The role of secondary nucleation in epitaxial growth: the template model

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The traditional view of epitaxial growth of a crystal on an underlying substrate, having appropriate lattice matches, is that the growth proceeds immediately and that nucleation considerations are unnecessary. In the case of substrates having limited dimensions, it is necessary to ensure that the dimensions of the critical secondary nucleus do not exceed the dimensions of the substrate crystal. It is shown that this condition is very important when polymeric substrates are used. In essence, there is a necessity for the elementary growth 'template' of the depositing polymer to fit the elementary existing lamellar template of the substrate. For the case of polyethylene growing on a polypropylene substrate, it is shown that a simple theory explains all the known facts and resolves a current controversy involving epitaxy *versus* nucleation for that system.

(Keywords: epitaxial growth; secondary nucleation; template model)

INTRODUCTION

Primary nucleation is generally recognized to fall into two classes, instantaneous and sporadic. The instantaneous class is usually identifiable as some form of heterogeneous nucleation (i.e. some form of interface involving a different material). The sporadic curve is often referred to as homogeneous nucleation, in which the crystallizing substance forms its own three-dimensional primary nucleus. In reality the sporadic (i.e. time-dependent) nucleation process may be caused by chemical changes in the melt. Secondary nucleation is the process by which crystals grow after they have been nucleated by the primary process. In this process an essentially two-dimensional nucleus of the crystallizing substance must form on the crystal face and may be regarded as a two-dimensional form of homogeneous nucleation.

A mechanism which is often mistakenly regarded as a form of heterogeneous primary nucleation is epitaxy. In this mechanism there is a match of lattices between the foreign material and the crystallizing substance which essentially results in a continuation of the growth of the crystal of the foreign material, but through the addition of the crystallizing substance. This addition may occur through secondary nucleation or by surface roughening dependent on the crystallizing substance. However, in the case of polymers it is generally recognized that secondary nucleation is the prevalent mode of crystal growth.

Epitaxial growth is well known and the basic requirements for its occurrence in atomic and molecular systems are well established. The phenomenon has many important industrial uses, especially in the semiconductor industry. Generally, a lattice match is required in which the discrepancy between the lattice parameters of the two substances can be no more than 13%. Additionally in the case of non-cubic crystals, such as organic molecules and polymers, there must be a second lattice match normal to the first one. The cases that have been studied most frequently are those related to elemental solids in which the crystal may have growth through a surface roughening mechanism rather than by secondary nucleation[1] and so the deposition of the critical nucleus has not received much attention.

In the crystals of many hydrocarbons and in all semicrystalline polymers, the crystal dimensions cannot be regarded as infinite in all directions, largely because of the limited lamellar thicknesses that generally occur. Additionally, the critical nucleus of a polymer is a single stem, or perhaps a few stems, and so has one crystal dimension of the same order as the lamellar thickness. In the case of polymers epitaxially depositing on substrates there must be an appropriate crystal dimension in the substrate that is greater than the critical nucleus size. When a polymer deposits epitaxially on a polymeric substrate the constraints become considerable as there must be some matching of some lamellar dimensions between polymer and substrate.

The epitaxial growth of polyethylene on polypropylene has been studied for several years and has become an accepted fact[2–5]. A lattice match occurs between the two polymers which is well inside the expected requirements. The epitaxy principle has been used for bonding by polyethylene of highly oriented polypropylene sheets[6]. Studies of the temperature dependence of epitaxial growth of polyethylene on oriented polypropylene substrates have recently raised questions regarding the validity of the epitaxial mechanism[7]. The authors could not find any traces of ordered epitaxially grown polyethylene crystals for crystallization temperatures above 120°C. Films quench crystallized into ice water, and hence crystallizing at temperatures below 120°C,

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0032-3861/94/16/3373–04

showed a high degree of epitaxial order. Additionally, crystallization at 115°C generated some epitaxial order, but crystallization by slow cooling to 118°C did not generate epitaxy. Epitaxy would have been expected to function most effectively at low supercoolings where the crystals are growing slowly and more perfectly, and where competition from other primary nucleation mechanisms would be minimized. As a result of these studies Petermann and Xu[7] suggested that a heterogeneous nucleation controlled process was occurring.

