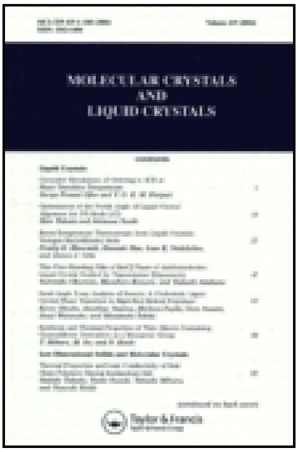

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Models for Understanding Processing Properties of Intrinsically Conductive Polymers

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Models for Understanding Processing Properties of Intrinsically Conductive Polymers

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Since their discovery in 1977 the intrinsically conductive polymers (ICP) have been considered unprocessable. This implies a main drawback for applied research and potential applications.[1,2] The main characteristic of ICPs which lead scientists to this conclusion and earlier attempts to overcome unprocessability by chemical means have been reviewed in Reference 3.

The aim of the research project which we started 1982 was nevertheless to find methods for processing unmolded ICP raw materials in powder form after polymerization either in pure form or in polymer blends. Our results have been published continuously,[4–9,17]), indicating flow properties of the pure ICPs and—on the other side in heterogeneous polymer blends—dispersability and percolation behavior, provided that the chemical synthesis of the raw ICP powders leads to purer and morphologically more uniform products.

In the meantime our research has created further new results which confirm our earlier findings and allow better processing results in homogeneous pure and heterogeneous polymer blend form. These results demand also a theoretical investigation in order to understand why ICP homopolymers now are processable despite the fact that their solubility and thermal properties have not been changed. Our present models for understanding processing properties of ICPs[8,10,11] will now be described.

PROCESSING OF PURE ICPs: "THERMODUCTILITY"

Our earlier experiments for molding pure ICPs resulted in products whose morphology has drastically been changed but which have been inhomogeneous and in some cases not completely "fused."[5,6,7] The process, like the processing of thermoplastic polymers, is based on the application of pressure (shear) at high temperatures. ICPs are however not thermoplastic in the common sense. The conditions required are much more drastic and the process is therefore much more complicated. Flow processes occur during deformation[5,7] and we therefore propose to describe ICPs as "thermoductile."

We are now able to produce almost any desired molding with almost any ICP on a small run basis. We are still limited by the availability of suitable raw materials. The molded articles we produce today are homogeneous, virtually regardless of the wall thickness. From the mechanical point of view some of them are very strong and extremely rigid (work is in progress to obtain quantitative data). The molded articles show a very high surface tension, their (electro-)chemical properties are not changed by the processing. Therefore it is possible to posttreat the molded articles, thereby forming layers of different

