

REVIEW PAPER

MORPHOLOGY - ELECTRICAL PROPERTY RELATIONS
IN POLYMERS

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ABSTRACT

In a review of this length, it is impossible to include all relevant references to every section of a subject as large as that of electrical properties. I have, therefore, only presented the most pertinent references and have restricted the review to well-established facts. This has naturally excluded some of the very interesting, but controversial, subjects of present research.

It should be clear from the review that researchers are only beginning to investigate morphological effects in some areas and that it will be some time before comprehensive investigations are reported. This is largely because polymer scientists familiar with morphology have rarely taken an interest in properties other than dielectric relaxation. The physicists and electrical engineers, who have generally carried out the research in other electrical properties, have had little knowledge of morphological detail. Paradoxically, those areas in which morphology is likely to be of greatest significance, electrets and breakdown, have received least attention.

This review has endeavored to introduce the non-polymer scientist to morphology and to review, in a concise manner, well-established relations existing between morphology and electrical properties.

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INTRODUCTION

Over the past several years the use of polymers in the electrical industry has increased remarkably. This has been, in the main, due to two major commercial developments. The first of these has been the overwhelming acceptance of cross-linked polyethylene and associated polymers as insulation in power transmission cables; the second being the emergence of polymer electrets as important acoustical devices. All of the major polymers used for these purposes are semi-crystalline and as such many of their properties are extremely dependent on the fractional crystallinity present and on the size, shape, and orientation of the individual crystals. Over the past decade, due to the perfection of new characterization techniques, it has become possible to determine just those parameters and hence to study systematically their effects on bulk properties. Such investigations already have shed much light on mechanical behavior and are beginning to lead to tailor-made products. It is likely that related investigations into certain electrical properties will be just as productive.

Although a vast literature exists on the electrical properties of polymers, much of this is on dielectric dispersion. This major research area grew up not as an electrical engineering discipline or as an area of materials science, but as an extension of physical chemistry. For many years now it has been used to study and characterize the molecular structure and properties

of polymers. An extensive literature also exists on the conductive properties of polymers; a field which has grown up as a part of solid state physics and often with neglect of chemical microstructural variables. In both areas, however, there exists a substantial amount of information on the morphological effects although no major systematic investigations or even comprehensive reviews are to be found.

Electric breakdown is now being studied intensively in a number of laboratories. Much of this effort has been prompted by failures in the field of transmission cables after only a few years service. It is already clear that the major contributory factors are the physical and morphological structures present rather than the chemical nature of the polymer.

One technique useful in the preparation of polymer electrets is the orientation of permanent dipoles through control of the orientation of the crystals containing dipoles. Such technology requires not only a knowledge of the control of morphology and its relation to piezoelectricity but also a knowledge of the effects of mechanical deformation on morphology.

It is, therefore, an appropriate point in time for a review of the characterization of morphological detail, its relation to electrical properties, and its control through processing.

2. MORPHOLOGICAL STRUCTURE AND CONTROL

Here we are concerned with the physical structure of the polymer, with the presence of more than one phase. The variables which need to be discussed and, if possible, controlled are

- (1) the fraction of each phase present;
- (2) the size and shape of the phase domains;
- (3) the orientation of the phase domains;
- (4) changes in any of the above with temperature and time.

There are four basic classes of polymer systems in which phase separation is known to occur. These are

- (i) *semicrystalline polymers*, in which the phases present are amorphous and crystalline;
- (ii) *block and graft copolymers* [1] and *blends of polymers*; here effectively two incompatible polymers are forced to exist together in the solid state and do so by forming a two phase system where domains of one component are dispersed throughout a matrix formed by the second;
- (iii) *phase separated random copolymers* in which highly polar or ionic groups are attached randomly to the polymer chain: because of the basic incompatibility of the organic and inorganic groups, a separation occurs in which the inorganic groupings form domains dispersed within the organic polymer matrix; and
- (iv) *compounded polymers* in which any of the above systems has added to it a, generally, inorganic powder or filler such as carbon black, alumina, silica, etc. This fourth group would also include filled non-crystalline polymers.

In the following sections each of the above classes will be discussed in some detail and examples given of pertinent commercial systems.

2.1 Semicrystalline Polymers

Unlike most metallic and many ceramic materials, polymers are invariably only partially crystalline [2-5] and their morphology cannot therefore be rationalized in terms of a simple granular structure. The equivalent of the metallic grain is the polymer single crystal which until recently [6] could only be produced by crystallization from solution.

2.1.1 Single Crystals

A typical single crystal of a polymer is a thin plate rhombohedral in shape (Figure 1). The thickness is only a few hundred Angstroms whereas the other dimensions are generally 1 to 100 μm . Electron diffraction experiments as early as 1938 showed, contrary to expectations, that the molecular axis was parallel to the thinnest dimension. It was not, however, until 1957 that Keller [7] suggested that the only rational structure possible was one in which the molecule folds regularly (Figure 2). The crystal thickness, and hence the fold length, is determined by the supercooling in a precise way. The experimentally determined dependence of thickness on inverse supercooling was known some time before it was predicted theoretically in the adaptation of secondary nucleation theory [8] by Lauritzen and Hoffman [9]. A detailed account of the theory is beyond the scope of this review; however, the relevant equation is

$$l = \frac{2\sigma_e T_m}{\Delta H \cdot \Delta T} \quad (1)$$

where l is the thickness, T_m the melting point or dissolution point, ΔH the heat of fusion, ΔT the supercooling, and σ_e the surface free energy of the fold surface. T_m , ΔH and σ_e are constants and are known for most systems.

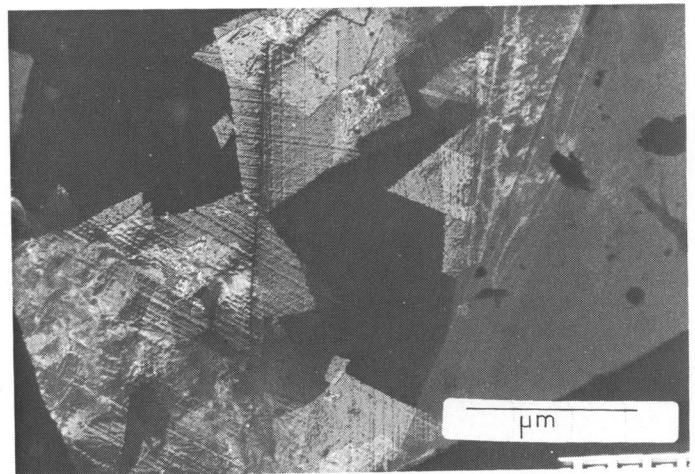


Fig. 1: Single crystals of high density polyethylene. Dark field image using (110) and (200) reflections; (photograph supplied by Dr. J. R. White).

