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Eutectic solidification of the pseudo binary system of polyethylene and 1, 2, 4, 5-tetrachlorobenzene

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This paper describes a study on the solidification of the pseudo binary eutectic system, consisting of unfractionated linear polyethylene and the faceted growing diluent 1, 2, 4, 5-tetrachlorobenzene. Crystallization under eutectic conditions resulted in very fine-grained structures, which were found to depend on the growth rate. This rate of solidification was varied by pulling the polymer solutions through a fixed temperature gradient of 3° C mm^{-1} at different speeds ranging from 1 to 216 mm h^{-1}. Fibrillar polymer crystals with lateral dimensions of about 0.5 μm remained after removal of the solid diluent. At rates of solidification in the region of 2 to 20 mm h^{-1}, the fibrils appeared to be aggregated in domains of well oriented structures, closely resembling the complex regular structures of the eutectic Sn–Bi system. At higher speeds the fibrillar crystals formed an irregular three-dimensional network. The polymeric structures grown from more dilute mixtures were characterized by rectangular holes originating from the growth of faceted primary diluent crystals. Despite the complexity of the crystallization of the highly entangled polymer solutions there appears to be quite some similarities between the eutectic polymeric system investigated and faceted/non-faceted atomic or small molecular eutectics.

1. Introduction

Controlled solidification of small molecular and atomic eutectic systems has been studied extensively in the last two decades and a number of the composite materials, produced *in situ* by applying this technique, have already found their application because of unique mechanical and physical properties [1–3]. Except for the eutectic-type minimum in the melting temperature/composition diagrams of copolymers [4, 5] and a theoretical treatment of heterodisperse polymers as eutectic systems [6], hardly any notice has been paid to the subject of eutectics in polymeric systems.

The theory of melting point depression of Flory and Huggins predicts that a eutectic point may be observed in macromolecular systems [7] and more specific in an athermal polymer solution if the melting point of the solvent is not too low in comparison with that of the polymer [8]. As shown in previous papers [8, 9] the pseudo binary system consisting of nonfractionated linear polyethylene and the diluent 1, 2, 4, 5-tetrachlorobenzene complies with this requirement. The melting point diagram of this eutectic-type system, as determined by means of differential scanning calorimetry, is presented in Fig. 1. A calorimetric study pointed out this this phase diagram depended strongly on kinetic factors as indicated by the formation of the metastable polymer solid state [8]. In addition to this problem, other characteristics of macromolecular systems, such as the heterodisperisty in chain length, the entanglement structure of concentrated polymer solutions and the remaining amorphous phase in the solid polymer, make the eutectic solidification in these

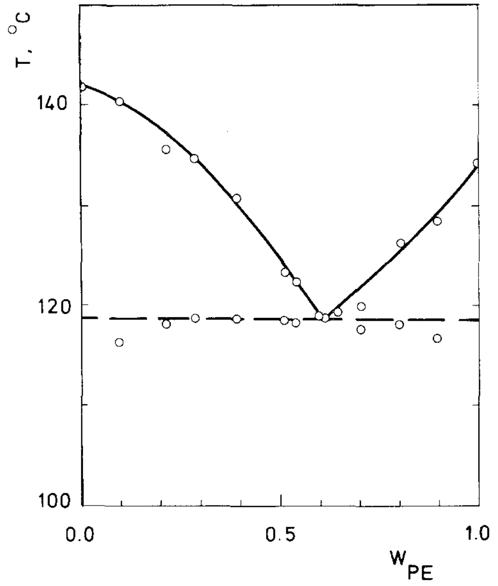

Figure 1 Melting point diagram of the pseudo binary system of polyethylene and 1, 2, 4, 5-tetrachlorobenzene, as determined by differential scanning calorimetry. W_{PE} indicates weight fraction of polyethylene.

systems much more complex than in atomic and small molecular eutectics.

Nevertheless, eutectic solidification of binary systems of a polymer and a low molecular weight compound provides a method for growing polymer composites *in situ* and a unique way of dispersing crystalline additives such as dyes and nucleating agents. It also may be an excellent method for producing porous materials by removal of the small molecular component from the solidified eutectic mixture. For these reasons investigations were undertaken to elucidate the microstructure of these kind of systems and a study of the influence of the rate of solidification on the morphology has been made in order to gain some understanding of the mechanism of this mode of crystallization.

2. Experimental details

2.1. Materials

The experiments in this study were carried out with unfractionated linear polyethylene, Marlex 6009, with the following molecular characteristics: $\bar{M}_n = 8 \times 10^3$, $\bar{M}_w = 13 \times 10^4$, as determined by ebulliometry and light scattering in α-chloronaphthalene at 125° C respectively. The diluent was 1, 2, 4, 5-tetrachlorobenzene having a melting point of 141.5° C. Since impurities are known to affect strongly the eutectic microstructures [10, 11], both components were purified. The polyethylene was recrystallized from para-xylene and the diluent from petroleum ether.

