, half esters of maleic acid, etc.). Examining these structures, the following considerations can be made:

- a. These polymers have the basic structure of the starting epoxies, but they copolymerize through double bonds, while epoxy resins add to the oxirane ring cross-linking agents with active hydrogen atoms.
- b. In comparison with unsaturated polyesters, they have ether bonds, few ester bonds, high level of aromatic rings.
- c. The unsaturated carbon-carbon double bonds are always at the end of the molecule.
- d. By varying the molecular weight of the starting epoxy resin, the distance of the reactive unsaturations can be changed and consequently the lattice width.

We have synthesized in our labs a wide range of products which, after copolymerization with unsaturated difunctional (styrene) or polyfunctional (polyacrylates and polyallylic) monomers, show some features interesting both for the type of processing (for instance, easy cross-linking by UV curing) and for the final properties of the composites obtained (good mechanical properties, high elongation at break, high heat distortion temperature).

Structure H outlines the possibility of modifying G-type structures by reacting the hydroxyl groups distributed in the chains of the base epoxy resin with other monomers; for instance with anhydrides to obtain carboxylated polymers which can be thickened with MgO and used as matrices in SMC and BMC.

Structure I shows new polyurethane-type products with unsaturated cross-linkable groups. A variation of the starting alcohols and isocyanates leads to the synthesis of a great variety of polymers with interesting properties, in particular with

regard to wettability and adhesion of the resins to glass fibres. It may be seen that there are many possibilities of making new structures or of modifying existing products.

Structure I shows how it is possible, to obtain tridimensionally cross-linked matrices containing imide-type rings through double bonds polymerization reaction. Fig.2/A shows the mechanical properties of these new structures.

4. INVESTIGATIONS OF MATRICES BY GEL PERMEATION CHROMATOGRAPHY (GPC)

GPC has proved to be a very important investigation technique for unsaturated thermosetting resins, both for synthesis and molecular characterizations.

Fig.3 shows as an example the values of number average (M_n) weight average (M_w) and zeta average (M_z) molecular weights for some of our typical commercial products.

It is well known that these quantities are connected with some properties. For instance, tensile strength is correlated with M_n . Melt and solution viscosities are more dependent on M_w , while M_z is correlated with the viscoelastic properties. It is evident that a knowledge of these quantities is of great help in the development of existing products and of new ones. GPC analyses have proved extremely important for correlating "thickening" rates of sheets of reinforced unsaturated polyesters (SMC) in the presence of second-group alkali metal oxides or hydroxides. It is well known from literature that polyesters, through the oxygen atoms of end-type carboxyl groups, make co-ordination complexes of different kinds with metal compounds or metal ions according to the scheme shown in Fig.4. The strong molecular weight increase due to these reactions leads to a fast and considerable increase in viscosity. While it is well known that thickening rate is correlated with the amount of water (Fig.5) we have found that it is also correlated with M_z and M_w (Fig.6).

5. COPOLYMERIZATION INITIATORS

Unsaturated thermosetting matrices, dissolved as stated in unsaturated monomers (usually styrene), are pasty liquids with relatively low viscosities at room temperature, which can be cured or cross-linked through free radical polymerization. Free radicals for initiating the polymerization process usually originate from organic peroxi initiators which are added to the resins. Some unsaturated resins are also polymerized by UV curing: visible light cross-linking reaction is also at an advanced stage of investigation

Two initiation types are known:

- initiation through redox mechanism
- initiation by thermal decomposition

Initiation through redox mechanism

This technique is normally used to generate free radicals and have at room temperature the polymerisation reaction, which would not take place with peroxides, owing to their high thermal stability. The mechanism is based on the reaction of some peroxides with specific promoters or decomposition accelerators.

The most used peroxides are ketoperoxide and hydroperoxides, whose structures are shown in Fig.7. Promoters or accelerators are transition metal (cobalt) salts or tertiary aromatic amines (dimethylaniline): reaction mechanisms are also shown in Fig.7. Cobalt salts, also in their oxidised form, can decompose the initiators (reaction 2). Reaction 3 shows that free radicals can also be destroyed by cobalt: it is therefore necessary to work with an optimised promotor quantity, as experimentally proved. Reaction 4, on the other hand, shows that decomposition of benzoyl peroxide into free radicals can only take place through complex formation with dimethylaniline. Recent studies have demonstrated that the cross-linking properties of methylethylketone peroxides greatly depend upon the composition and the nature of the unsaturated resin. The lower the amount of dimer form in the initiator, the shorter the curing times in orthophthalic resins; the opposite is true for vinyl ester structures. Attempts have been made to replace disubstituted aromatic amine - type promoters (owing to their toxicity) with special amides derived from acetoacetic acid: first results are quite promising.

Initiation by thermal decomposition

Thermal decomposition of most peroxides is a first order reaction, i.e. reaction kinetic is proportional to the reactants' concentration. The main quantities to be taken into consideration are the half-life time as a function of the rate constant and the activation energy.

$$t \frac{1}{2} = \frac{0,693}{K} \quad K = A e^{-AE/RT}$$

Peroxides with a lower activation energy have a more uniform decomposition rate in a wider temperature range.

A practical quantity useful for selecting the most suitable initiators for moulding, is the temperature at which their half-life time is 10 hrs. Fig.8 shows the most significant initiators, among which particularly interesting are the new perketals and di-tertiary-butylperoxides, whose stability depends on the nature of substituents R1 and R2. The higher the electron-donor effect, the lower the stability. Further research has proved that mixtures of initiators can give optimal results, which cannot be achieved with single initiators.

