

# MORPHOLOGY OF FILLED SYSTEMS

## 10.1 CRYSTALLINITY

The crystalline structure of composite materials can be highly varied. The measurements of crystallinity show how the combined interference of the various components of the composite influences the structure. Filled material is composed of crystalline and amorphous regions separated by an interphase which is a diffuse boundary between these two states. The crystallinity of the binder material depends on the fraction of crystalline structures and on their size. Filler may affect both the fraction and the size of crystallites. But, those two measures of crystalline structure are often insufficient and the measurement of crystallinity may give confusing information if the results are taken without further analysis of the fine structure of the material. Table 10.1 gives examples of the effect of fillers on material crystallinity from the current literature.<sup>1-13</sup>

**Table 10.1. Effect of fillers on crystallinity of polymers**

Polymer	Filler (%)	Processing method	Polymer crystallinity, %	Composite crystallinity, %	Reference
UHMWPE	bauxite (45)	extrusion	52	28	1
PTFE	ferrite (14)	hot pressing	60	57	2
LDPE	talc (11)	film	51	61	3
PP	kaolin (0.3)	hot pressing	63	46	9
PP	kaolin (7)	hot pressing	63	58	9
PP	CaCO <sub>3</sub> (30)	compression	67	68	10
PP	talc (30)	compression	67	78	10
PA-66	GF (80)	compression	40-45*	36-45*	11
PP	TiO <sub>2</sub> (30)	injection	45-47**	46	13
HDPE	TiO <sub>2</sub> (30)	injection	62-65**	63	13

\*depends on annealing temperature in a range from 20 to 300°C

\*\*depends on specimen taken either from skin or core (filled material uniform)

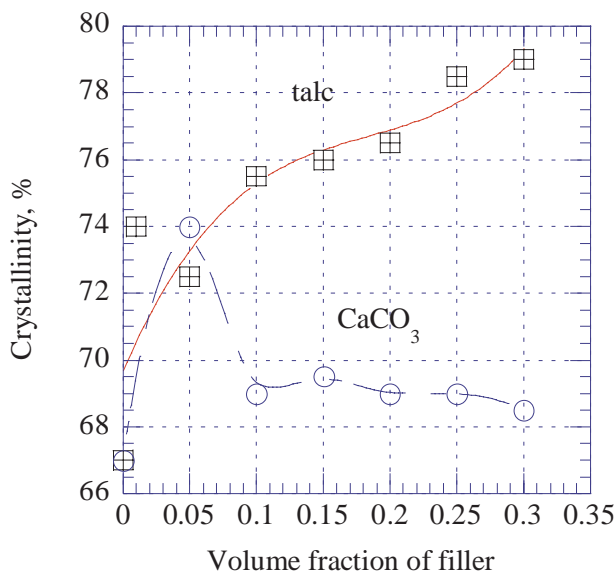


Figure 10.1. Crystallinity of PP composites as a function of CaCO<sub>3</sub> and talc concentration. [Adapted, by permission, from Pukanszky B, Belina K, Rockenbauer A, Maurer F H J, *Composites*, **25**, No.3, 1994, 205-14.]

It is difficult to conclude from the data in Table 10.1 whether the filler addition increases or decreases crystallinity. The lack of a clear pattern in the results is caused by differences in filler treatment and processing which cause the development of different structures as the material crystallizes. These points will be further discussed in the next paragraphs.

Figure 10.1 shows the effect of the addition of fillers to polypropylene on its crystallinity.<sup>10</sup> This study was conducted under the same conditions for all specimens tested. There is a difference in the effect of CaCO<sub>3</sub> and talc. Calcium carbonate lacks surface functional groups so it tends to have a very small influence on crystallinity and the crystallization behavior. Talc has interacting functional groups on its surface which cause the increase in crystallinity along with the concentration increase.

Several studies<sup>2,3,9</sup> have shown that small additions of filler cause substantial changes in crystallinity (either a large increase or decrease). Whether it was an increase or decrease in crystallinity, these small additions caused a substantial increase in tensile strength and a reduction in elongation. This indicates that the crystalline structure is formed by a nucleation process (see below) which is capable of producing reinforcement.

Surface treatment of a filler may also affect crystallinity. Phosphate coating on talc increased the crystallinity at a low concentration of coating (up to 0.5%). But there was a decrease in crystallinity when the talc was coated with higher concentrations of phosphate.<sup>6</sup>

Other fillers also produce variable degrees of crystallinity depending on their surface treatment. Carbon black is such an example. Graphitization of carbon black may increase surface crystallinity by 30%.<sup>4,5</sup>

## 10.2 CRYSTALLIZATION BEHAVIOR

Crystallization rate, nucleation, size of crystalline units, crystalline structure, crystal modification, transcrystallinity, and crystal orientation are the most relevant characteristics of crystallization behavior in the presence of fillers.<sup>7,10,14-34</sup> Here the discussion is focused on crystallization rate. The other topics are discussed in the following sub-chapters.