Theoretical prediction of σ_e is very difficult and intrinsically dependent on the model chosen for the structure of the fold surface. The representation in Figure 2 is an idealized structure of tightly folded chains. It is also possible that a looped surface could occur as well as a non-adjacent reentry or "switchboard" surface [10,11]. Although the exact structure remains a matter of some controversy, recent elegant studies of the deformation transformations [12] in single crystals can only be rationally explained in terms of a predominance of the regularly folded structure, at least for polyethylene. Although inaccessible theoretically, values of σ_e have been determined precisely by experimentation [13] and are to be found in the literature for common polymers. The amount and structure of folded chain material is of relevance to electrical properties since often the material found in a fold may be chemically impure segments rejected from the crystal. These chemical microstructural irregularities may give rise to low temperature-high frequency dispersion, serve as trapping sites, or form electrically weak sections.

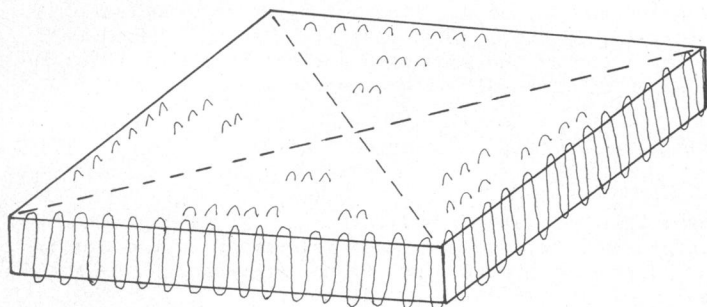


Fig. 2: Schematic diagram of chain folding in a polymer crystal.

The fold surfaces themselves are of course non-crystalline and, as such, contribute to the always fractional value of crystallinity. Single crystals are generally 80 to 90% crystalline and because of that, differ intrinsically from single crystals of other materials. They do, however, contain dislocations and defects just as do crystals of other materials [14]. Presumably they would also form trapping sites for conductive species.

Macroscopic single crystals were recently produced by the technique of solid state polymerization [15-17]. In this technique the monomer is crystallized in as perfect a state as possible and then polymerization is initiated either thermally or by the use of irradiation. If the change in volume on polymerization is negligibly small, a virtually perfect polymer crystal is produced. The unique structural feature of these crystals is that the chains are not folded at the surface, they are extended-chain crystals. Crystals produced by this method so far have been poly(di-acetylenes) which are conjugated systems expected to have unique optical and electrical properties (Figure 3).

2.1.2 Spherulites

When crystals grow from concentrated solutions or melts they do not attain the perfect shape of the crystals referred to in the previous section. They are highly dendritic and the characteristic shape produced by melt crystallization is that of a thin long ribbon

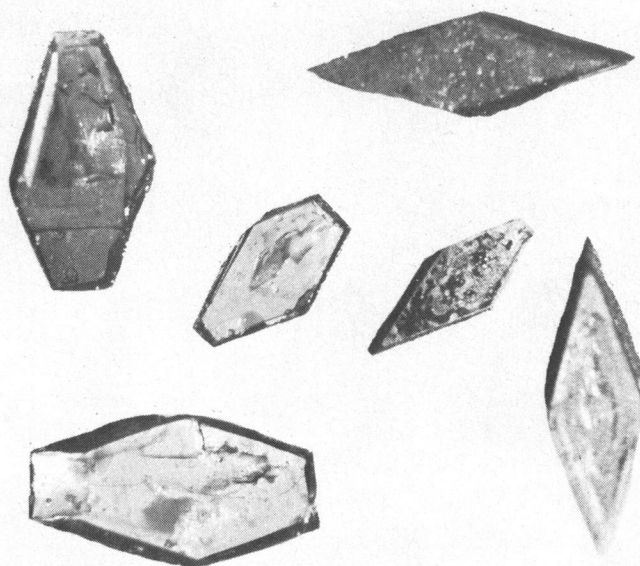


Fig. 3: Small Crystals of bis-(p-toluene sulphonate) of 2,4-hexadiyne-1,6-diol photographed in polarized light. Monomer crystals are at left; polymer crystals at right. The electric vector of the light is horizontal (photograph supplied by Dr. D. Bloor).

known as a lamella (Figure 4). Nor do they occur as isolated species, they are found in spherulitic arrays (Figure 5). This is a direct consequence of the nucleation process. A single crystal is nucleated at its center and may even have been nucleated by high molecular material rather than a foreign particle [18]. In the bulk there are two possible mechanisms [5,19] if the melt is isotropic (i.e. with no imposed strain). The first of these is *heterogeneous* nucleation in which the crystals are nucleated on foreign matter and grow outwards in a radial manner (Figure 6). The second is *homogeneous* nucleation in which the polymer produces its own nuclei on which the first crystals grow. These first crystals then "spawn" new crystals alongside them [13] leading to the development of a sheaf and ultimately to the *spherulite* (Figure 5). The spherulites then continue to grow until they impinge on one another resulting in truncation and their final appearance as polyhedra of about twelve faces. They completely fill

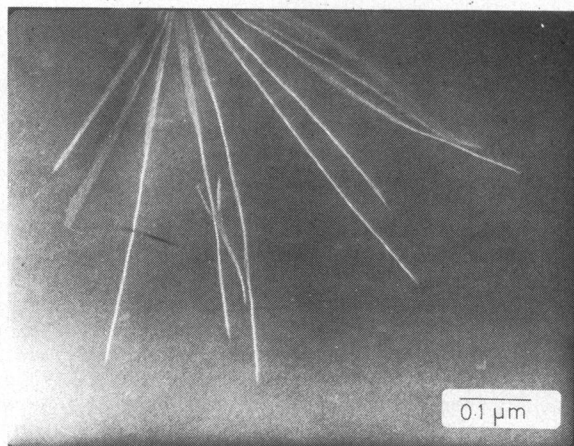


Fig. 4: Crystalline lamellae in cis polyisoprene.

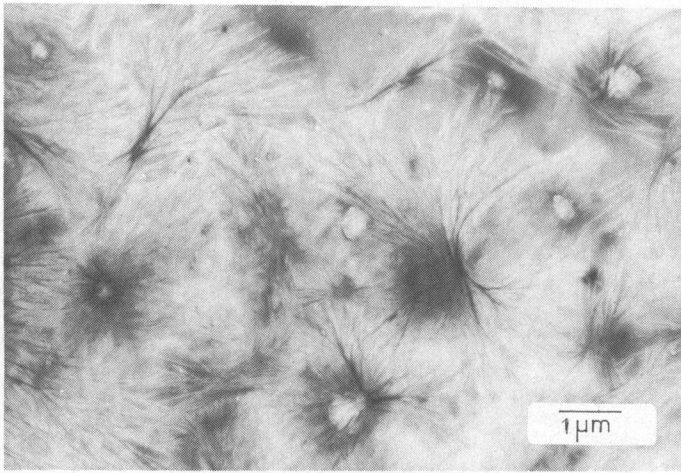


Fig. 5: Spherulites in *cis*-polyisoprene.