2.2. Sample preparation

Solutions of polyethylene in 1, 2, 4, 5-tetrachlorobenzene were prepared by intensive mixing of the powdered components are subsequent homogenization at 200° C for 1 h in a sealed glass tube, with an internal diameter of 4 mm and a length of about 60 mm. The polymer solutions were solidified unidirectionally in a fixed temperature gradient of $3° \mathrm{C\,mm^{-1}}$ by pulling the specimens out of an oven unless indicated otherwise. The temperature of this oven was kept at 200° C during all the crystallization experiments.

The microstructure of the crystallized mixtures were studied on fracture surfaces of the samples, which were obtained by breaking the specimens in liquid nitrogen. After removal of the solid diluent by sublimation under reduced pressure at 60° C these fractured samples were examined in the scanning electron microscope (Jeol JSM U3).

2.3. Differential scanning calorimetry

Thermal analysis on the pseudo binary system of polyethylene and 1, 2, 4, 5-tetrachlorobenzene was carried out in order to establish the composition of the mixture from which both components crystallize simultaneously. For these measurements samples were used of about 5 mg of mixtures with different compositions, which were homogenized in sealed aluminium pans at 200° C for 30 min. Subsequently the specimens were cooled down with rates ranging from 0.5 to $16° \mathrm{C\,min^{-1}}$ in a differential scanning calorimeter (Perkin Elmer DSC-model 1B). This instrument was calibrated according to standard procedures.

3. Results

3.1. Eutectic composition

Crystallization of the polymer solutions has to be divided in the crystallization of eutectic solutions and of mixtures which have a composition different from the eutectic one, so called off-eutectic solutions. Solidification of eutectic mixtures is characterized by the simultaneous crystallization of the components from the liquid phase. Cooling of off-eutectic solutions results at first in the crystallization of the excess of one component, in primary crystals, until the remaining solution has reached the eutectic composition.

The eutectic composition and temperature of the polyethylene solutions are not exactly known [8], due to the fact that the melting point diagrams of polymeric eutectic systems are determined by kinetic factors. However, in crystallization experiments, carried out in a differential scanning calorimeter, the composition of the pseudo binary mixture of polyethylene/1, 2, 4, 5-tetrachlorobenzene for which only one crystallization exotherm occurred, appeared to be independent on the rate of solidification. This composition, which is referred to as the eutectic composition, was found to be 55% w/w polyethylene in 1, 2, 4, 5-tetrachlorobenzene. The fact that this eutectic composition turned out to be independent of the cooling rate may be a result of a favourable liquid structure in the eutectic mixture [9].

3.2. Off-eutectic solutions

A typical example of the polymeric structure that remained after sublimation of the diluent from a solidified off-eutectic mixture with an excess of tetrachlorobenzene is given in Fig. 2. The presented scanning electron micrographs are taken from the macromolecular material grown from a 10% w/w solution of polyethylene in 1, 2, 4, 5-tetrachlorobenzene. Fig. 2a shows cross-sections through this polymeric structure in the direction of solidification, which is from the bottom to the top of this micrograph, and perpendicular to it. Rather long canals, well oriented in the growth direction, can be discerned in this porous material. An enlarged view of this structure, Fig. 2b, discloses the rectangular habit of the holes, which originate from the formation of the faceted primary crystals of the diluent.

The present structures obtained by crystallization of off-eutectic solutions clearly exhibit the influence of the temperature gradient, in which they were grown. The primary crystals of the diluent were found to be well oriented in the direction of the growth, as illustrated in the scanning electron micrographs of Fig. 2. In contrast to the temperature gradient, the rate of solidification hardly affected the morphology of the crystallized off-eutectic mixture. The structures grown at low rates of $10\,\mathrm{mm\,h^{-1}}$ in a temperature gradient of $3°\,\mathrm{C\,mm^{-1}}$ differed only slightly in the lateral dimensions of the holes from those as obtained by pouring out the dilute polymer solution on a cold glass plate. In the material solidified in the latter way (the scanning electron micrographs of Fig. 2), the primary diluent crystals had a somewhat smaller diameter than in the specimens grown with $10\,\mathrm{mm\,h^{-1}}$. This is in accordance with the effect of the cooling rate on the number and size of crystals usually found.