In this paper, it is demonstrated that the results of Petermann and Xu are easily explained when attention is paid to the process by which crystals grow, namely secondary nucleation. It is shown that the reported behaviour would be expected when an additional requirement is placed on epitaxy between two polymers, namely that the stem length in the depositing crystal cannot be greater than the crystal dimension in the substrate characteristic of the lattice match directions.

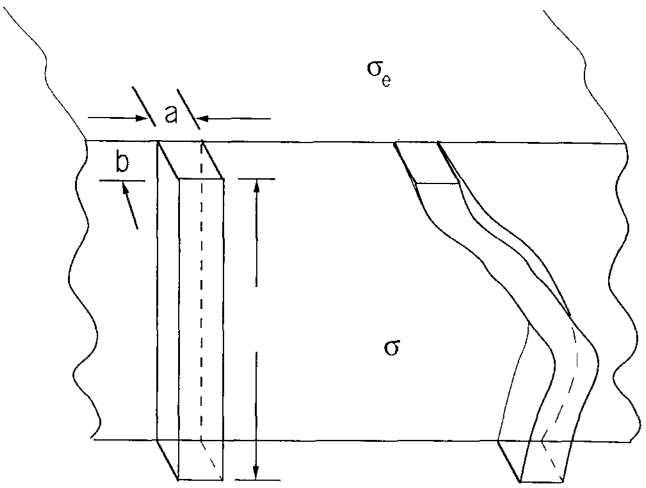

Figure 1 Schematic diagram of single stem deposition: left, immediate crystalline register; right, partial register

EXPERIMENTAL

Long periods of polypropylene and polyethylene were determined by Campbell[8] and Lambert[9] using the 10 m camera of the SAXS facility at the National Center for Small Angle Scattering at Oak Ridge National Laboratories. Lamellar thicknesses were obtained by multiplying the long period by the WAXS determined crystallinity.

THEORETICAL

When a material deposits on a substrate by epitaxial matching the need for primary nucleation of the crystal is eliminated. However, the crystal can only grow by either secondary nucleation or surface roughening[1,10]. In the case of polymers it is widely accepted that surface roughening is highly unlikely and that crystal growth proceeds by secondary nucleation. Essentially, the polymer molecule must deposit on the substrate in the same manner as it would during lamellar growth.

Secondary nucleation theory can be treated in a simplified manner as a continuous process or, more accurately, as a stepwise addition of stems[10–12]. Common to all approaches is the generation of a critical secondary nucleus which has a length of similar size to the lamellar thickness of the substrate, which for conventional crystal growth is the crystal of the material that is being deposited. Unless this secondary nucleus of critical size is generated, growth does not proceed.

In the case of the Hoffman–Lauritzen theory[12,13] the critical nucleus is a single stem and the criticality is attained through it being of an appropriate length (*Figure 1*). The thermodynamics of the process involves a surface energy term ($2bl\sigma$) which is partially offset by the free energy of fusion released by the deposition ($abl\Delta G_f$). The chain probably does not add as a chain-extended unit, but as a partially organized chain which deposits on the surface and then reorganizes in the chain extended form. It therefore incurs all of the surface energy on deposition but only part of the free energy of fusion will be released initially. The remainder will be released as lattice register is attained by sections of the chain. This phenomenon is usually represented as:

$$\text{deposition} \qquad \Delta\phi_1 = 2bl\sigma + \Psi abl\Delta G_f \tag{1a}$$

$$\text{lattice registry} \qquad \Delta\phi_2 = (1-\Psi)abl\Delta G_f \tag{1b}$$

where $0<\Psi<1$. Clearly the barrier to critical nucleus formation is the magnitude of $\Delta\phi_1$.