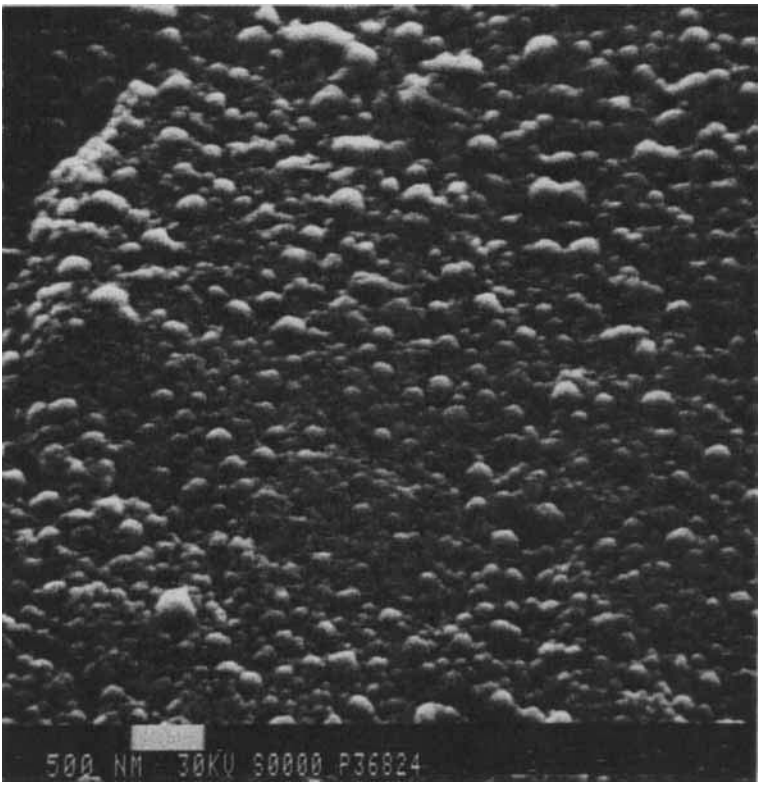


FIGURE 1

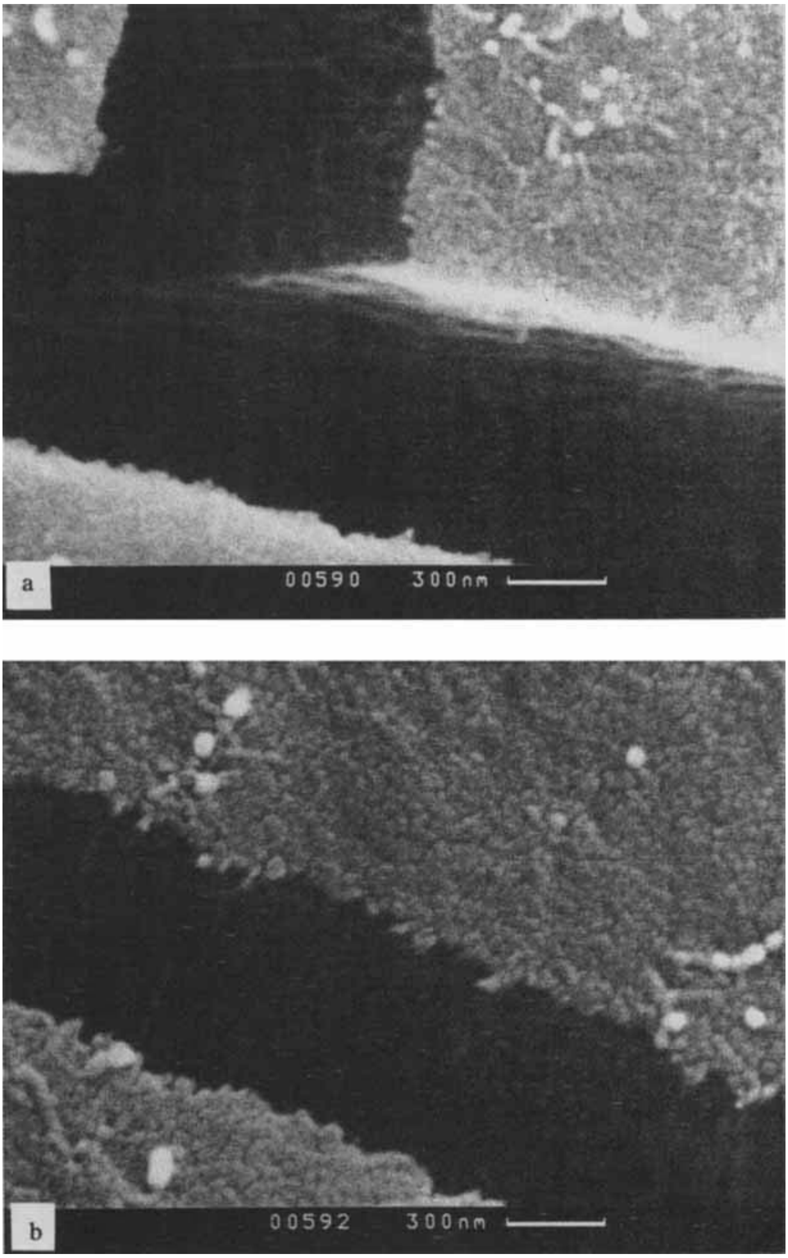


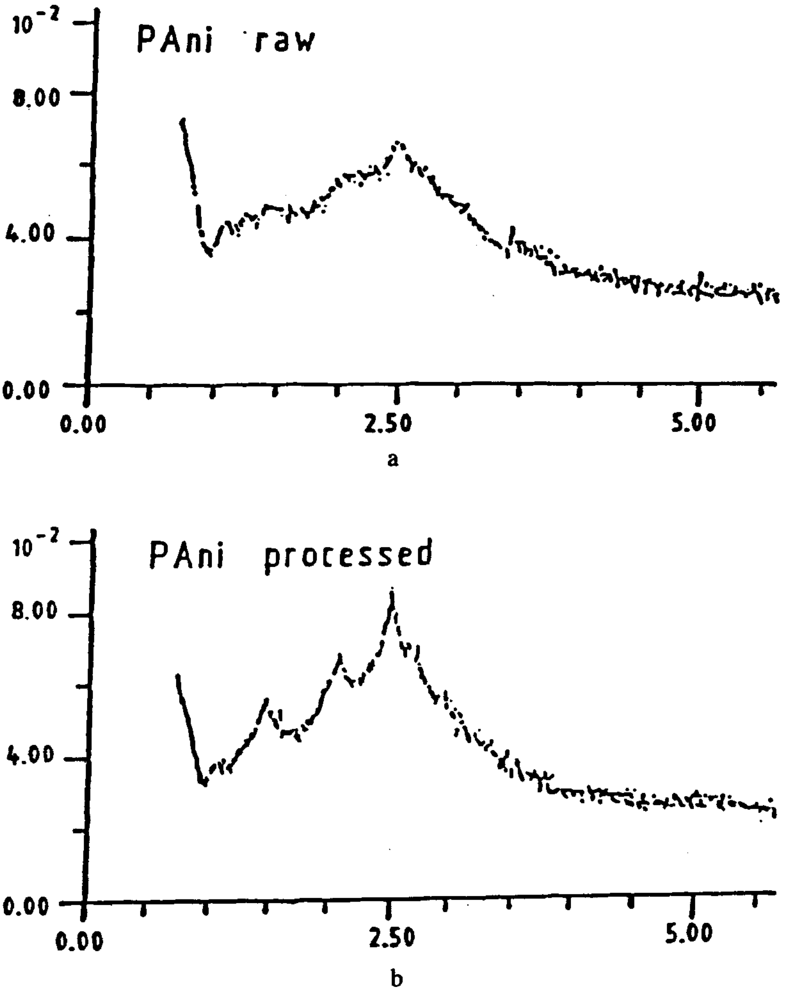
FIGURE 2

conductivities or properties. Additionally they can be subjected to mechanical secondary treatment. We have succeeded in cutting slices as thin as 15 μ. The moldings can be drilled, milled, ground and polished. Microtom sections with a thickness of 1 μ are transparent and birefringent. The scanning electron microscope reveals the same structures as we have described previously. The original globular primary morphology has disappeared and is replaced by a new compact, highly oriented and obviously rod-like morphology (Figures 1 and 2). X-ray structure analyses[12] show an increasing crystallinity as a result of the deformation (Figure 3). Unlike our earlier "products," the morphological and X-ray results are now reproducible in all samples where they are evenly distributed and display characteristic features for different polymers.[17]

FLOW MODEL

To date there is no ICP homopolymer in which a glass transition point or even a melting point has been observed. At present they are regarded as solids. Nevertheless we have proceeded on the assumption that what we observed is genuine flow, i.e. that the products obtained are not just the result of sintering processes. Instead the initially disordered polymer chains from different primary particle flows i.e. are sliding relatively to each other, crystallizing in the process as shown in our model (Figure 4). One conceivable way of describing this could be to regard ICPs as undercooled liquids that have solidified in amorphous form, i.e. as "glasses." Some of the phenomena occurring during our deformation could then be interpreted as pressure-induced crystallization (cf. pressure-induced crystallization during solid state extrusion of high density polyethylene).[14] Additionally we can report now, that the product which has been molded once from a powder to a compact, "fused," molded item, can be transformed once again to an article of another form, an analogy to reprocessability of thermoplastic polymers. This experiment proves the ability of the polymer chains or the primary morphological units, the rod-like morphological elements, of sliding relative to each other.

It remains to be seen whether this concept is correct and if so, whether the flow involved is that of a solid (similar to the ductility of metals or the "creep" of polymers) or of some other (extremely viscous) liquid.[5,6] Until this point is resolved, we propose now to use the term "thermoductility" to describe this flow property of ICPs.



a

b

FIGURE 3

POLYMER BLENDS WITH INTRINSICALLY CONDUCTIVE POLYMERS

The preparation of polymer blends between insulating conventional polymers (regardless whether thermoplastic or not) and intrinsically conductive (homo-)polymers by physical means starting after separate