Kinetic studies by Differential Scanning Calorimetry (DSC)

In our previous works we have shown the importance of copolymerisation conversion, obtained from DSC data, on the mechanical properties of one of our unsaturated polyester resins of isophthalic structure (Fig.8A). It can be seen from the figure that tensile strength (TS) tensile modulus (E) and heat distortion temperature (HDT) increase with an increase in the degree of conversion (degree of curing) and reach the maximum values only for a degree of conversion (A) of 99.5%. The percentage elongation at break already reaches a maximum at 99% conversion. We have reported previously (Fig.8B) that glass transition temperature (Tg) increases with A, up to 100% conversion. We have also found that, when the thermal cycles are continued beyond 100% conversion, Tg keeps rising. Within the CNR programme, in our labs we have carried out more detailed investigations on polymerisation Kinetics via redox initiation and via thermal decomposition of peroxides, with the aim of obtaining fundamental information for future developments of com-

posites based on thermosetting matrices. Basic knowledge of this type is essential for the development of processing techniques and for the improvement of the final products' performance.

Kinetics of redox polymerisation

Copolymerisation of unsaturated isophthalic polyesters with styrene in the presence of promoters (cobalt octoate) and with different initiators, has been observed with a differential calorimeter operating under scanning conditions (DSC). In this way we were able to obtain typical temperature data such as polymerisation start (PS), polymerization end (PE) and maximum polymerization rate (MPR). With a computer we have also calculated the decrease of polymerization enthalpy (ΔH_p), the activation energy (AE) and the logarithm of the rate constant ($\ln k$) as a function of temperature.

Fig.9 shows the data for an unsaturated isophthalic polyester dissolved in styrene and treated with a promoter and different initiators: methylethylketone peroxide, tertbutylperoxyisobutyrate and a mixture of the two. With methylethylketone peroxide (System A) copolymerisation starts at 24°C and ends at 155°C with an enthalpy decrease (ΔH_p) of 212 J/g.

With tertbutylperoxyisobutyrate (System B) initiation reaction takes place, as could be expected from half-life data, at a higher temperature (85°C). The activation energy is much higher (116 KJ/mole vs. 34 KJ/mole for System A). This means that reaction rate of System B is more sensitive to temperature changes. System C, i.e. the mixture of the two initiators, leads to a two-stage kinetic. There is a first reaction starting at 25°C and ending at 85°C with much lower enthalpy decrease ($\Delta H_p = 15$ J/g vs. 212 and 84 J/g of System A and B).

The second reaction starts at 85°C with an enthalpy decrease of 60 J/g. With System C the total enthalpy decrease amounts to 75 J/g. It is well known that high ΔH_p values during polymerization cause internal stresses in the laminate and consequently poor mechanical properties and fractures.

Fig.10 shows the variation of the rate constants with temperature. It can be seen that copolymerization with methylethylketone peroxide (Curve A) is faster than the reaction initiated by tertbutylperoxyisobutyrate (Curve B). It should be emphasized that the slope (i.e. the activation energy AE) of Curve A is lower than the slope of Curve B, and this means that co-polymerization reaction, initiated with methylethylketone peroxide, is less dependent on a temperature increase.

Two reactions (Curves C1 and C2) are observed when mixtures of the two catalysts are used. At temperatures above 30°C reaction C1 is faster than System A, whereas reaction C2 is slower than System B and takes place only at relatively high temperatures. From calculations, at 30°C reaction rates C1/A/B are (when C1=100) in the following ratio: 100/47/0.37. At 70°C ratios C1/A/B/C2 are as follows: 100/0.08 0.008/0.001.

Reaction C2 at this temperature is so slow as to be negligible, and so is the enthalpy variation. From this observation it can be seen that a knowledge of the reaction kinetic and parameters is important in order to achieve a high reaction rate with low heat development.

Fig.11 (equations 1,2,3,4 and 5) shows the equations used for calculating the activation energies (AE) and the conversions (α) vs time. For the above system A, B and C, knowing the rate constants at different temperatures (Fig.10) we have calculated the conversions vs. time and temperature (Fig.12).

These data are very important for the study of processing and transformation parameters. In Fig.13 is shown another example of kinetic control. Other systems have been examined and the influence of accelerators based on copper compounds has also been evaluated. It can immediately be seen that use of these compounds leads to two reactions, both with System A (with methylethylketone peroxide) and with System B (with acetylacetone peroxide). A first reaction with lower PS, much lower ΔH_p (44 J/g for System A1 vs. 188 J/g of System A and 47 J/g of System B1 vs. 115 J/g of System B); the second reactions (A1(2) with PS 123°C and B1(2) with PS 87°C) have negligible rates as shown in Fig.14.

The use of a mixture of the two peroxides, still with Cu complex (A1 and B1) lowers the reaction starting temperature; it slightly reduces ΔH , in comparison with A1 and B1 and strongly compared with A+B (38 J/g vs. 233 J/g of A+B). On examining the rate constant curve vs. temperature (Fig.14) it can be seen that copper-based systems show a higher rate than copper-free systems. The rate constants ratios B1/A1/A/B at 50°C, according to calculations (when B1 = 100), are 100/52/12/02.