In more concentrated off-eutectic solutions with an excess of the diluent the habit of the primary solvent crystals changed remarkably. These crystals grew from a 40% w/w solution of polyethylene in 1, 2, 4, 5-tetrachlorobenzene in a stepwise mode. This is probably caused by adsorption of macromolecular material on crystal

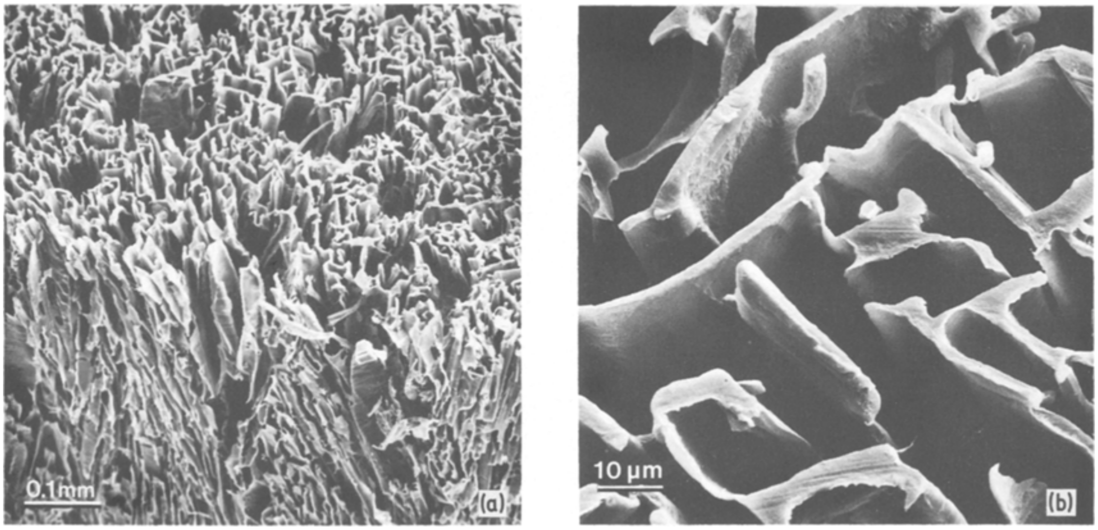

Figure 2 Scanning electron micrographs of the polymeric structure that remained after sublimation of the diluent from an off-eutectic mixture of 10% w/w polyethylene in tetrachlorobenzene, solidified by pouring out on a cold glass plate. The rectangular and quadratic holes in these micrographs originate from the faceted primary diluent crystals.

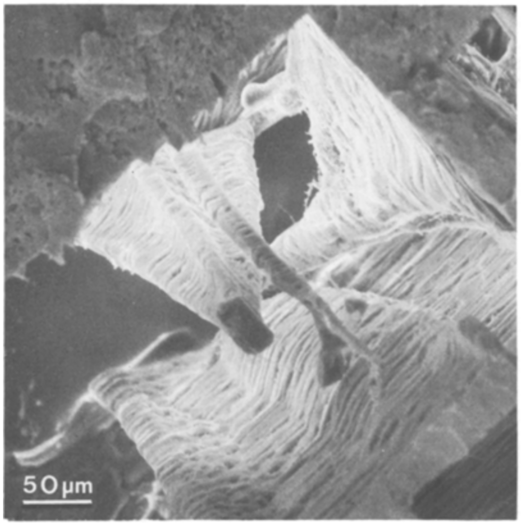

Figure 3 Scanning electron micrograph of the porous polymer material that left behind after removal of the solid diluent from a 40% w/w solution of polyethylene in tetrachlorobenzene, solidified with 10 mm h^{-1} in a temperature gradient of 3° C mm^{-1}. This micrograph discloses the hopper-like habit of the primary diluent crystals grown from concentrated solutions.

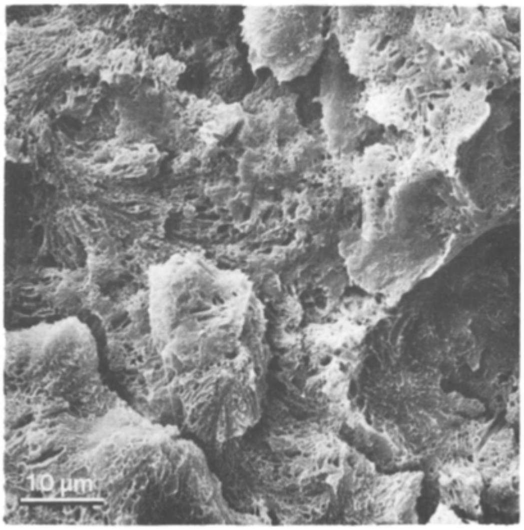

Figure 4 Micrograph of the spherulitic polyethylene structure that remained after removal of the solid diluent from a eutectic mixture, which was solidified by quenching in cold water.

surfaces. The morphology of the primary crystals was quite similar with the hopper-like crystals of bismuth [12]. The polyethylene structure grown around these modified crystals is shown in Fig. 3. The scanning electron micrograph presented in this figure, was taken from a fracture surface perpendicular to the growth direction of a specimen solidified with 10 mm h^{-1}.