The theory of secondary nucleation generates an equation relating l to the supercooling, ΔT, which is given by the equation:

$$l = -\frac{2\sigma_e T_m^0}{\Delta H_f \Delta T} + \delta l \tag{2}$$

where l is both the critical nucleus length and the pre-thickened lamellar thickness. So, at any given crystallization temperature, a certain minimum value of l must be attainable or crystallization cannot proceed.

In the case of the epitaxial deposition of a polymer on a substrate, it is still necessary for the critical value of l to be attained, although the value might be modified slightly because of the difference in the σ values of the two polymers. To a first approximation, it can be assumed that the critical value of l remains fixed at that characteristic of secondary nucleation for the polymer concerned.

Consider now a substrate of another polymer, having a characteristic lamellar thickness, l', and crystallinity, χ'. The depositing stem will have a characteristic critical length, l, which will be inclined to the lamellar normal of the substrate crystal at an angle Θ determined by the lattice match (*Figure 2*) and so the maximum crystal substrate dimension available is $l'/\cos\Theta$. If $l<l'/\cos\Theta$ then the stem will deposit and a critical nucleus is generated.

If $l>l'/\cos\Theta$ then it has to be recognized that the section of depositing molecule that lies on the amorphous phase cannot generate any free energy of fusion, but still incurs the lateral free energy penalty, so equation (1) becomes:

$$\Delta\phi_1 = 2bl\sigma + \Psi ab\Delta G_f l'/\cos\Theta \tag{3a}$$

$$\Delta\phi_2 = (1-\Psi)ab\Delta G_f l'/\cos\Theta \tag{3b}$$

The surface free energy term is positive and constitutes the inhibition to permanent deposition. The second term is negative and the driving force for crystallization. However, it has now been proportionately reduced over its value during normal crystal growth. The critical energy for secondary nucleation has been increased by an

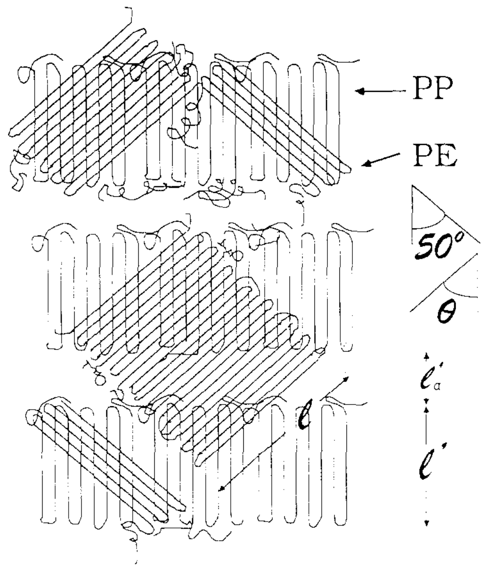

Figure 2 Epitaxial deposition of polyethylene on polypropylene

amount equal to:

$$\Psi ab\Delta G_f(l - l'/\cos\Theta) \qquad (4)$$

For an attempted deposition of one stem on two adjacent lamellae of the substrate the maximum increase in the critical energy of nucleation will be:

$$\Psi ab\Delta G_f(l - l'_a/\cos\Theta) \qquad (5)$$

where l'_a is the thickness of the amorphous phase in the direction of l'. If the depositing lamella has a critical stem length greater than the value in parentheses in equation (5), then two substrate lamellae have to be involved in the process and the free energy of formation of the critical nucleus begins to decrease. To summarize, the need for deposition of a critical nucleus appropriate to the depositing polymer, requires that there be a match of elementary lamellar templates of the two crystals involved.

DISCUSSION

In any attempt to deposit a first stem which has a critical length greater than the crystal dimension accessible to it on the substrate crystal under lattice match conditions, there is a significant increase in the free energy of formation. Effectively, the impediment will be such that deposition can occur only if the value of l does not exceed that of $l'/\cos\Theta$. The only way in which this impediment could be offset would be if there were a strong attraction between the molecules of the substrate and the depositing polymer. Such events are rare in polymers, as evidenced by the general tendency for the liquid state of blends to be phase-separated. Certainly this is not the case in the polyethylene–polypropylene system, but might be attained for appropriate pairs of polar polymers especially if they were both capable of hydrogen bonding.