The second reactions rates of the copper-based system A1(2) and B1(2) and (A1+B1)2 are negligible. In fact (when A1 + B1 = 100) the rate constant ratios A1 + B1/(A1+B1)2/A1(2)/B1(2) at 80°C, from calculations are 100/0.028/0.026/0.016.

Morphological investigations

The importance of wettability and adhesion of the matrices to the glass fibres used as reinforcement in the composite is well-known. Insufficient wettability and adhesion of the matrices to the reinforcement are believed to be responsible for the unsatisfactory mechanical properties of the composite and for microfractures, which take place when the manufactured piece undergoes dynamic stresses. A knowledge of the parameters regulating fibre wettability is of fundamental importance. In order to obtain a good adhesion between reinforcement and matrix it is essential (though not sufficient) that the reinforcement surface be wet. Good adhesion should be obtained when the cosine of the contact angle ($\cos \theta$) approaches unity, that is, θ approaches zero. When $\theta = 0$ maximum wettability is achieved. A good adhesion, when the surface is wet requires a good interaction between forces of the same type on the fibre-matrix contact surface. This means that there must be interactions between the dispersion, hydrogen bond and polar forces, having respectively a surface energy of E_d , E_h , E_p . As part of the research carried out by CNR and the general investigations on the factors influencing the fibre-matrix adhesion at CNR labs of Arco Felice, a study was made on the wettability of some unsaturated matrices on commercial glass fibres sized in different ways.

First investigations were carried out by measuring the contact angles, using optical microscopy with the "tangent method": this consists of observing the profile of a drop of resin on the fibre under testing and measuring the contact angle. Fig.15 shows the contact angles for each type of fibre vs. different resins. The following considerations should be made on the results obtained:

- The results obtained have to be considered only qualitative, as also seen from the dispersity of the data. This can be explained by the type of investigation method, as well as the non-homogeneity of the sizing of the fibre under testing.
- The measurements were taken by extracting from the strand (a combination of single filaments) a single sized filament, damaging in this way its uniformity,

which is essential for the reproducibility of the results.

c. Even though on a qualitative basis, the results are promising and lead to the following considerations:

1. Wettability depends on both sizing and resin types.

2. There seems to be no correlation between percentage of unsaturation (C=C % in fig.15) and wettability.

3. By increasing the amount of styrene, the contact angle is reduced, in this way improving the wettability.

4. The cohesive energy density and solubility parameter, which we have theoretically calculated, could have an influence provided that wettability takes place when the sizing is dissolved. The sizing is dissolved if its cohesive energy density or its solubility parameter are similar to those of the matrix. This idea is attractive, and research is continuing at SAVID and CNR labs to confirm its validity, with a more sophisticated technique. With the same unsaturated polyester-based matrices and glass fibres used in the study of wettability, we made SMC formulations with the following ratios: unsaturated polyester in styrene, polyvinylacetate, fillers, glass, equal to 37/3/10/50. Morphology studies of said composites compression-moulded, have been carried out at CNR labs of Arco Felice, by scanning electron microscopy (Philips SEM 501). We have examined a wide range of specimens taken from the most significant areas of the moulded piece (curves, ribs, flat surface and so on). Four photomicrographs are given of two composites which differ only for the molecular weight of the unsaturated polyester matrix. It can be seen from a comparison that composite no.2 has a better fibre-matrix adhesion than no.1 both in Section 2F (parallel to the rib) and in Section 2FC (perpendicular to the rib). The better adhesion of no.2 explains its better impact resistance than no.1. Correlations with contact angles were not found, also because the applied methodology was not the most suitable. An improvement in this technique is under way: first results appear promising and lead us to expect a correlation between polymer structure and wettability.

CONCLUSIONS

We believe that the development of thermosetting composites depends not only on the synthesis of new structures, but also on advanced studies on the characterization of the matrices, of curing kinetics, and of interfacial and morphological phenomena.

These studies, rapidly developed in many countries, are fundamental for a radical improvement in the performances of composites with a thermosetting matrix.