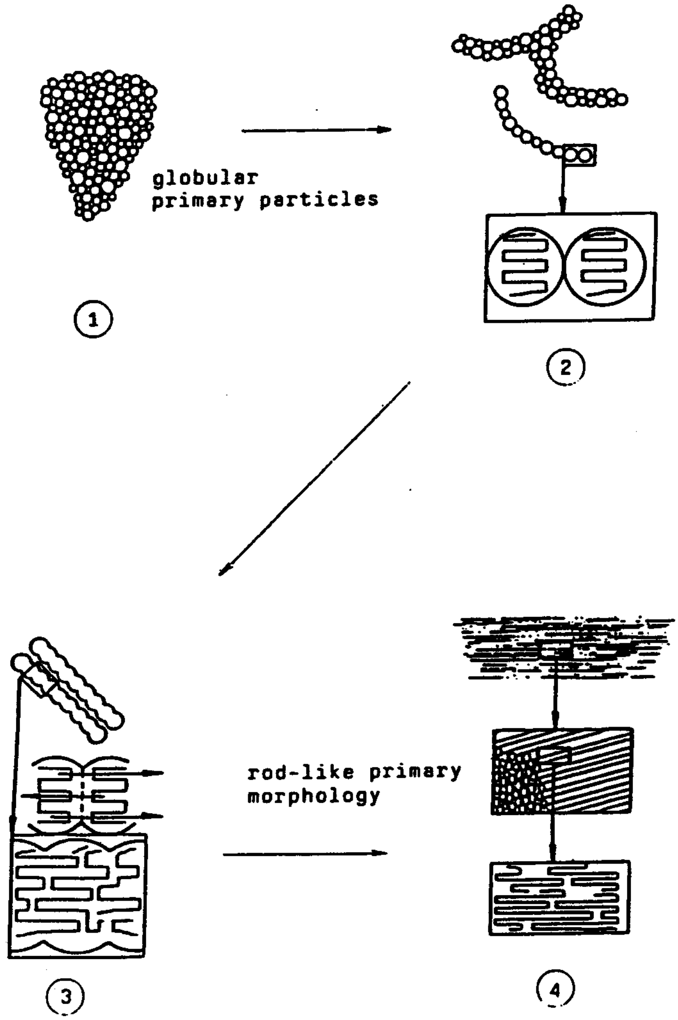


FIGURE 4

completed polymerization of the single components provides not only several practical but also fundamental theoretical problems:

1. It proved to be much more complicated to distribute ICP powders in conventional thermoplastic methodes than it was to disperse pigments or conductive carbon blacks. ICPs form huge aggregates,

so that we decided first to try to disperse them in low concentrations.[5,6]

2. It is a commonly held view (cf. References 15, 16, and the literature in 8 and 10) that the conductivity of carbon black compounds results from the statistical distribution of highly structured aggregates of carbon black and that above a certain critical volume concentration, these aggregates contact each other thereby forming continuous conductive pathways. On this basis the aim of polymerizing an ICP powder suitable for blends would have to be the formation of especially highly structured fine aggregates (which has been tried by other groups). We in contrast tried to polymerize dispersable ICP powders, which—again according to common belief—would "never" percolate in a polymer blend.

Nevertheless we observed percolation behaviour with our ICP powders which along with progress in polymerization techniques and development of new blending methods became better dispersable.[8,17] In the meantime we have improved these processes even more, thereby getting lower percolation thresholds down to 3.5 vol% and lower saturation concentrations at about 25 to 35 vol% of ICP in polymer blends (Figure 5 [13]).

This enables us now to announce that we can provide processable polymer blends on a laboratory scale and a limited number of matrices to other research groups for their fundamental and basic applied research.

On the basis of the percolation theory (21, cf. also 16, 20) it is not possible to explain a percolation behavior of globular primary ICP particles which are fully dispersed below percolation point. The percolation theory is based on the assumption that articles which have no interactions with the matrix are statistically distributed therein. This enables the theoreticians to describe a percolation behavior mathematically with a purely statistical and mechanistic view. In the case of polymeric compounds which contain conductive carbon blacks, the theory results in the model that highly structured aggregates of irregular and non-symmetrical shape are statistically distributed in the matrix.

Not only that percolation of fully dispersed ICP globules was theoretically not "allowed," but also other findings from our research and development work on carbon black compounds convinced us, that it was not the aggregates of carbon black but their primary particles which we should regard as the elements responsible for the percolation process. The formation of continuous conductive paths, we postulated, is not due to statistical laws, but results from the strong