Crystallization kinetics is estimated from the Avrami equation:<sup>20</sup>

$$\tau_c(\theta) = \tau_c(\infty)[1 - \exp(-K\theta^n)] \quad [10.1]$$

where:

$\tau_c(\theta)$	amount of crystalline material at time $\theta$
$\tau_c(\infty)$	maximum amount of crystallinity reached after the completion of the primary crystallization (the Avrami equation does not account for secondary crystallization)
K	temperature dependent factor
$\theta$	time
n	exponent related to the dimensionality of crystallites

This equation deals with the temperature-dependence and crystallite-size-dependence of crystallinity. Frequently, the crystallization half-time,  $t_{1/2}$ , is reported in the research data. The time to reach one half of the total crystallization is  $t_{1/2}$ . The time to achieve maximum crystallization is  $\tau_c(\infty)$ . Figure 10.2 shows the relationship between  $t_{1/2}$  and temperature, T, for silica-filled PDMS. The value for  $\tau_c(\infty)$  is higher for the filled system than for the unfilled system. The value increases as the temperature increases. Only a small difference was noted for two different filler loadings. The temperature shift shows that less supercooling is required with the filled than with the unfilled system. Fillers produce a nucleation effect which initiates the crystallization process.<sup>20</sup>

Figure 10.3 shows the effect of silica concentration on crystallization rate. This behavior is independent of temperature but the absolute value of the crystallization rate is temperature dependent.<sup>20</sup> Two mechanisms must operate to give such behavior. For lower volume fractions of filler (below 0.26) the crystallization rate is high because more nucleation sites are available. Adsorption of polymer on the surface of silica organizes the adsorbed layer which causes a more ordered structure to develop as the material cools down. When the concentration of silica increases, the silica particles form obstacles to the free movement of crystallizing chains and crystallization is stopped at a filler volume fraction of 0.45. Before this happens, the rate of crystallization gradually decreases. At higher concentrations of filler, there is an insufficient number of polymer molecules adsorbed and crystalline structures do not form because of conformational constraints. The maximum rate of crystallization is determined by two competing processes: nucleation and impingement.

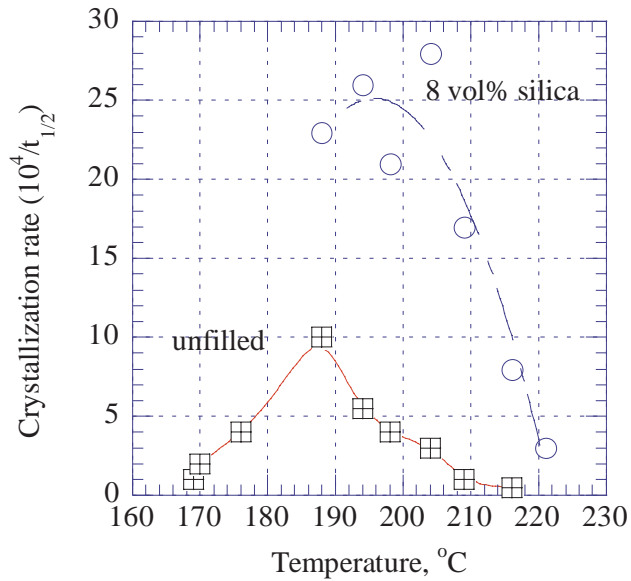


Figure 10.2. Crystallization rate of PDMS filled with silica. [Adapted, by permission, from Ebengou R H, Cohen-Addad J P, *Polymer*, **35**, No.14, 1994, 2962-9.]

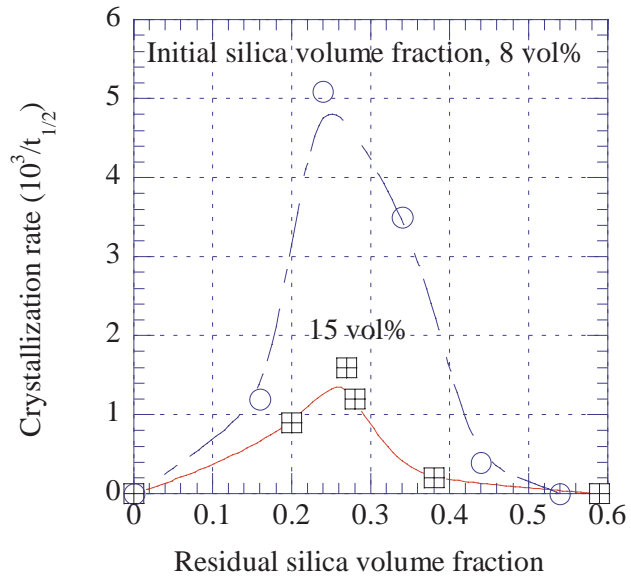


Figure 10.3. Crystallization rate as a function of silica volume fraction in PDMS. [Adapted, by permission, from Ebengou R H, Cohen-Addad J P, *Polymer*, **35**, No.14, 1994, 2962-9.]