FIG. 1 TYPICAL STRUCTURES OF UNSATURATED THERMOSETTING MATRICES

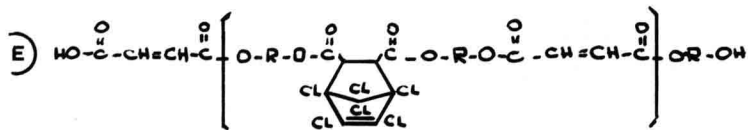
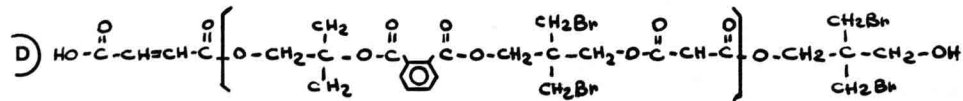
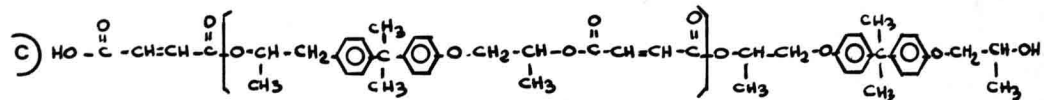
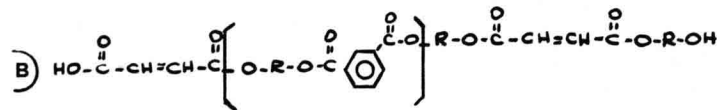
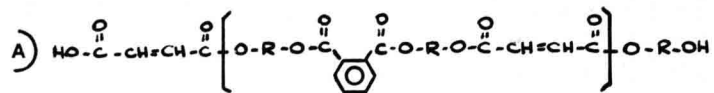
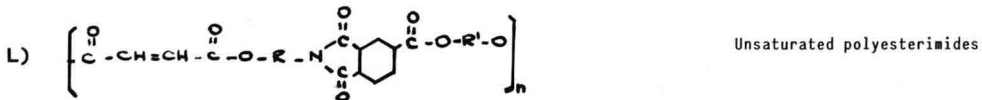
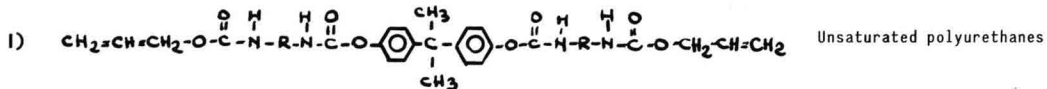
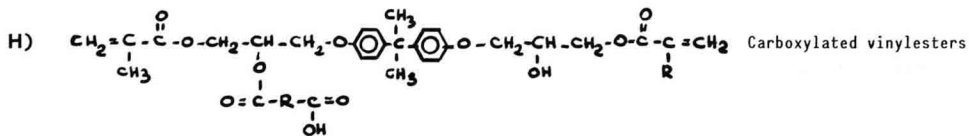
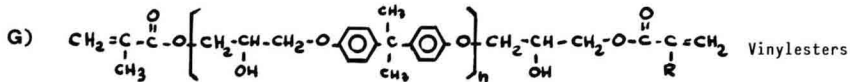


FIG.2 STRUCTURE OF NEW UNSATURATED THERMOSETTING MATRICES



RESIN TYPE PROPERTY	Epoxyacrylic LMW	Epoxyacrylic MMW	Epoxyacrylic C T B N	Unsaturated Polyurethane MDI	Isophthalic Polyester	Orthophthalic Polyester
Tensile strenght (MN/m^2)	80	70	70	85	70	67
Tensile modulus (MN/m^2)	4.100	3.700	3.500	4.000	4.100	4.500
Flexural strenght (MN/m^2)	125	130	110	135	120	105
Flexural modulus (MN/m^2)	3.850	3.400	3.400	3.600	3.800	4.100
Elongation at break (%)	2,8	6,3	5,6	3	2	1,8
H D T ($^{\circ}\text{C}$)	135	90	85	93	115	60

FIG. 2/A MECHANICAL AND THERMAL PROPERTIES OF NEW MATRICES AND OF CONVENTIONAL UNSATURATED POLYESTERS

LMW = Low Molecular Weight

MMW = Medium molecular Weight

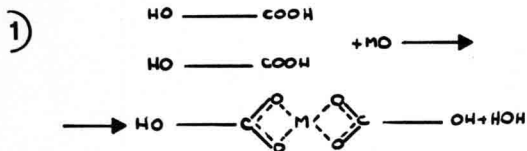
CTBN = Carboxy Terminated Butadiene Acrylanitrite Rubber modified

MDI = Methylenediisocyanate

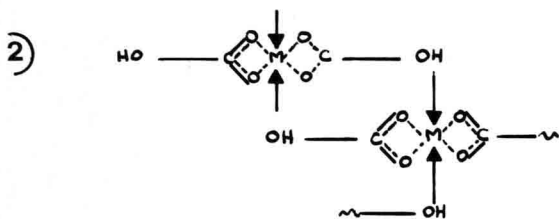
MATRIX TYPE	MOLECULAR WEIGHTS				
	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	\bar{M}_z	\bar{M}_z / \bar{M}_w
ORTHOPHTHALIC	1.240	2.900	2,33	6.700	2,3
ISOPHTHALIC	2.600	14.600	5,6	132.000	-
BISPHENOL-TYPE	2.700	19.300	7,14	64.700	3,35
CYCLOPENTADIENE-TYPE	820	2.600	3,17	15.800	6
URETHANE-TYPE	1.600	4.490	2,8	11.950	2,66
VINYLESTER	1.591	5.590	3,5	17.300	3,1

FIG. 3 MOLECULAR WEIGHTS OF VARIOUS THERMOSETTING MATRICES

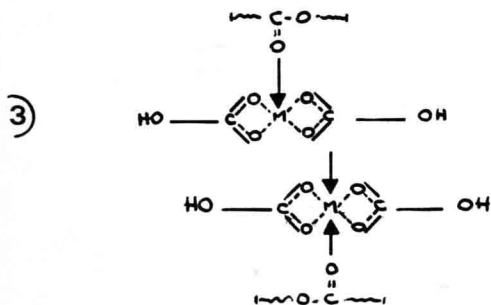
FIG.4



Bond between end-type carboxyl groups of polyester molecules and metal atoms.