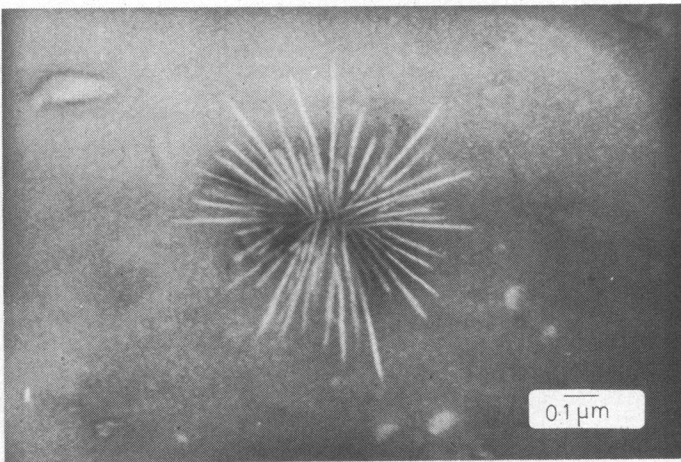


Fig. 6: Heterogeneously nucleated spherulite in *cis*-polyisoprene.

the volume of the material and resemble grains in a metallic element to which they are often confusedly interpreted as being equivalent. This is not however the case since all the material, both crystalline and amorphous, is contained within them, the radiating crystals being separated by the amorphous material.

The crystalline fraction (commonly referred to as the *crystallinity*) is generally determined by the degree of perfection of the chemical microstructure and as such is controlled by the synthetic process. There are rare examples of polymers in which the crystallinity may be adjusted by more than a few percent through thermal treatments. These are generally low crystallinity polymers of high melt viscosity and low crystallization rate. The most important commercial example is poly-(ethylene terephthalate) which may be made in a totally amorphous form through rapid thermal quenching. Crystallinity may be determined through a number of experimental techniques [3] the most used being differential scanning calorimetry and X-ray diffraction. A major problem, however, is that the value obtained generally depends on the technique used. This is intrinsic to polymer structure since there exists a transition zone between the amorphous and crystalline phases rather

than a clear boundary. The simplest and smallest transition zone would be an idealized tightly folded surface which would only extend for a few Angstroms. But since this simplistic model is unlikely to apply to the surfaces of crystals in a bulk polymer, a more realistic estimate would be of tens of Angstroms. In practice the "boundary line" is imposed by the measuring technique. For technological purposes comparative data are satisfactory and statistical differences between techniques of ca. 5 to 8% are not overly critical.

Two other variables, spherulite size and lamellar thickness, can be controlled. Early processing studies showed that a small spherulite size was conducive to good mechanical properties [20,21]. Although scientific reasons for the relations were not understood, and are now only becoming apparent [22-24], the achievement of a small spherulite size became a general consideration in plastics processing. This has been attained in two ways, both maximizing the number of primary nuclei present. Addition of nucleating agents increases the number of heterogeneous nuclei and hence decreases the ultimate size a spherulite can achieve. Homogeneous nucleation is controlled by the temperature of crystallization and may be described using primary nucleation theory [9, 25, 26]. This is similar to and indeed is a progenitor of the secondary nucleation theory referred to earlier. The following equation may be used

$$I = I_0 \exp\left(-\frac{\Delta H^*}{kT}\right) \exp\left(-\frac{\Delta \phi^*}{kT}\right) \quad (2)$$

where I is the rate of nucleation, I_0 a pre-exponential factor, ΔG^* the free energy of activation of the elementary diffusion process and $\Delta \phi^*$ the free-energy of formation of a critical size nucleus.

$\Delta \phi^*$ is a negative quantity giving rise to a positive exponential factor. The overall result is a curve of nucleation rate versus temperature as shown in Figure 7. A maximum in the nucleation rate and hence a minimum in the spherulite size occurs as temperature of crystallization decreases. Rapid cooling in a plastics forming process is usually enough to ensure that the minimum is achieved.

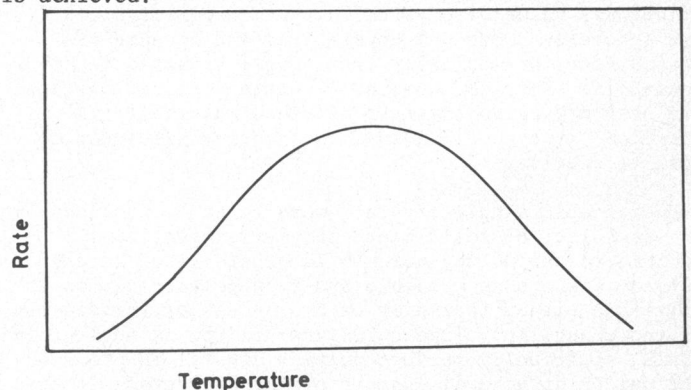


Fig. 7: Nucleation rate by homogeneous nucleation versus temperature for a crystalline polymer.

Such a procedure also determines the lamellar thickness through equation (1). Both spherulite size and lamellar thickness could be determined independently through use of both a nucleating agent and thermal control. Most common processes involve the use of pressure as well as temperature in the forming stage. Examples of these are compression, injection and extrusion molding. Pressure is a thermodynamic variable and the

"constants" in the theories and equations referred to so far are all pressure dependent. The study of the effects of pressure on polymer crystallization is in its infancy, but experimental investigations have recently [27,28] made possible a prediction of ways in which both nucleation density and the rate of crystallization of a lamella will be affected. It is believed that, in the future, careful control of pressure will enable physical properties to be predicted through the much finer control of the crystallization process.

Crystallization, in practice, generally begins at the cooled surface of the polymer. The lamellae radiate inwards from the surface nucleating points (Figure 8). This naturally results, because of early surface impingement, in the formation of columnar structures. Hence, even in systems which are strain-free there is never a totally uniform morphology.