Finally, solidification of off-eutectic mixtures with an excess of polyethylene resulted in the generation of an incomplete porous structure, due to the formation of primary polyethylene sperulites.

3.3. Eutectic solutions

In this study eutectic solutions were solidified over a wide range of crystallization rates and directional solidification was accomplished in a temperature gradient of 3° C mm^{-1} with speeds varying from 1 to 216 mm h^{-1} as well as by quenching the specimens in cold water in order to induce rapid crystallization of the components.

A scanning electron micrograph of the porous polymeric structure which remained after sublimation of the solid solvent from the quenched eutectic mixture is given in Fig. 4. A degenerated type of sperulites can be discerned in this material. These structures originate from the fast simultaneous crystallization of the polymer and the diluent, as could be established by direct microscopic observations of the crystallization of thin eutectic films.

By directional solidification of eutectic solutions in a fixed temperature gradient more defined morphologies were obtained. Two regions of solidification rates could be distinguished in which different eutectic structures developed.

Fig. 5 shows a typical example of the morphology of the polymeric material that remained after removal of the solvent from the eutectic solution, which was solidified with a rate in the range from 20 to 216 mm h^{-1}. The porous material appeared to consist of fibrillar polyethylene crystals as was revealed in the scanning electron microscope (Fig. 5a). A more detailed micrograph, as presented in Fig. 5b, of these structures shows that the fibrils are heavily branched and have a transverse diameter of about 0.5 μm. No influence of the direction of solidification or crystallization rate on the morphology or fibril dimensions could be established in specimens solidified at different speeds in this range of growth rates. The scanning electron micrographs of Fig. 5 were taken from a fracture surface perpendicular to the growth direction of a sample which was crystallized with 216 mm h^{-1}. Fracture surfaces along the solidification direction exhibited similar pictures in the electron microscope.

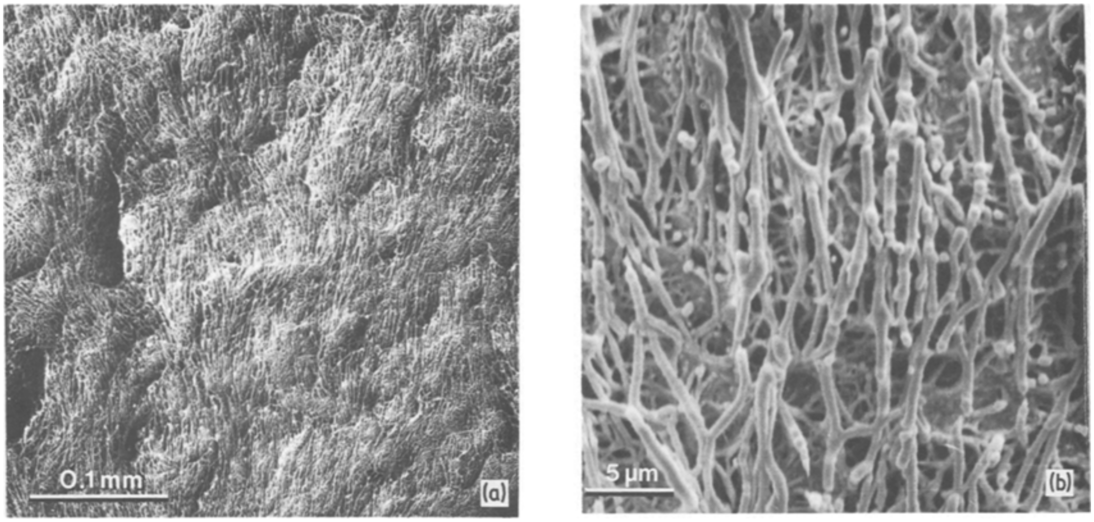

Figure 5 Scanning electron micrographs of the fibrillar polymeric microstructure that left behind after sublimation of the solid diluent from a eutectic mixture, which was solidified unidirectionally with 216 mm h^{-1} in a temperature gradient of 3° C mm^{-1}. Growth direction out of paper.