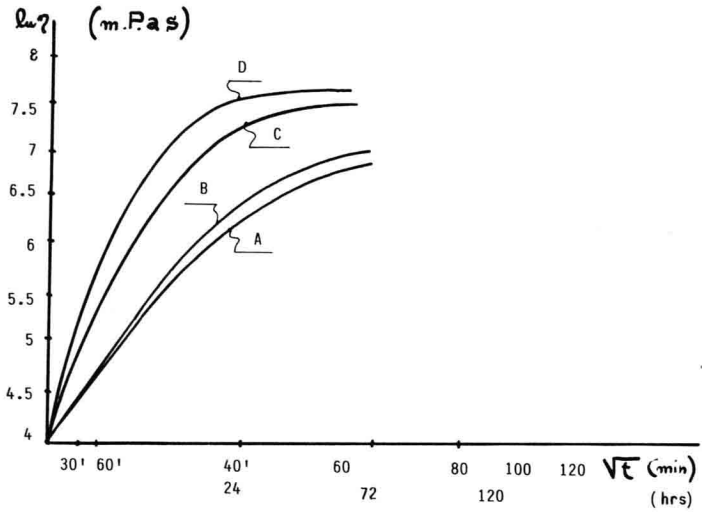


Co-ordination at end-type hydroxyl groups of polyester molecules with metal-carboxyl compounds.



Co-ordination of ester groups with metal-carboxyl compounds

FIG. 5



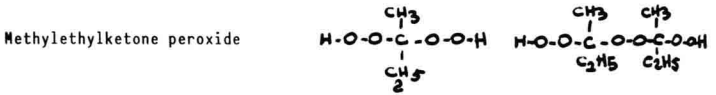
Influence of water content on the chemical thickening of a carboxylated polyester resin

A	Mole ratio H_2O / MgO	0.12
B	" " " "	0.16
C	" " " "	0.44
D	" " " "	0.7

POLYESTER RESIN PROPERTY	A	B	C	D
Acid number on dry resin (mgKOH/g)	35,2	36,2	36,6	36
H_2O (%)	0,05	0,05	0,05	0,05
Final viscosity after 24 hrs. (mPa.s at 20°C)	320.000	800.000	1.000.000	16.000.000
\bar{M}_n	2.200	2.200	2.300	2.200
\bar{M}_w	11.000	12.000	18.500	38.500
\bar{M}_z	145.000	165.000	290.000	780.000
\bar{M}_z/\bar{M}_w	13	13,75	15,6	20,25
\bar{M}_w/\bar{M}_n	4,9	5,4	7,9	17,6

FIG.6 CHEMICAL AND MOLECULAR CHARACTERIZATION OF DIFFERENT POLYESTER RESINS FOR SMC

FIG.7



- ① $R-O-OH + CO_3^{2+} \rightarrow R-O\cdot + OH^- + CO_3^{3+}$
- ② $RO-O-H + CO_3^{3+} \rightarrow R-O-O\cdot + H^+ + CO_2^+$
- ③ $R-O\cdot + CO_3^{2+} \rightarrow R-\bar{O}\cdot + CO_3^+$

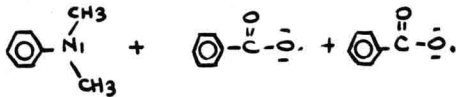
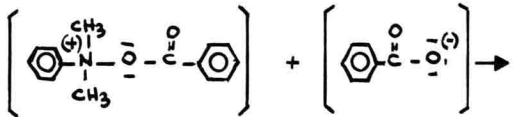
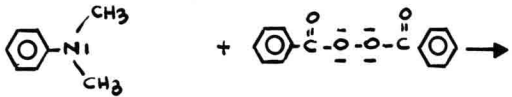


FIG. 8

	Temperature at which catalyst half-life is equal to 10 hrs. °C	Working Temperature °C
$\text{C}_6\text{H}_5\text{C}(=\text{O})\text{O}-\text{O}-\text{C}(=\text{O})\text{C}_6\text{H}_5$	73	90 - 130
Benzoyl Peroxide		
$\text{C}_6\text{H}_5\text{C}(=\text{O})\text{O}-\text{O}-\text{C}(\text{CH}_3)_3$	105	135 - 165
Ter-butyl-perbenzoate		
$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{O}-\text{O}-\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_5$	115	140 - 175
Dicumyl Peroxide		
$\text{CH}_3\text{C}(\text{CH}_3)_2\text{O}-\text{O}-\text{C}_6\text{H}_7$	73	90 - 130
Ter-butyl-peroxoate		
$\text{C}_4\text{H}_9-\text{O}-\text{O}-\text{C}(\text{R}_1)(\text{R}_2)$	92 - 110 ⁽¹⁾	120 - 170
Di-ter-butyl-peroxide		