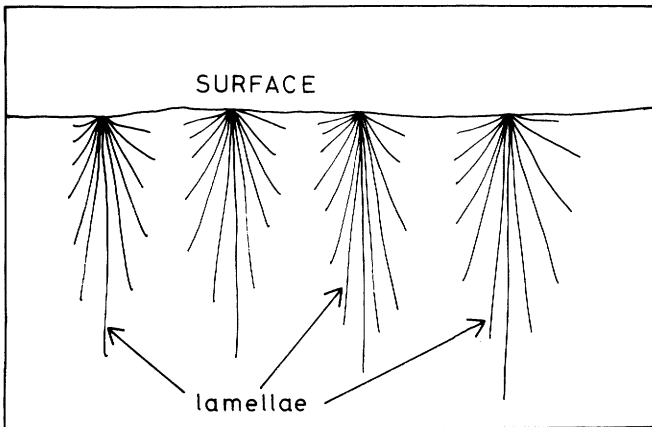


Fig. 8: Schematic representation of surface nucleation.

2.1.3 Orientation

The most common of the processes used in the fabrication of plastics components involve the molten polymer being impelled through a barrel. In the case of extrusion molding, used in fabrication of transmission cable, the polymer is pushed through a die. This process imparts a strain to the melt and the molecules become elongated and hence partially oriented. Crystallization invariably follows after this part of the process and hence occurs in a strained melt. The resultant morphology depends on the amount of strain present [28,29]. A strain of about 50% results in oriented spherulites (Figure 9) whereas strains of 100% and above generally result in row nucleation. Here, instead of the crystals radiating outwards from a central nucleating point, they are nucleated on the surface of a fiber (Figure 9). The fiber is formed as a result of the orientation, alignment and subsequent crystallization of sections of polymer chain. At strains of 300% and above, not normally encountered in processes other than fiber extrusion, the strain-induced crystallization predominates and the lateral growth of folded-chain crystals is eliminated. Only the fibrous species are then present.

The formation of a row nucleated morphology has a profound effect on the physical and, particularly, the mechanical properties. An anisotropic material results in which the properties in the direction of the axis of the row nucleus differ from those perpendicular to it. Fibers exhibit the most anisotropic behavior of all polymeric materials.

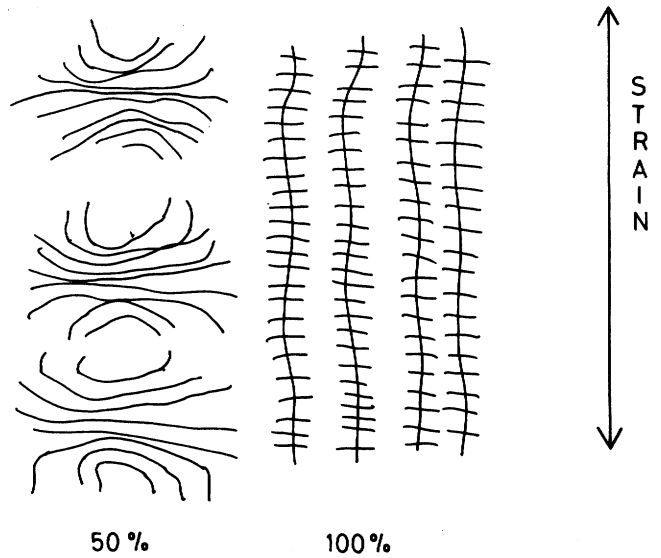


Fig. 9: The effect of pre-orientation on crystalline morphology.

2.2 Block and Graft Copolymers; Blends

The problem of compatibility in polymers is a serious one and is the subject of considerable research. Generally, the thermodynamics of mixing of two polymers are such as to predict incompatibility [30]. A mixture of polymers, however produced, should therefore result in a multiphase material. The major component would be expected to form the matrix in which will be randomly distributed pockets or domains of the minor component.

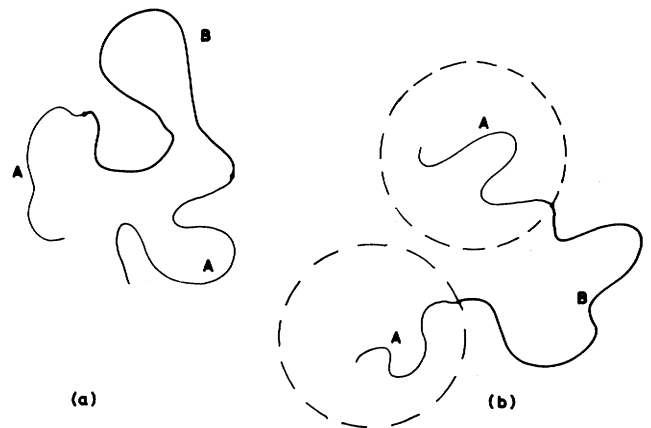


Fig. 10: Schematic representation of (a) a block copolymer molecule and (b) the molecule when incorporated into the morphological structure.

A special way of producing such a system is block copolymerization [1]. Here the different polymeric species are present in the same molecule (Figure 10a). Most common commercial plastics of this type are terblock copolymers where the molecule consists of a long section of polymer A, followed by a long section B, followed by a second long section of A. The result is a molecule containing fundamentally incompatible sections. When phase separation occurs, as it must, the domain size is controlled by the actual lengths of each sub-unit present in the molecule. Each molecule must itself be present in both domain and matrix (Figure 10b). This results in a strong material which may be rubbery or glassy depending on the components, but which is reprocessable.

Graft copolymers are made by attaching lengths of polymer B to a molecule of polymer A. The morphological structures are similar to those of the block copolymers. Very special arrangements of the domains can be achieved in the block copolymers [30] through careful control of the sub-unit lengths. Normally, however, in commercial specimens random morphologies are observed with domain dimensions of a hundred or so Angstroms.

Blended systems have morphologies similar to those of the block copolymers. If crystallization occurs the results are more complicated since a second different morphology is being superposed. If the major component crystallizes the domains of the minor component will be scattered throughout the amorphous phase of the major component [32]. Some systems do exhibit partial compatibility [33,34]. One system is known in which the crystals are of one polymer and the amorphous phase a mixture of the two with no domain formation [35].

2.3 Phase-Separated Random Copolymers

The majority of commercial plastics tend to be copolymers rather than homopolymers. This is generally because properties can be controlled to a considerable degree through the incorporation of small amounts of a second monomer into the polymer chain. Incorporation is generally random and incompatibility does not occur.

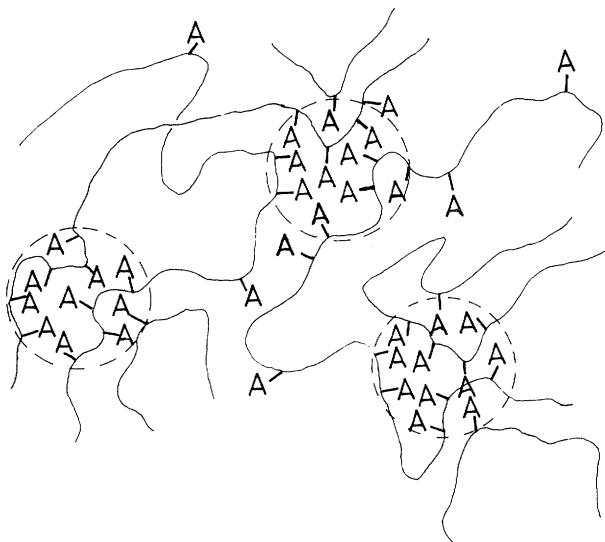


Fig. 11: Schematic representation of domain structure in an ionomer.