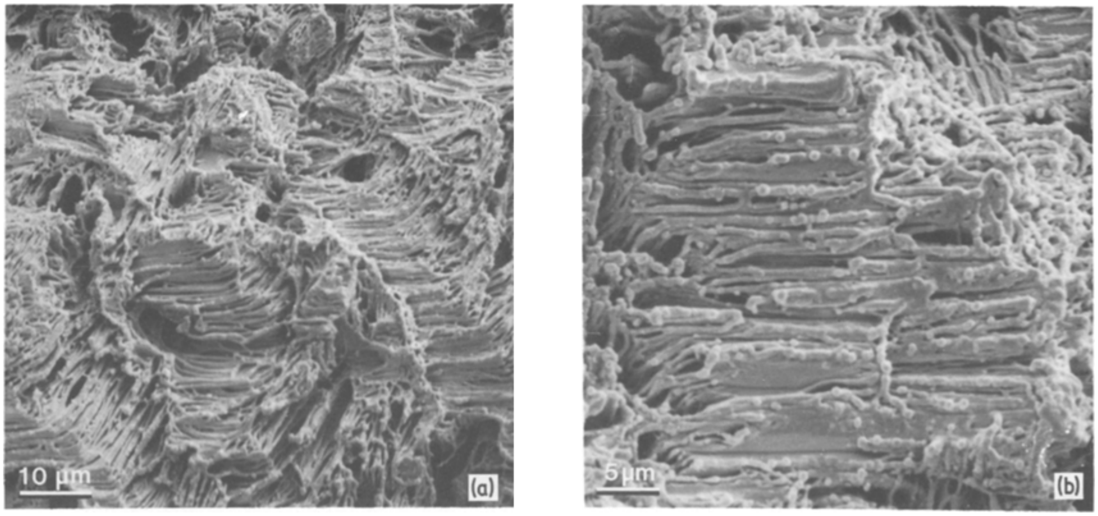

Figure 6 Scanning electron micrographs of the complex regular polymeric microstructure that remained after removal of the solid diluent from a eutectic mixture, which was solidified unidirectionally with 10 mm h^{-1}. Growth direction out of paper.

The presented structures were grown from a 55% w/w solution of polyethylene in tetrachlorobenzene, which corresponds with a polyethylene volume fraction of about 0.75. In this rather loose fibrillar polymeric structure the polymer volume fraction seems to be substantially lower than 0.75. This may be the result of some deformation of the macromolecular material upon breakage of this particular specimen.

In the other region of pulling rates, which ranged from 2 to 20 mm h^{-1}, a different eutectic microstructure was obtained. In the micrograph of Fig. 6a showing a fracture surface of the eutectic mixture, that was solidified unidirectionally at 11 mm h^{-1}, domains of oriented close-packed polyethylene fibrils can be discerned. The present structure has characteristic features in common with the "complex regular" eutectic microstructure of the non-faceted/faceted Sn–Bi eutectic [13]. Similar with the structures grown at faster speeds, the rate and direction of solidification did not affect the morphology of the polymer/

diluent eutectic. In all cases, the material that was left behind after removal of the solvent, appeared to be built up from 0.5 μm thick polyethylene fibrils (Fig. 6b).

Eutectic solutions which were solidified at rates lower than 2 mm h^{-1} did not show any orientation or regularity in morphology. The mixtures crystallized in rather degenerated structures at these low rates, which is a quite common phenomenon in low molecular weight and atomic eutectics [14]. However, the possibility that this irregularity of the morphology is caused by instability of the temperature gradient or non linearity of the pulling rate should not be ruled out.

3.4. Coupled region

Well defined eutectic microstructures without primary crystals of one component are generally grown in a narrow composition region around the eutectic point. However, in studies of off-eutectic mixtures [15, 16] it has been shown that also these solutions could be solidified with a primary crystal-free eutectic morphology if proper temperature gradients and growth rates were applied. The concentration range in which this specific mode of eutectic crystallization can be carried out, is usually referred to as "the coupled region".

In the present eutectic system composed of polyethylene and the diluent 1, 2, 4, 5-tetrachlorobenzene a coupled region was observed for off-eutectic mixtures with a small excess of the solvent. A schematic representation of this region where coupled growth of the both components occurred, is given in the graph of Fig. 7.

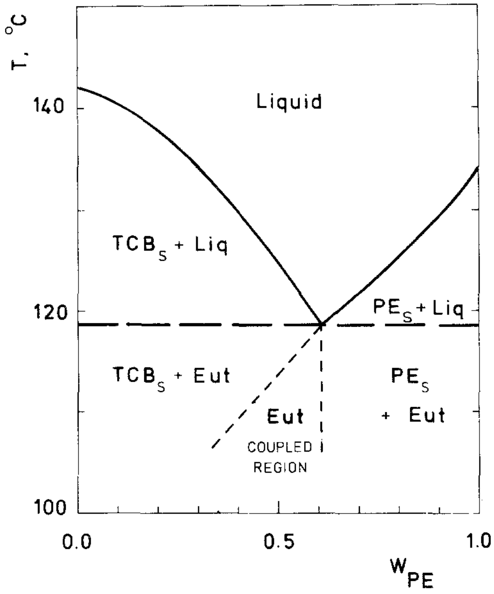

Figure 7 Schematical representation of the coupled region in the phase diagram of the system polyethylene/ 1, 2, 4, 5-tetrachlorobenzene.