(1) Depends on the nature of R₁ and R₂

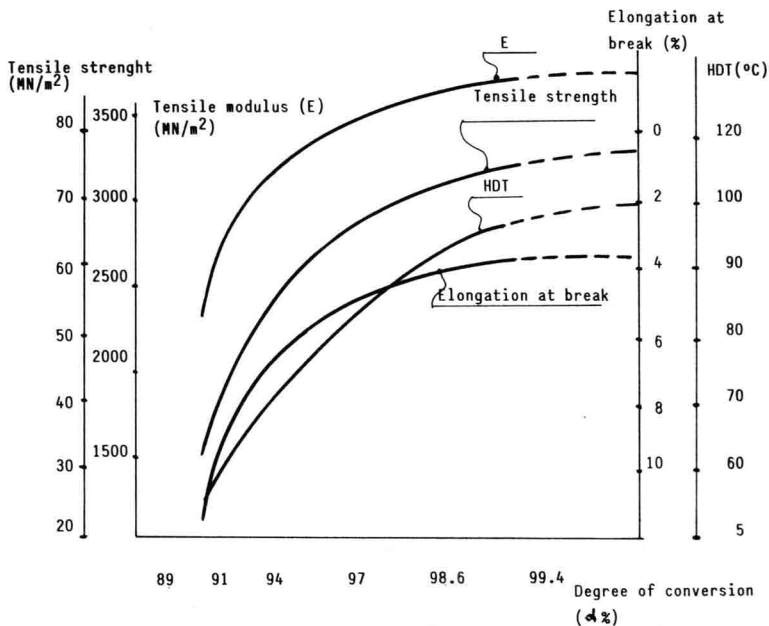
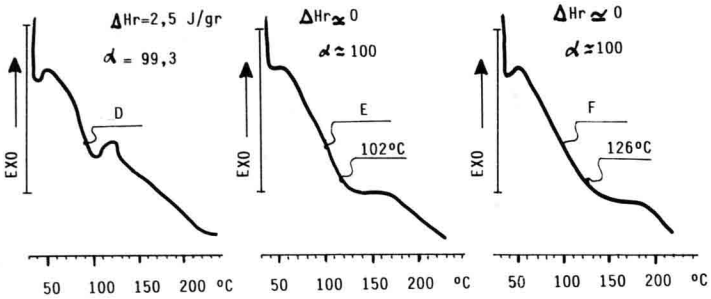


FIG. 8 A Influence of the degree of conversion ($\Delta\%$) on the mechanical and thermal properties of Neoxil 268 N castings

FIG. 8 B



Influence of polymerisation conversions (α) on D 24hrs/25°C + 3hrs/80 °C
 glass transition temperature (T_g), of Neoxil E 24hrs/25°C + 3hrs/100°C

268 N

F 24hrs/25°C + 3hrs/120°C

ΔH_r = residual enthalpy of polymerization

SYSTEM		A	B	C
<u>Catalysis:</u>				
Co ⁺⁺	(%)	0,006	0,006	0,006
Initiator	% (Methylethylketone peroxide)	1	-	1
Initiator	% (Ter-butylperoxy-isononoate)	-	0,5	0,5
<u>Thermal properties:</u>				
PS	°C	25	85	25
MPR	°C	86	108	83
PE	°C	155	145	85
Hp	J/g	212	184	15
AE	KJ/mole	34	116	174
PS	°C	-	-	85
MPR	°C	-	-	110
PE	°C	-	-	140
Hp	J/g	-	-	60
AE	KJ/mole	-	-	162

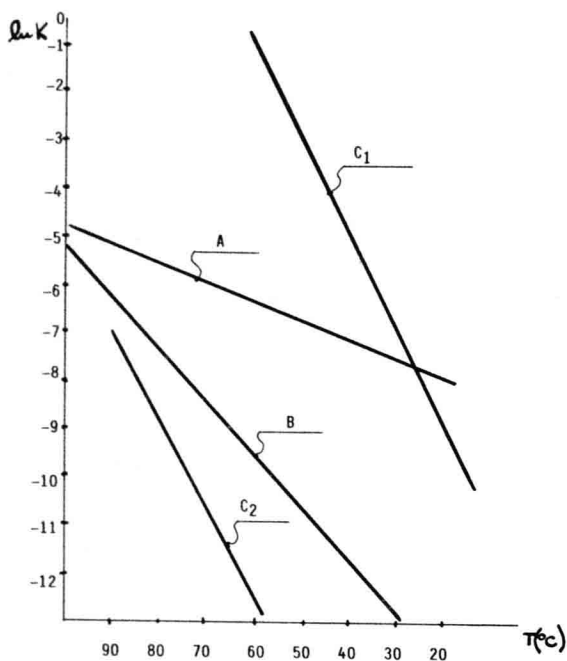
} first
reactions

} second
reaction

FIG. 9 COPOLYMERIZATION OF UNSATURATED ISOPHTHALIC POLYESTER WITH STYRENE: THERMAL PROPERTIES BY DSC ANALYSIS WITH DIFFERENT CATALYSES

- PS = Temperature of polymerization start
 MPR = " " maximum polymerization rate
 PE = " " polymerization end
 Hp = Enthalpy of polymerization
 AE = Activation energy

FIG. 10



Copolymerisation rate constant for isophthalic polyester with styrene vs. temperature. Promotor Co^{++} 0,006%

A Methyleneethylketone peroxide 1 %

B Ter-butyl-peroxy-isononoate 1 %

C { Methyleneethylketone peroxide 0,5 %
Ter-butyl-peroxy-isononoate 0,5 %

FIG. 11

Example of calculations of kinetic parameters

$$1) \quad \frac{d \ln K}{dT} = \frac{AE}{RT^2}$$

$$2) \quad \int_{TA}^{TB} d \ln K = \frac{AE}{R} \int_{TA}^{TB} \frac{dT}{T^2}$$

$$3) \quad \ln K_{TA} - \ln K_{TB} = -\frac{AE}{R} \left[\frac{1}{TA} - \frac{1}{TB} \right]$$

$$4) \quad AE = \frac{[\ln K_{TA} - \ln K_{TB}]}{\frac{1}{TB} - \frac{1}{TA}} \times 8.32 \text{ [KJ/mole]}$$