If, however, the second monomer has highly polar or ionic side groups, incompatibility can result. As in the block copolymers domain formation occurs; however, the situation is more complicated since the alien monomer is randomly placed. As a result the domains are more diffuse (Figure 11) and must contain hydrocarbon chain sections. They are generally 50 to 80 Å in size [36]. Examples of these materials are ethylene-methacrylic acid ionomers (Du Pont's Surlyn^(R)) [37], polyether urethanes [38] and the new thermoplastic elastomers of Exxon based on EPR [39].

2.4 Compounded Systems

Most commercial plastics are intentional blends of a polymer or polymers with, among other things, mineral fillers. The object of the compounding exercise is to improve mechanical properties as well as to reduce the cost of the end-product significantly. There is therefore a specific multiphase structure present in the material. The structure will depend drastically on the size and volume of the filler as well as on the ability of the polymer to adhere to the filler. Fillers are generally classified [1] according to whether or not chemical bonding or strong interactions occur between the filler and the polymer.

3. ELECTRICAL BEHAVIOR

3.1 Dielectric Constant and Loss

The dielectric behavior of plastics is not too different from that of low molecular weight organic molecules. Four basic types of polarization are present [40-42] and all give rise to loss mechanisms in the appropriate region of the electromagnetic spectrum (Figure 12). That occurring in the lowest frequency range, interfacial polarization, will be discussed in the following section. Here we will concentrate on the one most widely studied, orientation polarization.

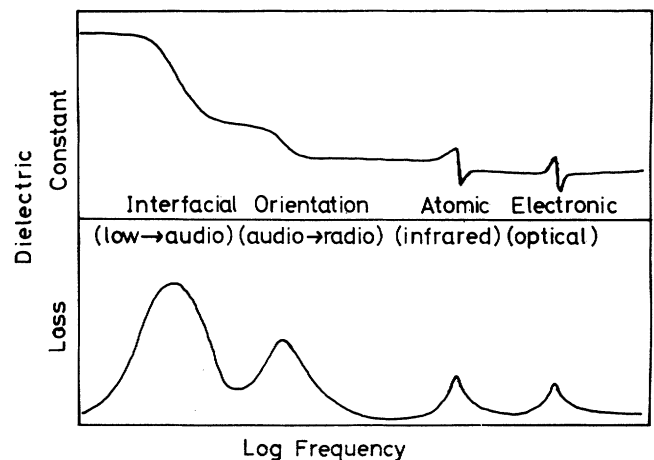


Fig. 12: Dielectric behavior of plastics as a function of frequency.

This particular type of relaxation process has been studied mainly as a means of investigating molecular motions in polymers. One of the most important parameters usually obtained is the activation energy of any particular process. It is normally obtained from the slope of a plot of the logarithm of the frequency of maximum loss versus the reciprocal temperature. The

values so obtained are often a good indication of the molecular scale of the process occurring.

In semi-crystalline polymers the dielectric loss peaks can arise from motions of polar groups in either of the two phases present. Increased crystallinity would enhance the magnitude of peaks arising from crystalline regions and depress those associated with non-crystalline regions. The best known example of this effect is the difference between low density (ca 50% crystallinity) and high density (ca 85% crystallinity) polyethylenes [43]. Polyethylene is essentially non-polar; however, slight oxidation produces sufficient dipoles for the loss peaks to be monitored. The major relaxation observed for the high density polymer is associated with the crystalline phase and peaks at about 60°C, (Figure 13). For the low density polymer this peak was suppressed and the peak at 0°C associated with amorphous regions was enhanced. Oxidation of polyethylene produces relatively large polar side groups which can be only partially incorporated into the crystals. The peaks observed cannot therefore be quantitatively related to the crystallinity. Random copolymers of polyethylene containing a few percent of carbon monoxide [44,45] do however incorporate the smaller polar groups into the crystals. This results in a near quantitative relation between the relative areas of loss peaks and the crystallinity (Figure 14). A comparison between Figures 14c and 13 will emphasize the importance of this effect on the loss maxima.

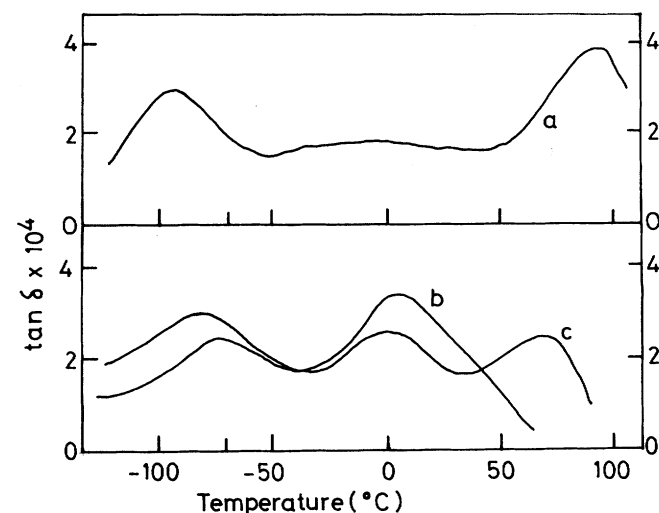


Fig. 13: Loss tangent of polyethylene at 10 kHz for (a) high density polyethylene (b) quenched low density polyethylene and (c) annealed low density polyethylene (after Mikhailov et al [42]).

Orientation of the crystals is also an important effect. The effect of stretching a film of the ethylene-carbon monoxide copolymer on its dielectric properties was determined [45]. Dipolar groups incorporated into such a crystal have a specific location relative to the crystalline lamellae (Figure 15a). Deformation of a specimen through elongation causes the molecular axis to be oriented in the direction of the deformation. Such a process naturally results in the dipole in becoming oriented perpendicular to the deformation axis. Hence the dielectric constant and loss must increase when measured across the thickness of

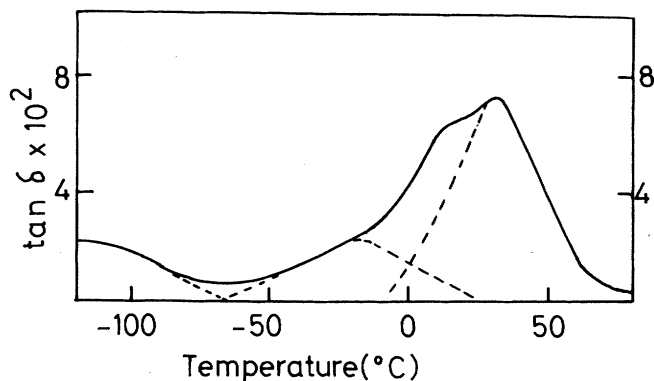


Fig. 14: Loss tangent of a copolymer of ethylene with 1.0% carbon monoxide at 100 Hz. This polymer is a low density polyethylene (after Phillips et al [43]).