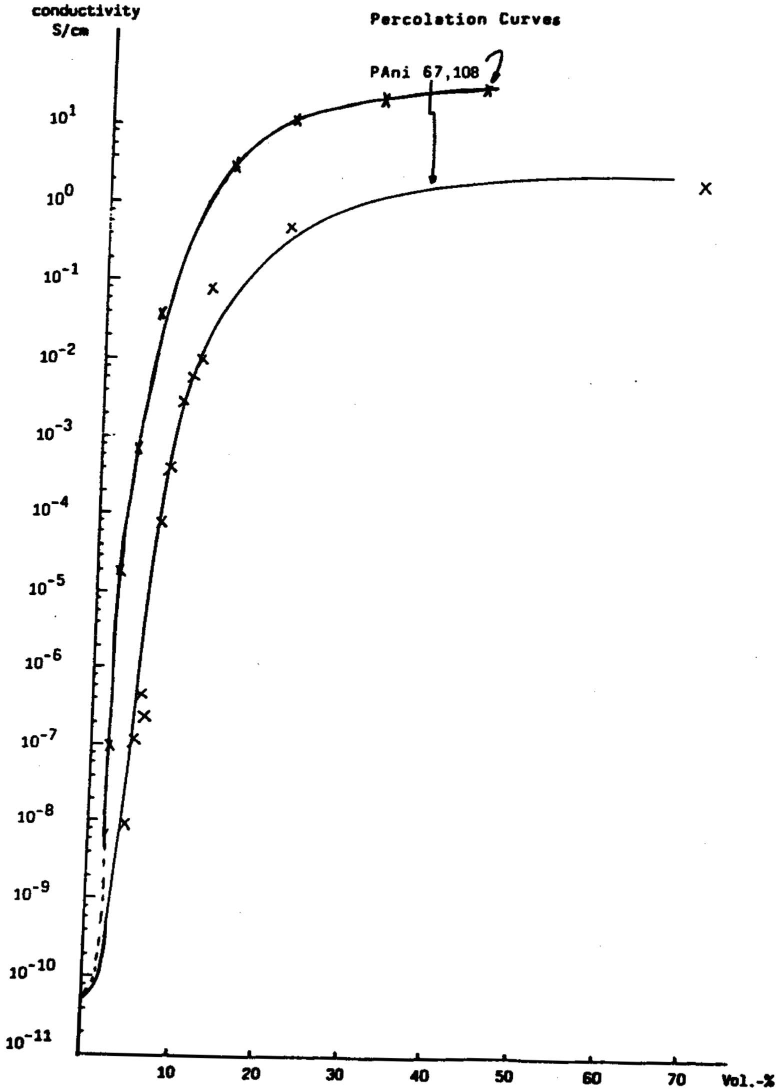

conductivity
S/cm
Percolation Curves
PAni 67,108
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10
20
30
40
50
60
70
Vol.-%

FIGURE 5

interfacial interactions between the dispersed primary carbon black (and ICP) particles with the matrix forming the conductive pathways above the percolation point due to energetic reasons.[8]

From this we went on to develop the working hypothesis that we should polymerize fully dispersable powders of conductive polymers and perform percolation tests following the dispersion principle. Surprisingly this resulted recently in a distinctly lower percolation and saturation behaviour (see Figure 5[13]).

According to our latest scanning electron microscope studies, conductive carbon black in a concentration below the percolation point in a thermoplastic matrix is evidently present in the form of completely dispersed isolated primary particles (Figure 6 [10,11]). The carbon black aggregates which have been used as models for percolation theory until now, have not been found by us below the percolation point. At the percolation point, however, we find, in addition to isolated dispersed primary particles, those linear or network-like structures of agglomerated black particles to which the compound owes its conductivity (Figure 7 [10,11]). This simultaneous appearance