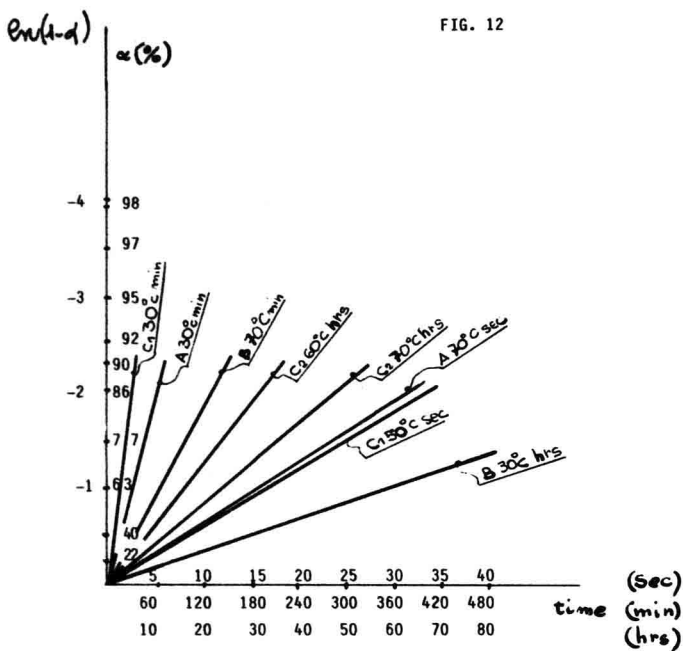
$$5) \quad AE = \text{SLOPE} \times 8.32$$

$$6) \quad \frac{d\alpha}{dT} = K [1-\alpha]^n \quad \text{for } n=1$$

$$7) \quad \int \frac{d\alpha}{1-\alpha} = K \int dT$$

$$8) \quad T = \frac{\ln(1-\alpha)}{K}$$

$$9) \quad \frac{d\alpha}{dT} = [K_1 + K_2 \alpha^m] [1-\alpha]^n$$



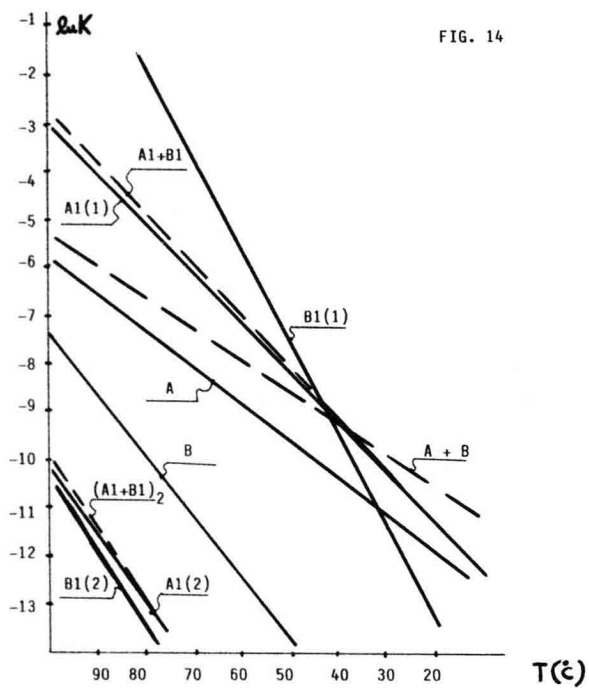
Degree of conversion vs. time and temperature in copolymerisations of isophthalic polyester with styrene

- A Methyl ethyl ketone peroxide 1 %
- B Ter-butyl-peroxy-isononoate 1 %
- C { Methyl ethyl ketone peroxide 0,5 %
Ter-butyl-peroxy-isononoate 0,5 %

SYSTEM		A	A1	B	B1	A + B	A1 + B1
Catalysts:							
Co ⁺⁺ (%)		0,015	0,015	0,015	0,015	0,015	0,015
(Cu - OR)		no	yes	no	yes	no	yes
Initiator % (methyl-ethylketoneperoxide)		1	1	-	-	0,5	0,5
Initiator % (acetyl-acetoneperoxide)		-	-	1	1	0,5	0,5
Thermal properties:							
PS	°C	85	67	96	60	75	67
MPR	°C	120	90	130	75	114	90
PE	°C	160	108	155	87	155	112
ΔHP	J/g	188	44	115	47	233	38
AE	KJ/mole	66	101	132	158	58	95
PS	°C	-	123	-	87	-	123
MPR	°C	-	140	-	105	-	145
PE	°C	-	175	-	124	-	175
ΔHP	J/g	-	36	-	25	-	55
AE	KJ/mole	-	219	-	184	-	194

FIG.13 COPOLYMERIZATION OF UNSATURATED ISOPHTHALIC POLYESTER WITH STYRENE: STUDY OF THE INFLUENCE OF INITIATOR TYPE AND OF COPPER COMPLEXES. DATA FROM DSC ANALYSIS.

FIG. 14



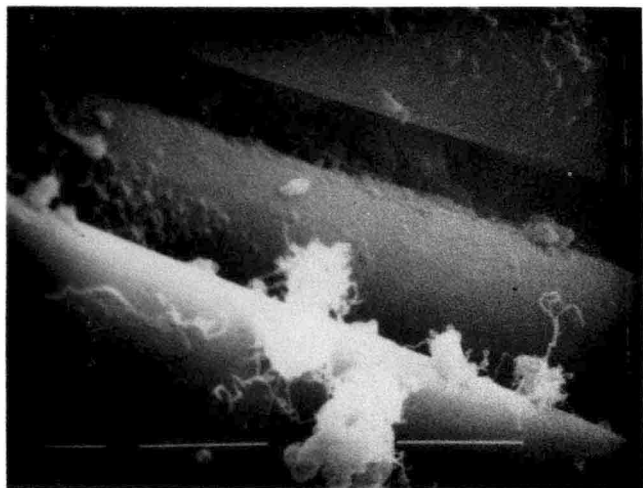
Copolymerisation rate constants for isophthalic polyester with styrene vs temperature. Promotor $Co^{++}0.015\%$.