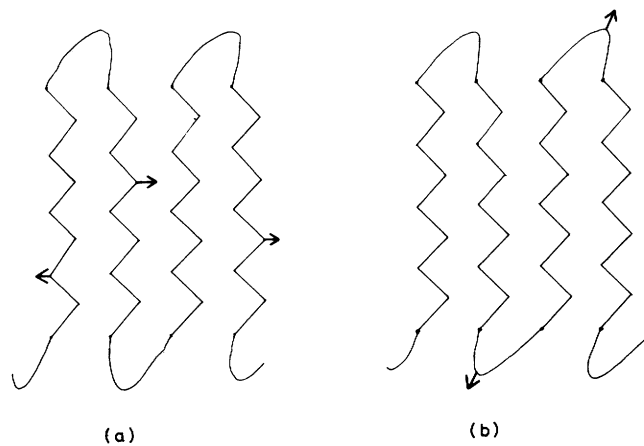


Fig. 15: Schematic representation of the location of dipoles in (a) the interior and (b) the folds of a polymer crystal.

the film [46,47]. Generally, therefore we can say that for dipoles located perpendicular to the polymer chain dielectric constant and loss will increase with deformation of the film. Conversely, those few polymers which possess dipoles in the chain direction the dielectric constant and loss should decrease with film orientation. An example of the latter might be polyphenylene oxide.

One unique feature of polymer crystals, not found in any other material, is the fold or loop found on the surface normal to the chain (Figure 15b). These folds, although part of the crystal in the broadest sense of the word, are in fact non-crystalline. Any loss associated with dipoles located in the folds will naturally increase with crystallinity and be affected by orientation. The fraction of dipoles located in folds must be relatively small compared to those in the interior of the crystal and any losses should be relatively small. No report is to be found in the literature proving the existence of such a mechanism although an interactive process involving folds and interior chains has been

proposed for polychlorotrifluoroethylene [47,48]. More detailed investigations of this mechanism using polymers of varying lamellar thicknesses and hence fold surface areas showed the loss to be primarily associated with the interior dipoles [49,50].

The relaxation processes so far discussed generally occur at elevated temperatures and relatively low frequencies. At cryogenic temperature or high frequencies loss peaks are often found which again vary with crystallinity [42]. These are the so-called γ peaks which generally occur for audio and radio frequencies below -60°C , but for microwave frequencies are important at room temperature. They have generally been ascribed to re-orientation of chains at defects in the crystalline structure and are found, amongst others, in PCTFE [48] polyoxymethylene [51] and polyethylene terephthalate [52].

A number of other studies are to be found in the literature, but the exact effects and mechanisms involved are not too clear and so will not be discussed in this general review.

3.2 Interfacial Polarization

One of the most important, but oft neglected, effects in commercial polymers is interfacial polarization [53-56]. Although normally associated with the physical dispersion of one phase in a second continuous plastic phase there are many other situations in which it occurs. The phenomenon is due to the presence of two phases, one of much higher conductivity than the other.

Naturally, a crystalline polymer contains two phases. The amorphous phase will give rise to higher mobilities than the crystalline phase. If the amorphous phase contains sufficiently large numbers of conducting species, such as in the polyamides [57-60] interfacial polarization results. It is generally manifest both by the presence of a large loss peak and by dc conductivity.

The phase-separated morphologies discussed in an earlier section also give rise to interfacial polarization. Segmented polyurethanes [38] as well as ionomers [36,37,61] show these effects. The most startling effects have been observed in polymers containing acid side groups where dielectric constants of several hundred have been reported. These polymers, the polyethylene phosphonic acids [62-64,36] and the polystyrene sulphonic acids [65] are thought to be phase-separated but detailed structures and mechanisms are still a matter of speculation.

Interfacial polarization is most commonly caused by the mundane operation of adding filler to a plastic to alter other properties. The earliest example of this was the incorporation of carbon black into rubber [66] and was the first analysis of complex relaxation behavior in terms of dc conductivity, orientation polarization and interfacial polarization (Figure 16). In this case the conducting phase was not the amorphous plastic but the carbon black.

If a filler is non-conducting it will not, of course, introduce interfacial polarization. It will, however, alter the dielectric constant through a law of mixtures effect [67] and will introduce its own relaxation processes. A review of these aspects of the subject is available in the literature [68].

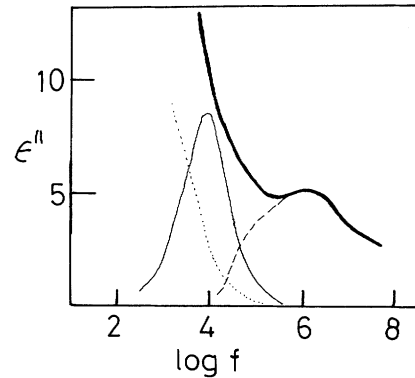


Fig. 16: Dielectric loss versus logarithm of frequency for carbon black filled Butaprene^(R) NM (after Carter et al [65]). [—: observed curve;: dc conductivity; — — —: interfacial polarization; - - - - -: orientational polarization]

Of considerable interest at the present time is the effect of water droplets on the dielectric behavior of cross-linked polyethylene insulation [56,69,70]. Water droplets give rise to interfacial polarization around 22 kHz at room temperature [56] and also to major losses between 0 and -40°C [69] which are also presumably interfacial. Cross-linked polyethylene contains not only water droplets as impurities but also acetophenone as an alien phase. Both of these give rise to major dispersions [70].

3.3 Conduction

Generally, polymers can be excellent insulators or occasionally good conductors. The majority of polymers encountered are insulators, regardless of how they have been prepared or processed. Insulating ability is a natural result of covalent bonding. Conductivity, when it does exist, is generally by ionic impurities.

Intrinsic electronic conduction occurs in polymers containing alternating single and double bonds in their backbone. This type of structure can give rise to a conjugated π -bond system. A pathway has been formed, under such circumstances, along which the electron can travel. The actual measured value of conductivity in such a system will be controlled by the ability of the electron to hop from one chain to the next [71].