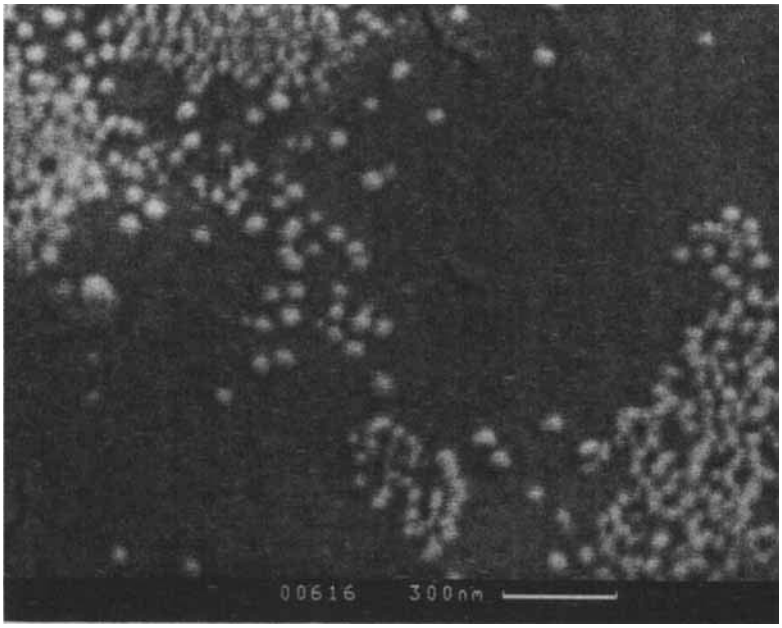


FIGURE 6

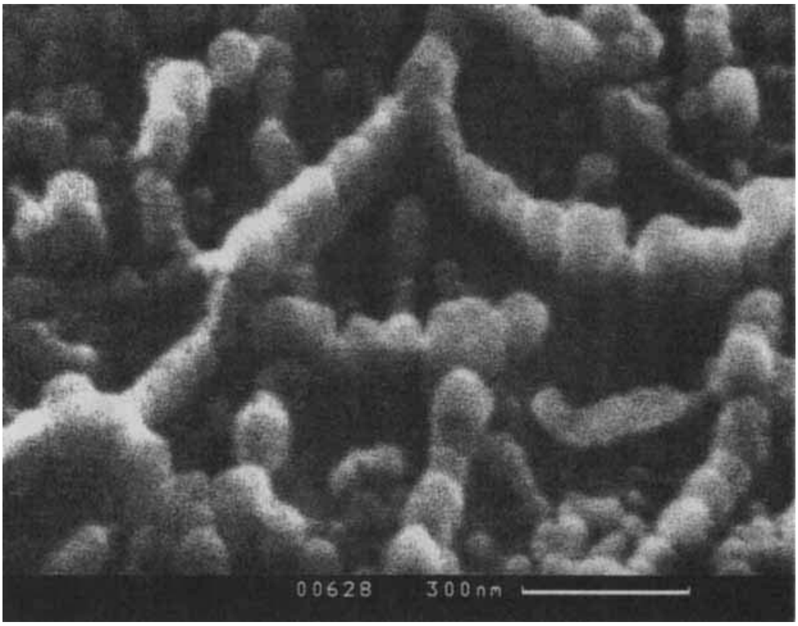


FIGURE 7

of both the dispersed and the agglomerated structures is strong experimental evidence in favor of our hypothesis[8]; at the percolation point there is an equilibrium between adhesive forces which causes dispersion and cohesive forces which cause agglomeration.

By examining the carefully prepared PS-carbon black-systems under SEM two additional conclusions have to be drawn:

1. The dispersed primary particles of carbon black are surrounded by an immobilized layer of significant thickness.
2. The dispersed particles with their layer are not uniformly, statistically distributed in the whole matrix but are obviously concentrated in layers comparable to seams (see Figure 8a and Figure 9).[10]

Our present model for a thermodynamically driven percolation mechanism[11] is as follows: Just below the percolation point, the carbon black particles, including their immobilized adsorbed matrix shell, fill the whole volume of the layer. Besides that, most of the matrix volume is free from carbon black. By adding new dispersed carbon black primary particles with their shell, the layers would be overfilled.