A typical example of the structures obtained by crystallization of off-eutectic solutions in the coupled region is given in Fig. 8. Here scanning electron micrographs are presented of the polyethylene structure which remained after removal of the diluent from a 40% w/w solution of polyethylene in tetrachlorobenzene, solidified by quenching in cold water. It should be noticed

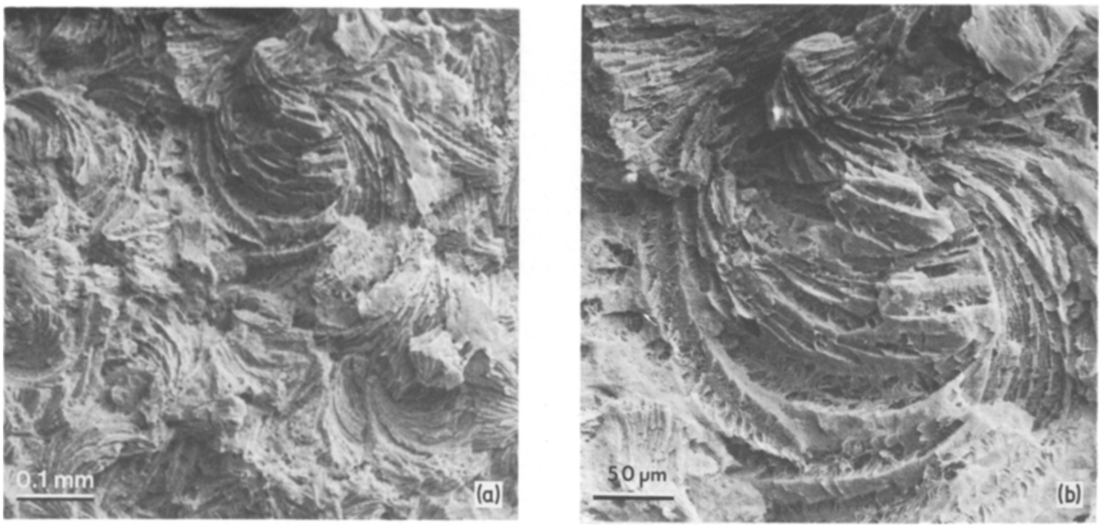

Figure 8 Scanning electron micrographs of the spherulitic polymer eutectic microstructure that left behind after removal of the diluent by sublimation from a 40% w/w solution of polyethylene in tetrachlorobenzene, which was solidified by quenching in cold water.

that, in contrast to the pictures of Fig. 3 of the same solutions, in the present micrographs of these off-eutectic mixtures the large rectangular holes originating from the primary solvent crystals are lacking. The picture of Fig. 8a displays a spherulitic structure similar to the eutectic microstructure shown in Fig. 4. A more detailed micrograph of this material (Fig. 8b), exhibit that this structure grown from the off-eutectic solution is remarkably courser than that obtained by solidification of a eutectic mixture. This might be due to the greater amount of the diluent in the solidified solution. Attention should be paid to the curved shape of the diluent crystals in this eutectic microstructure. In off-eutectic solutions the tetrachlorobenzene primary crystals were found to have a whisker-like habit. The generation of the present curved crystals may be caused by adsorption and accumulation of macromolecular material on certain growth faces. It is to be expected that also the mutual transport of both components in the mixture is an important shape-determining factor.

Solidification of off-eutectic mixtures with an excess of polyethylene did not result in the formation of a complete eutectic structure without primary polymer crystals. The coupled region has therefore an asymmetric shape, as is frequently observed for non-faceted/faceted eutectics [17].

4. Discussion

The present data on the solidification of the pseudo binary system of heterodisperse polyethylene and the diluent 1, 2, 4, 5-tetrachlorobenzene show that this eutectic polymeric system has quite a number of features in common with non-faceted/faceted low molecular weight and atomic eutectics. The most conspicuous similarities between these systems are the complex regular eutectic microstructure and the asymmetric coupled region for the more diluted polymer solutions. The present system can clearly be distinguished from non-faceted/non-faceted and faceted/faceted eutectics, according to the classification of Hunt and Jackson [13] for atomic and low molecular weight eutectics, which do not display these characteristics.

The components of the first of these two groups of eutectics, non-faceted materials, grow with an atomically rough solid–liquid interface, similar to metals. Solidification of these eutectic systems is characterized by coupled growth of both components and results, under proper conditions, in general in the generation of lamellar or rod-like eutectic microstructures. This mode of solidification is mainly governed by the cross diffusion of both species ahead of the interface and the creation of different interfaces.