Polymers containing such bonds are generally quite complex [72], but the most studied are relatively simple polyacetylene [73] and poly(phenyl acetylene) [74]. Recent potentially exciting polymers belonging to this class are the poly(diacetylenes) [15-17]. These conjugated systems can be made as large macroscopic single crystals (Figure 3). As extended chain polymer crystals, they have unique anisotropic optical properties. Many of them should also have special electrical properties and, in theory at least, should be excellent conductors.

For the more common polymers, there are a number of interesting morphological effects. The volume resistivity for a number of polymers increases with crystallinity. Data of Sazhin and Podosenova [75] is given

in Figure 17 for poly(ethylene terephthalate) and polychlorotrifluoroethylene for a series of temperatures. Such a result is not unexpected since the ionic species can only pass through the amorphous phase. The resistivity also changes markedly at the melting point. Since the resistivity is so sensitive to crystallization, it was used to follow crystallization in these polymers by the same workers. Similar effects have been observed in poly(vinylidene fluoride) [76].

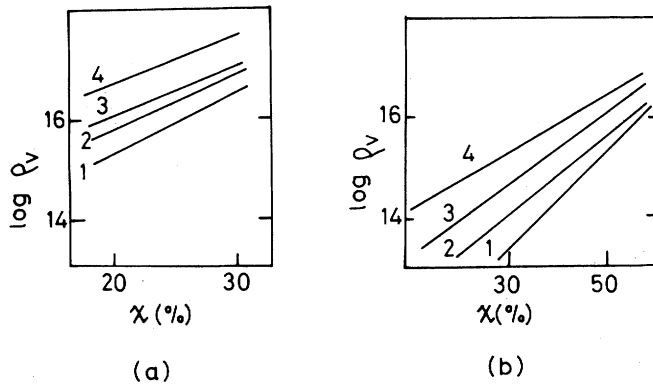


Fig. 17: Log volume resistivity versus degree of crystallinity for (a) poly(ethylene terephthalate) and (b) poly(chlorotrifluoroethylene) at (1) 114°C (2) 104°C (3) 92°C and (4) 89°C (after Sazhin and Podosenova [74]).

The effect of spherulite size on the conductivity of polyethylene, polystyrene and polyoxymethylene was determined by Kargin et al. [77], who found that conductivity decreased with spherulite diameter until a critical point was reached. This was when the diameter was equal to the film thickness. From this point, the conductivity increased to an asymptote. The phenomena have been explained in terms of the initial effect being due to increasing crystallinity and the ultimate effect being due to direct amorphous paths existing in the spherulite boundaries between electrodes.

Anisotropic effects have been studied in only one polymer, nylon 66 [78,79]. In nylon crystals the most important structural feature is the crystallographic plane along which hydrogen bonding occurs. Through mechanical deformation and, hence, orientation, the authors were able to measure the conductivity in the chain direction, along the hydrogen bonded plane and perpendicular to it. Conduction in the chain direction was always lowest; conduction in the hydrogen plane was greater than perpendicular to it. The data was interpreted as due to electron transfer along the hydrogen bonded pathway. The behavior changes with temperature (Figure 18). At a particular temperature, probably coincident with the onset of chain libration, the two planes show much closer values of conductivity. Nylon 66 is, coincidentally, the only polymer for which the conducting species has been clearly identified [80]. Hydrogen ions are responsible.

There is little more known about morphological effects in conductivity, although they are clearly of significance from the data reviewed above. The recent introduced technique of thermally stimulated conductivity (TSC) [81-83], provides a method of studying conductivity

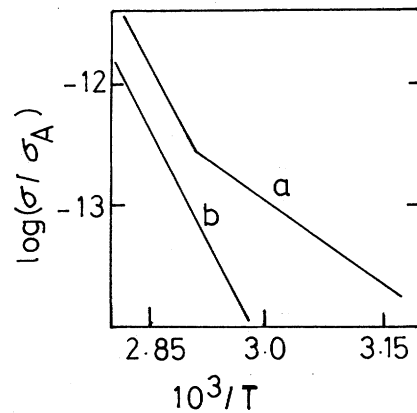


Fig. 18: Dependence of conductivity of nylon 66 on temperature (a) parallel to the hydrogen bonds and (b) perpendicular to the hydrogen bonds (after Miyoshi and Saito [78]).

and, through it, dielectric relaxation. So far, little has been done using controlled morphologies. However, data on poly(tetrafluoroethylene) is interesting [84]. The curves are reproduced in Figure 19a. Until now, it had generally been assumed that TSC only gave information on features occurring up to and including the glass transition. Comparison with dynamic mechanical data (Figure 19b) [85] clearly shows a relation between mechanical loss peaks and conduction peaks. These mechanical peaks are well understood and related to changes in the internal structure of the crystals. It is believed that morphological control of specimens used for TSC will be of major benefit to our understanding of conduction and of trapping in particular.

3.4 Piezoelectricity

The general phenomenon of piezoelectricity and related properties has become very important in recent years because of the advent of electrets [86,87]. There are two basic methods for the production of electrets. Cooling a molten polymer to a temperature below its melting point or glass transition whilst subjected to a large electric field is one method. In this technique, the orientation of permanent dipoles is partially retained. The second method involves the charging of the surfaces of the polymer film by irradiation, corona discharge, or other techniques. This latter technique is by far the most popular commercially [88].

The most thoroughly understood system is poly(vinyl chloride), which, although containing 10% crystallinity, can be regarded as amorphous. It follows the theory of Broadhurst et al. [89] in a most convincing manner. For crystalline polymers, however, the situation is not so clear. The most commonly used polymers for electrets are poly(ethylene terephthalate) (Mylar^(R)) and poly(tetrafluoroethylene) (Teflon^(R)). Naturally, these are the most heavily researched although poly(vinyl fluoride) and poly(vinylidene fluoride) are also the subject of much current investigation. In fact, Pfister et al. [90] were able to explain its behavior in terms of both charge-injection and a change in crystalline form. Murayama et al. [91] identified the β -crystal in poly(vinylidene fluoride) as operative in the piezoelectric response.

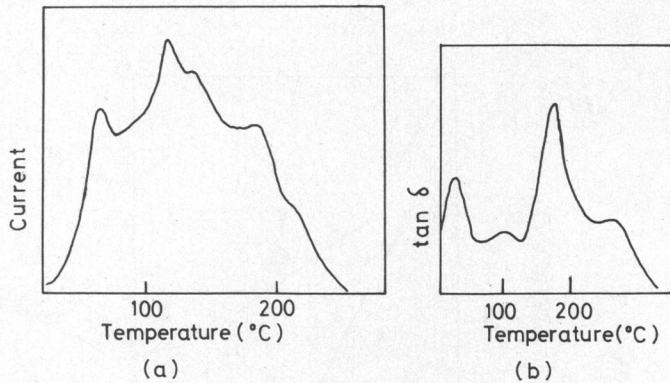


Fig. 19: (a) Thermally stimulated conduction curve of poly(tetrafluoroethylene), (after Perlman and Unger [83]); (b) Dynamic mechanical loss spectrum of poly(tetrafluoroethylene), (after Krum and Muller [84]).