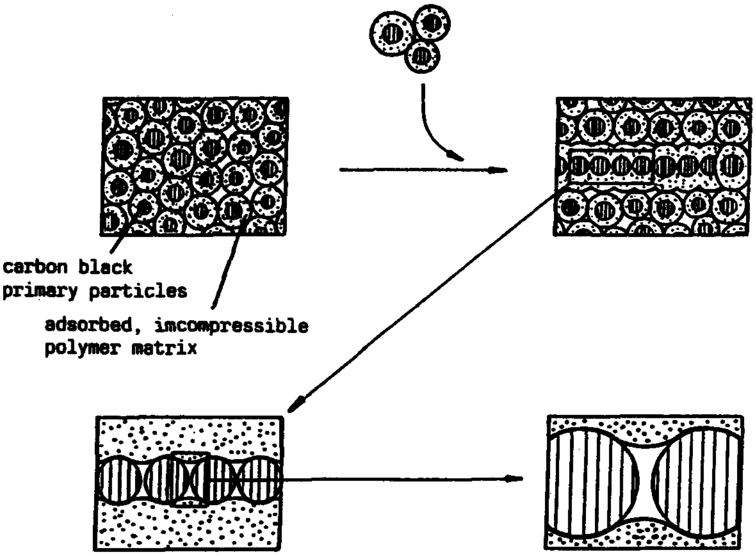


FIGURE 8

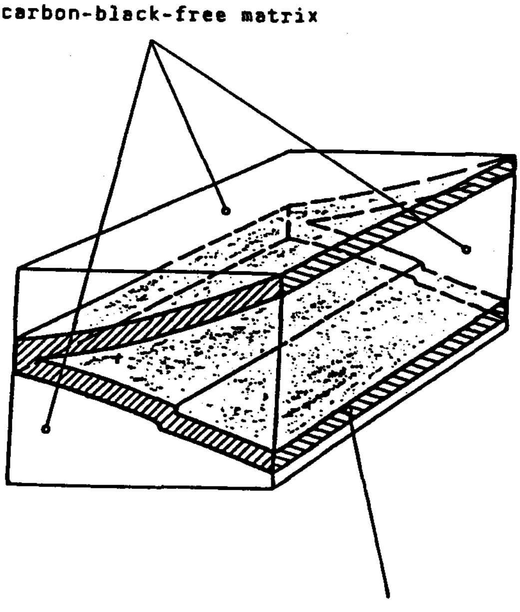


FIGURE 9

Therefore, driven by compression forces, the adsorbed shells of the two first carbon black particles begin to delaminate, thereby allowing the carbon particles to approach each other (see Figure 8). The next carbon black particle which "wants" to approach the two agglomerated particles has to approach from the opposite side, because this area has the higher surface tension (the region in between the first two agglomerated carbon black particles tends to deagglomerate again, leading to pressure from inside directed to "outside" which results in a lower surface tension). As a result of numerous delamination processes and agglomeration a linear network of *reversibly* agglomerated carbon black particles, surrounded by a tube-like shell, is formed (see SEM Figure 7 and model Figure 8d and 10).

This model is supported by investigations of the density dependence upon carbon black concentration,[11] Figure 11. Below the percolation threshold, the density increase is similar to what should be expected as the density of carbon black (1.8 g/cm^3) using an additivity rule. In the concentration region around the percolation threshold, the density does not increase anymore, but remains relatively constant. By further increasing the concentration of carbon black the density increases, but not any more with the same slope as below percolation. This supports very strongly our delamination model which include the formation of gas-filled, matrix-free room between the agglomerated carbon black particles.