The lamellar periodicity (λ, defined as the sum of the widths of the lamellae of both phases), of the obtained microstructures has been found to depend on the growth rate (R) in the following way

$$\lambda^2 \cdot R = \text{constant.} \tag{1}$$

This relationship has been derived theoretically by Jackson and Hunt [18]. The constant depends on the diffusion coefficient (D), eutectic temperature (T_E), the ratio of the lamellar widths of both phases (ξ), the heat of fusion of the components (L_1, L_2), the free energy required for the formation of the interfacial boundary between the two solid phases, ($\sigma_{1,2}$), and on the slopes of the liquidus lines at the eutectic point (m_1 and m_2).

For a eutectic system where both components are completely inmiscible in the solid state and both lamellae have an equal width Equation 1 becomes

$$\lambda^2 \cdot R = 14.8 \cdot D \cdot T_E \cdot \sigma_{1,2} \left(\frac{1}{L_1 m_1} + \frac{1}{L_2 m_2} \right) \tag{2}$$

Faceted growing materials have a nearly atomically smooth solid–liquid interface and are generally referred to as non-metals. In solidification of eutectic systems of two faceted growing materials the components grow independent of each other and the eutectic microstructure is built up from randomly mixed crystals of the two materials.

According to Jackson [19] the faceted or non-faceted habit of materials depend on a factor α, defined as $\xi \Delta S/R$. Here ΔS is the entropy of fusion, R is the gas constant and ξ is a crystallographic factor, in general equal to or slightly different from 1. If α is less than 2 non-faceted growth occurs, while for values of α greater than 2 the material crystallizes in a faceted manner. It should be noticed that this criterion is not supposed to hold for polymers, since their chain character differs essentially from the atomistic model on which the classification is based.

For the diluent of the system under investigation, 1, 2, 4, 5-tetrachlorobenzene, $\alpha = 7.0$, as derived from the enthalpy of fusion, and the growth of this material takes indeed place with crystalline facets. This is clearly illustrated by the structure in Fig. 2 from off-eutectic solutions with an excess of solvent, which show the rectangular and quadratic holes originating from the formation of the faceted primary tetrachlorobenzene crystals.

From the data presented in this paper it is evident that this polymer/diluent system has to be distinguished from faceted/faceted eutectics. These systems are characterized by the fully independent growth of the components upon solidification of the eutectic mixture. The spherulitic structures obtained by rapid crystallization, the fibrillar polyethylene network and the complex regular structures grown at lower rates, clearly demonstrate the effect of coupled growth in the polymeric system under eutectic conditions. In the case that the polymer and the diluent would have grown independent of each other from the eutectic solution, the morphology of the obtained structure should be characterized by randomly dispersed faceted diluent crystals in a polymer matrix, which was not observed.

The solidification of non-faceted/faceted eutectic systems leads in general to the generation of rather complex structures. According to a yet unpublished treatment of Van Suchtelen [20] these structures can be thought to be built up from a non-faceted/non-faceted lamellar or rod-like structure with a periodicity λ_{eut}, on which the cellular structure of the faceted growing component (with λ_{cell}) is superimposed. Under conditions where λ_{cell} has small dimensions in comparison with λ_{eut} the eutectic microstructure of the non-faceted/faceted mixture should resemble closely the structures found for non-faceted/non-faceted eutectics. When λ_{cell} is greater than λ_{eut} more complex morphologies should be obtained, which in general is observed. Nevertheless, also in these complex regular structures the fine structure should be governed by Equation 1. Whether or not this relation is applicable to polymeric systems, substitution of values for the different parameters of the system under study in Equation 2 leads to $\lambda = 0.6\,\mu$m, for $R = 10\,\text{mm}\,\text{h}^{-1}$, which is in close accord with the characteristic dimension of the complex regular structure of the present eutectic. The following values were used for the different quantities: heat of fusion of polyethylene = $70\,\text{cal}\,\text{cm}^{-3}$ and of the tetrachlorobenzene = $70\,\text{cal}\,\text{cm}^{-3}$; eutectic temperature 118° C; $\sigma_{1,2} = 80\,\text{erg}\,\text{cm}^{-2}$; slopes of the liquidus curves in the eutectic point = 40° C/volume fraction for both components [8]. The surface free energy, $\sigma_{1,2}$, was taken to be $80\,\text{erg}\,\text{cm}^{-2}$ which is a rather common value for atomic systems. This is the value of σ for the basal plane of polyethene crystals which in general has relatively large dimensions and is therefore likely to give the main contributions to the interfacial boundary. For the diffusion coefficient in relation [2] the coefficient of segmental diffusion ($D = 10^{-7}\,\text{cm}^2\,\text{sec}^{-1}$) has been used for this estimation, since the mobility of whole macromolecules is almost neglectable in concentrated polymer solutions. The movements of the polymer chains are limited to changes in conformation and it is to be expected that relaxation of the chains plays an important role in the simultaneous crystallization process of the polymer and the diluent.