If the critical stem length of the depositing polymer is much greater than that of the substrate crystal thickness then deposition might be possible involving a number of lamellae in the substrate. However, this event is also a remote possibility as lamellar thicknesses of most polymers are of similar magnitude.

For the case of polyethylene depositing on polypropylene, it is possible to test the theory using known values of lamellar thickness and the established angle of chain inclination in the epitaxial match. *Figure 3* shows the variations of lamellar thickness of the two polymers with crystallization temperature (T_c). Also shown by a horizontal line is the maximum dimension available ($l'/\cos\Theta$) in the polypropylene substrate of Petermann and Xu, calculated from the lamellar thickness data. It can be seen that the lamellar thickness of 'about 15 nm' generates a value of $l'/\cos\Theta$ which permits polyethylene lamellar thickness matches for T_c values below 120°C. The correspondence between theory and experiment in this respect is remarkable, considering the sensitivity of the temperature range predicted to the value of the lamellar thickness of the polypropylene substrate. An error of 1 nm measured in lamellar thickness (e.g. 14 nm thickness, quite possible for TEM evaluations) translates into a 3°C change in the predicted upper temperature for epitaxy. For a lamellar thickness of 14 nm the maximum predicted epitaxial temperature would have been 117°C. Such figures are, of course, at the lower limit for isothermal growth in polyethylene.

The observation that the measured lamellar thickness of polyethylene at ~120°C produces a template match with the lamellar thickness of the underlying polypropylene substrate is in one aspect surprising and indicates an anomaly in current theories of secondary nucleation. It is generally accepted that the initial lamellar thickness during deposition is smaller than that measured in a crystallized polymer. The amount of initial thickening is usually represented by γ, the thickening ratio, and may be estimated from the slope of a plot of melting point *versus* T_c. The value for polyethylene has been estimated to be about two by Weeks[14] for low supercooling growth, a figure which is generally accepted. If the value of the initial lamellar thickness of polyethylene is used, then even for the lowest supercoolings, the epitaxial deposition should occur. For the upper limit to be that determined by Petermann and Xu, the thickening of the initial stem must be an integral part of secondary nucleus formation rather than a subsequent event, as currently treated. It therefore appears necessary for secondary nucleation theory to be modified such that thickening of the first stem occurs on the same time-scale as the deposition of the second stem.

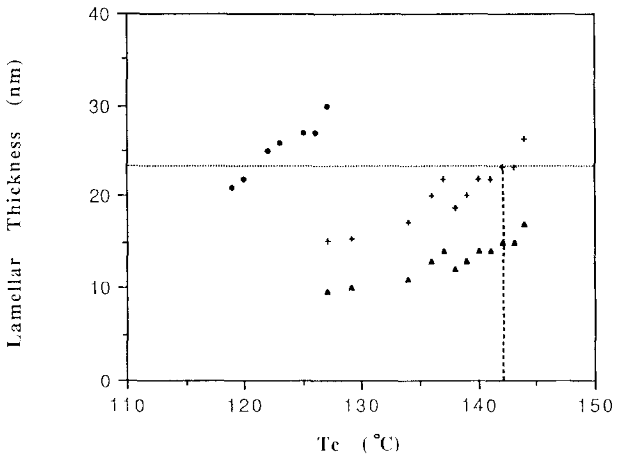

Figure 3 Lamellar thickness *versus* crystallization temperature for polyethylene and polypropylene: (●) polyethylene; (▲) polypropylene; (+) lamellar thickness of polypropylene divided by cos Θ