Electrets are often studied using the thermally stimulated conduction technique referred to earlier. Clearly, much careful work involving morphological control and TSC studies would be of considerable benefit to the understanding of electrets. It would indeed seem certain, to this author at least, that use of the known effects of controlled crystallization and prestrain would, after suitable development, produce special dipolar orientation and, hence, electrets.

3.5 Electric Breakdown

In all its ramifications, electric breakdown is a very difficult and often confused subject. The most interesting effect in polymers at the present time is the phenomenon of treeing in insulation. Trees are found to occur in all plastics studied, whether crystalline or non-crystalline.

Until recently, there had been little research into morphological effects, even though it had been known for many years [92] that the electric strength of crystalline polymers dropped abruptly on the approach to the melting point (Figure 20).

Recently, Wagner [93] was able to show that the discharge channels in both high density polyethylene and polypropylene were situated between spherulites. It is difficult to overstate the importance of this first morphological study to our understanding of treeing processes. This observation, of course, implies that the discharge channels follow the weakest pathway. Cross-linked polyethylene, which is the most widely used insulation material, is a very different polymer. It has a crystallinity of at most 50%, whereas the two aforementioned polymers have crystallinities between 80% and 90%. Polypropylene does contain non-crystalline atactic material, which naturally would segregate in the spherulite boundaries. HDPE, if crystallized carefully in order to produce large spherulites, permits low molecular weight material to separate. XLPE has been cross-linked and should have a relatively uniform structure with no analogous material present in the boundaries. It does, however, contain water droplets absorbed during the curing process as well as significant amounts of initiator by-products. Recently, Muccigrosso and Phillips [94] were able, using an etching technique, to show that large voids are present at the points where three or more spherulites impinge (Figure 21). These voids are identical to those previously observed [95] and regarded as randomly placed. Smaller voids and even

channels were also found to be present, but only in the spherulite boundaries. XLPE, therefore, appears to have present a network of voids of various sizes associated with spherulite boundaries which would provide a weak pathway for tree growth to follow.

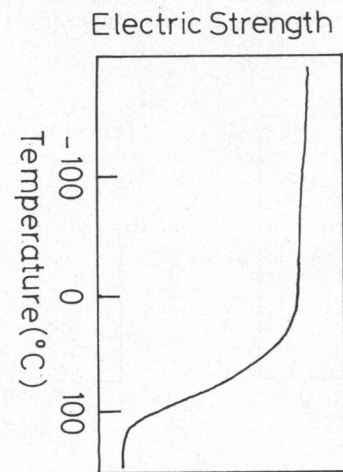


Fig. 20: Electric strength of polyethylene as a function of temperature (after Oakes [91]).

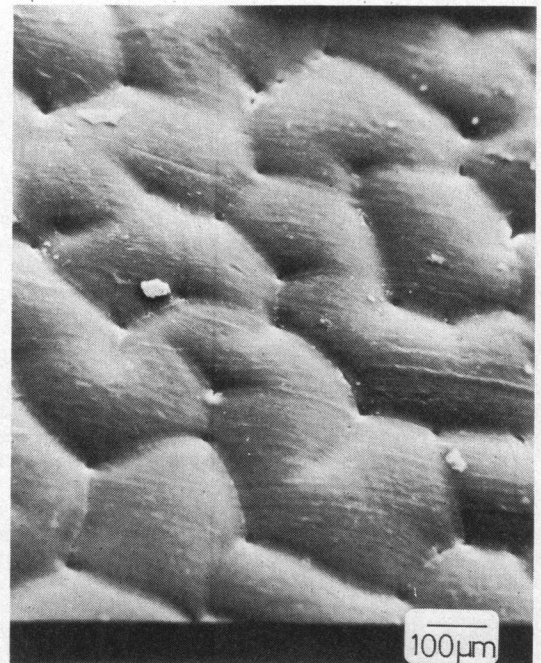


Fig. 21: Morphological structure of Cross-Linked Polyethylene.

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PSEUDO-SPHERULITE STRUCTURES IN CROSS-LINKED LOW-DENSITY POLYETHYLENE

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ABSTRACT

This paper describes evidence for the formation of secondary fissure structures, in low-density polyethylene (PE), and in cross-linked polyethylene (XLPE). These structures can be observed by optical and by scanning electron microscope techniques. The secondary fissures are not a volume effect like spherulites, but are associated with the fracture surface only. An explanation of this effect is given, as well as its relation to the observed electrical discharges in tree channels.

INTRODUCTION

Partially crystalline polymers contain internal microstructures called spherulites. These are well defined polyhedral bodies, grown from, and enveloped by, an amorphous matrix. The spherulites possess a lamellar structure, in which crystalline agglomerations of molecular chains and amorphous areas exist. Particularly large, clearly defined spherulites can be observed through the polarizing microscope, both in polypropylene and in high density polyethylene.

In earlier publications [1,2] attempts were made to find the relationship between the structure of a semi-crystalline polymer, and an electrical partial discharge therein. We concentrated first on the large polypropylene spherulites which were easiest to investigate. We demonstrated for the first time that discharge channels run along the spherulite boundaries [1]. Since these boundaries are regions of decreased structural strength, they offer lower resistance to electrical stress and permit the formation of discharge channels, Fig. 1.

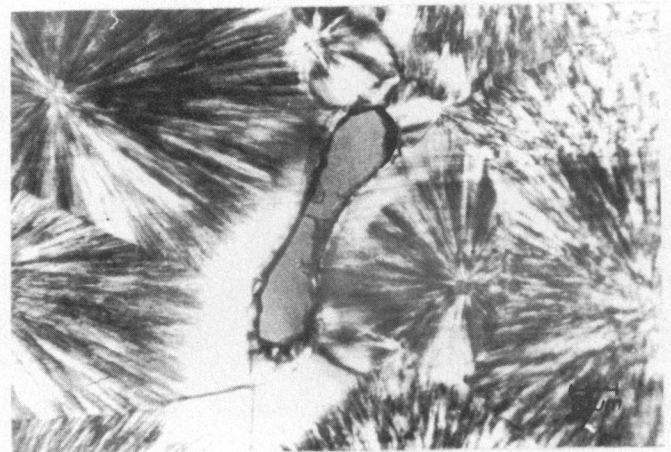


Fig. 1: Microtome section of a discharge channel located between polypropylene spherulites in polarized light. Specimen thickness 60 μm .