Our model implies that dispersion and agglomeration of carbon

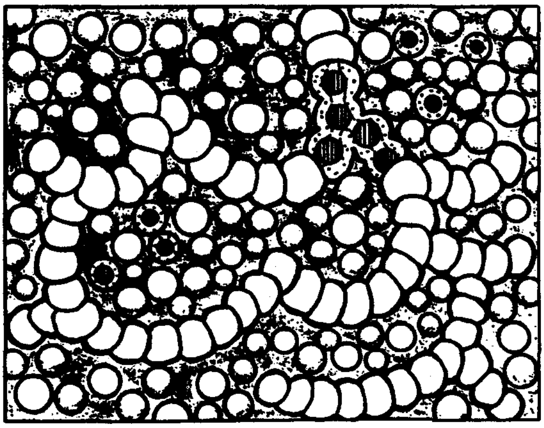


FIGURE 10

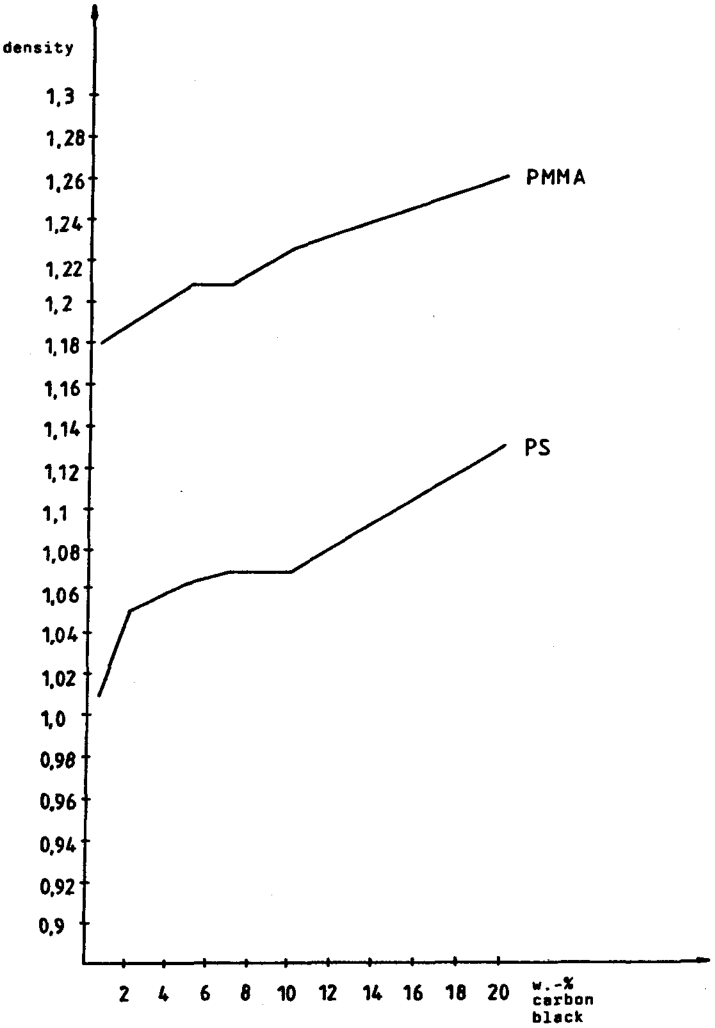


FIGURE 11

black particles is reversible. We have many experimental hints[8] which do support this statement. This is why we propose to describe the percolation point as being a composition which shows a thermodynamic balance between cohesion (agglomeration) and adhesion (dispersion) energy. This view may lead us also to a quantitative description of the percolation behavior, especially the percolation concentration by only using energy terms which describe the interaction of the dispersed carbon black or ICP particles with the matrix.

It may be interesting to note that, whereas we consider the percolation mechanism and percolation structures as being thermodynamically favored, they seem not to be kinetically favored. By applying temperature and time to compositions of polymers with different concentrations of carbon black, those compositions, which have concentrations below percolation now become conductive, i.e. that the "real" percolation curves always have to be worked out by using tempering techniques. Tempered compounds show also a different percolation structure when prepared for SEM investigations (Figure 12). It seems that the adsorbed tube-like shell adheres much more strongly and more efficiently as well as being better connected with the surrounding carbon black free matrix.

Using the new theory, we are now able to provide processable and flexible polymer blends with conductivities up to 20 s/cm for research purposes.

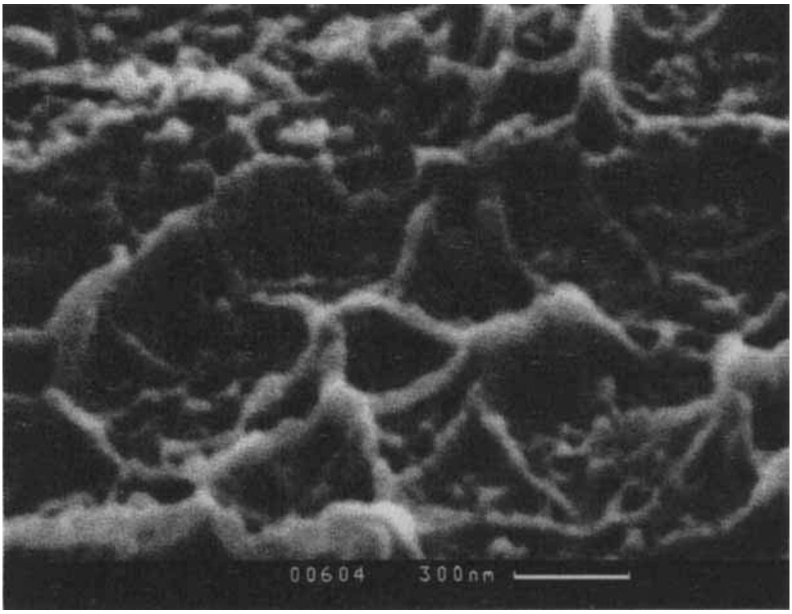


FIGURE 12

PROSPECTS

It seems to us that the novel properties of intrinsically conductive polymers, especially those combinations of properties that are not encountered in conventional materials, have yet to be fully appreciated by us all. With the availability of processable polymer blends, and also the availability of articles made of pure intrinsically conductive polymers and molded to any desired shape, we now have the opportunity to investigate the properties of this fascinating new category of materials with new opportunities to solve practical problems.

We invite research and development laboratories in universities and industry everywhere to join us in thinking about application-oriented research projects. For clearly defined projects we offer to make available, on a limited scale at present, and in return for a contribution to costs, moldings made of pure intrinsically conductive polymers (e.g. semi-finished goods) and moldable polymer blends incorporating intrinsically conductive polymers of various conductivity settings.

Acknowledgment

The results achieved in the course of five and a half years, would not have been possible without the support the project has received from Mr. Wolfgang C. Petersen, managing director and joint owner of Zipperling Kessler & Co. His sense of innovation and his readiness to take risks have given him the strength to ride out the constant setbacks in the course of the project and ensure that the necessary financial resource did not dry up.

The Federal Ministry for Research and Technology (W. Germany) has also given support to parts of the project. Without these additional funds it would certainly not have been possible to achieve these results in such a relatively short space of time.

It goes without saying that a project cannot be run on money alone. We should therefore like to express our thanks to the staff for their patience and commitment, and their readiness to follow up even the craziest of ideas (Susanne Blaettner, Frank Marten, Christian Funder, Olaf Siemers, and Holger Merkle).

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