The similarities between the eutectic system composed of polyethylene and 1,2,4,5-tetrachlorobenzene and non-faceted/faceted eutectics seems to point out that the polymer should have a non-faceted like habit. This leads to the idea that the monomer unit of the polymer has to be considered as the crystallizing entity in this solidification process, as was already done by using the segmental diffusion coefficient in the estimation of λ. For polyethylene the value for α is 1.1, if the entropy of fusion is taken per monomer unit, as is customary. According to Jacksons criterion, this indicates that the polymer has a non-faceted character indeed, if the polyethylene can be considered as an ensemble of segments. This, of course, completes the picture as outlined above. However, it is obvious that in the crystallization of eutectic polymeric systems the habit of the polymer cannot be conceived so simplified. The limited mobility of the segments due to the chain character of the macromolecules and the entanglement structure of concentrated polymer solutions make this solidification process much more complex. Also the remaining amorphous phase in the solid polymer gives rise to specific problems in the simultaneous crystallization of the polymer and a low molecular weight compound. Polymers can therefore not simply be classified as faceted or non-faceted growing materials. In fact, crystalline polymers form a special group of materials. In addition to the entanglement structure of their melts and concentrated solutions, the tendency to form metastable folded chain crystals, connected by tie molecules, which grow normal to the face with the lowest surface free energy make polymers distinguishable from the faceted and non-faceted growing materials. Nevertheless, from the presented data one may conclude that the polymer has a rather non-faceted character in eutectic solidification of the described polymer diluent system. And it is to be expected that in the formation of the microstructure of polymeric eutectic mixtures the cross diffusion of the polymer segments and the small diluent molecules ahead of the interface may play an important role.

Finally, some remarks should be made about the influence of the temperature gradient of 3° C mm^{-1} on the solidification of the eutectic mixture. The orientation of the primary diluent crystals over entire specimens of more dilute mixtures points to the fact that the unidirectional solidification process was not poisoned by large temperature gradients in the samples. Nevertheless, no effect of this mode of crystallization was found on the eutectic microstructures. A preliminary study on the unidirectional solidification of polymers showed that the applied temperature gradient of 3° C mm^{-1} was not sufficient to induce oriented crystallization of the polyethylene. Therefore the eutectic crystallization of the polymer/diluent system described in this paper is hampered by the spherulitic crystallization of the macromolecular material. The fact that the diluent crystals in the eutectic structures also appeared to be not oriented in the growth direction may be regarded as evidence for coupled growth of both components in the eutectic solidification process.

On the solidification of polymeric eutectic systems in temperature gradients which induces oriented growth of both components will be reported in a subsequent paper.

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References

1. G. A. CHADWICK, "Metallography of Phase Transformations" (Butterworths, London, 1972) p. 107.
2. J. D. LIVINGSTON, *J. Crystal Growth* **24/25** (1974) 94.
3. W. KURZ and P. R. SAHM, "Gerichtet Erstartte Eutekische Werkstoffe" (Springer-Verlag, Berlin, 1975).
4. O. B. EDGAR and R. HILL, *J. Polymer Sci.* **8** (1952) 1.
5. L. MANDELKERN, "Crystallization of Polymers" (McGraw-Hill, New York, 1964) p. 88.
6. G. I. ASBACH, H. G. KILIAN and F. H. MÜLLER, *J. Polymer Sci.-C* **18** (1967) 133.
7. M. HIRAMI, *Polymer* **8** (1967) 482.
8. P. SMITH and A. J. PENNINGS, *Polymer* **15** (1973) 413.
9. A. J. PENNINGS and P. SMITH, *Polymer* in press.
10. In [1], p. 121.
11. G. A. CHADWICK, in "Progress in Materials Science" (Pergamon Press, Oxford, 1965), Vol. 12 p. 143.
12. R. S. WAGNER and H. BROWN, *Trans. Met. Soc. AIME* **224** (1962) 1185.
13. J. D. HUNT and K. A. JACKSON, *Trans. Met. Soc. AIME* **236** (1966) 843.
14. G. A. CHADWICK, *J. Inst. Metals* **91** (1963) 169.
15. J. D. HUNT and K. A. JACKSON, *Trans. Met. Soc. AIME* **239** (1967) 864.
16. H. E. CLINE and J. D. LIVINGSTON, *Trans. Met. Soc. AIME* **245** (1969) 1987.
17. In [3], p. 113.
18. K. A. JACKSON and J. D. HUNT, *Trans. Met. Soc. AIME* **236** (1966) 1129.
19. K. A. JACKSON, "Liquid Metals and Solidification", (Amer. Soc. Metals, Cleveland, Ohio, 1958) p. 174.
20. J. VAN SUCHTELEN, private communication (1975).

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