- A Methyleneethylketone peroxide 1%
- B Acetylacetone peroxide 1%
- A1 Methyleneethylketone peroxide+Cu 1%
- B1 Acetylacetone peroxide + Cu 1%
- A + B { Methyleneethylketone peroxide 0,5%
- Acetylacetone peroxide 0,5%
- A1+B1 { Methyleneethylketone peroxide+Cu 0,5%
- Acetylacetone peroxide + Cu 0,5%

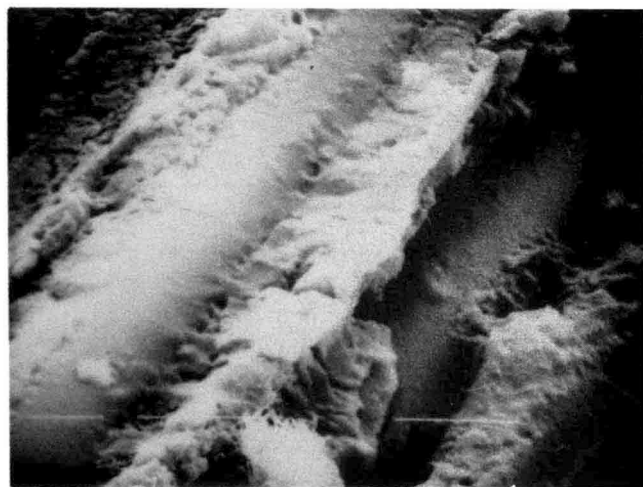
PROPERTY \ RESIN	722	722 HV	532	912
C = C (%)	10,6	10,6	13	14,6
Styrene (%)	34	26	34	34
<u>CALCULATED VALUES</u>				
Cohesive energy density (J/cm^3)	533	533	470	506
Solubility parameter ($J^{1/2} / cm^{3/2}$)	23	23	21,7	22,5
CONTACT ANGLE				
GLASS FILAMENT				
OCF glass fibre (insoluble sizing)	14 ₊₂	47 ₊₉	23 ₊₉	31 ₊₁₀
VETROTEX USA glass fibre (insoluble sizing)	35 ₊₆	46 ₊₉	39 ₊₁₄	14 ₊₅
VETROTEX ITALY glass fibre (soluble sizing)	17 ₊₄	49 ₊₉	32 ₊₈	21 ₊₆
OCF glass fibre (soluble sizing)	27 ₊₁	37 ₊₈	24 ₊₅	37 ₊₅

FIG.15 RESINS PROPERTIES AND CONTACT ANGLES BETWEEN MATRICES AND GLASS FILAMENTS

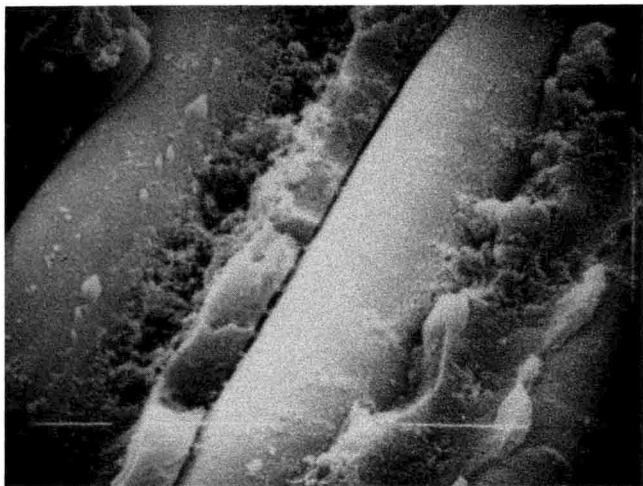
H V = High Viscosity



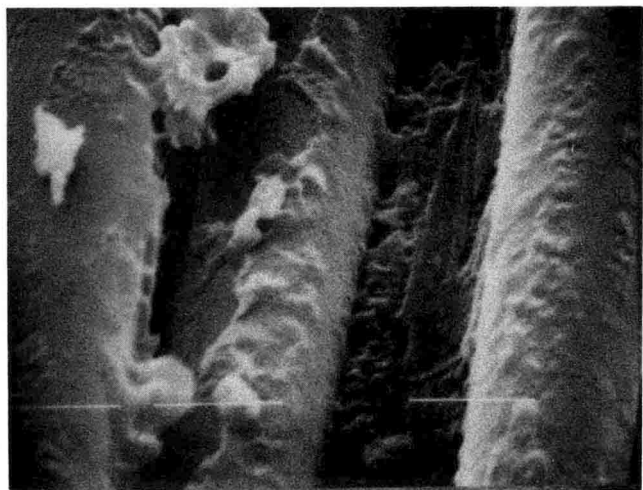
1 F (2500x)



2 F (2500x)



1 FC (2500x)



2 FC (2500x)