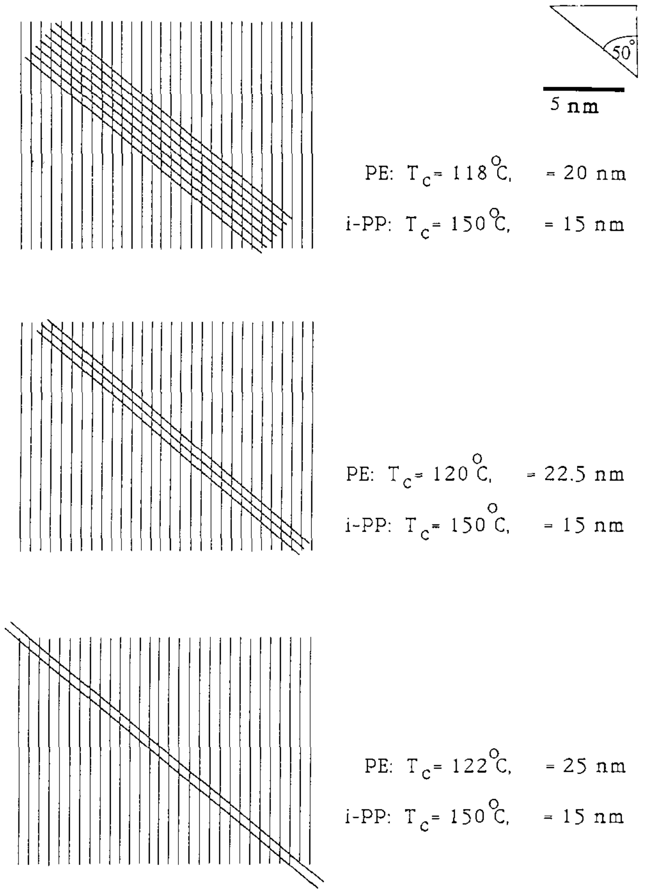

Figure 4 To-scale representation of the epitoxial deposition of polyethylene chains or polypropylene substitutes

It should be recognized that the model used here is relatively crude, not allowing for the influence of the folded chain on the underlying crystal perfection, nor for the effect of the mismatch between surface free energies of the two polymers. The model considers only the deposition of the first stem and does not attempt to evaluate the influence of limited substrate dimensions on the probability of additional stem depositions adjacent to the first one. There is a distinct possibility that the critical nucleus may consist of three stems, not one[15], under certain circumstances. For parallel chains and a fold surface normal to the chains the addition of more stems is limited unless the amorphous phase is overlapped by the additional stems. This effect is illustrated in *Figure 4*. A T_c of 118°C will permit seven chains and a T_c of 120°C permits only three chains before a potential problem exists. A comprehensive theory needs to be developed which considers all of these possibilities. However, the success of the preliminary approach reported here is very encouraging, providing a remarkable correlation between theoretical predictions and experimental results at this early stage.

It is likely that this effect will be applicable to polymer epitaxy on other substrates. In these cases the reason for the limitation in substrate dimensions would be dependent on the substrate. For instance, the phenomenon may be of importance in determining the behaviour of polymer blends and of polymers reinforced by polymeric fibres. In the case of solid nucleating agents, dislocation cells may be the controlling factor. Materials may be milled to produce a fine particle size, but in the milling process internal crystal domains may be created by the mechanical actions. Clarifiers[16,17] form string-like crystals of ~100 Å diameter thereby generating a limiting dimension and are believed to function by epitaxy. In carbon fibres, the edges of stacked graphite planes are adventitiously exposed at surfaces, dependent on manufacturing and processing conditions, and may be too small to permit epitaxy of thermoplastic matrices. It is anticipated that there be many other potential applications of the template principle.

CONCLUSIONS

Considerations of epitaxial growth of polymeric molecules on a polymeric substrate must involve the necessary requirements of secondary nucleation formation. In the case of polymeric substrates, the major requirement is that the lamellar thickness of the substrate be sufficiently large to accommodate a critical secondary nucleus of the crystallizing polymer.

ACKNOWLEDGEMENTS

This research has been supported partially through a scholarship to A. J. Greso from Martin Marietta Energy Systems and by the Polymers Program of the National Science Foundation (DMR-9107675).

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