Figure 10.4 shows the differences in the Avrami exponent for PVDF filled with carbon black and copper. In the case of carbon black, the rate of crystallization

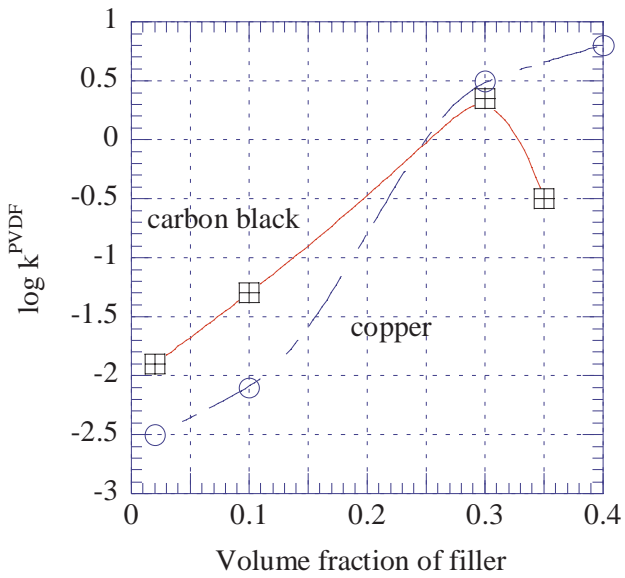


Figure 10.4. Avrami exponent vs. filler concentration for PVDF filled with carbon black and copper. [Data from del Rio C, Acosta J L, *Polymer*, **35**, No.17, 1994, 3752-7.]

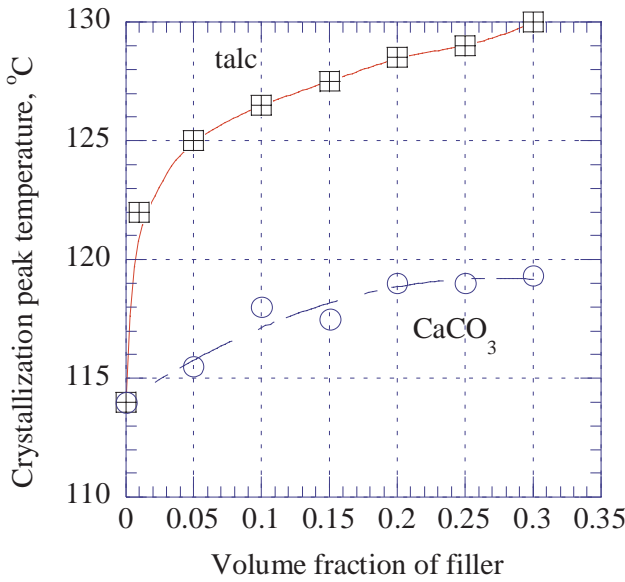


Figure 10.5. Crystallization peak temperature vs. volume fraction of filler. [Adapted, by permission, from Pukanszky B, Belina K, Rockenbauer A, Maurer F H J, *Composites*, **25**, No.3, 1994, 205-14.]

decreases above a concentration of 30% unlike in the copper-filled system. The difference is due to the differences in surface activities of the two fillers.<sup>19</sup>

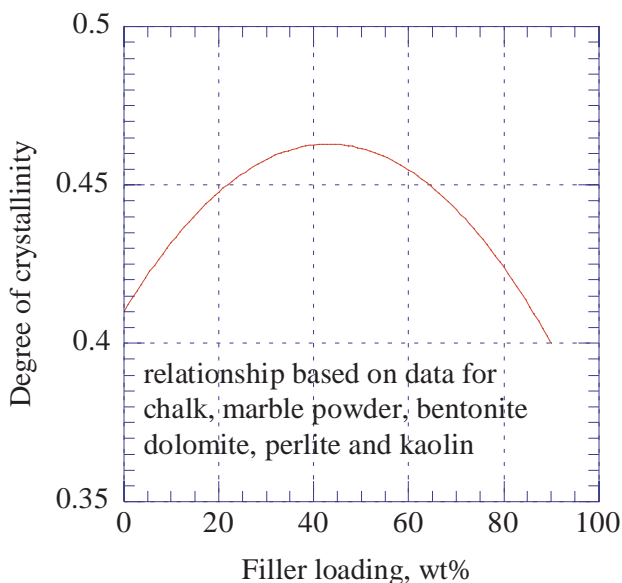


Figure 10.6. Degree of crystallinity vs. concentration of different fillers. [Adapted, by permission, from Minkova L, *Coll. Polym. Sci.*, **272**, No.2, 1994, 115-20.]

The above observations are similar to those obtained for peroxide-crosslinked polyethylene. An addition of filler, such as silica, results in an increased crystallization rate and a decrease in the crystallization half-time,  $t_{1/2}$ .<sup>21,22</sup>

Figure 10.5 shows the effect of fillers on crystallization peak temperature.<sup>10</sup> The effect of  $\text{CaCO}_3$  is much less pronounced than that of talc.

Figure 10.6 gives a summary of data on different fillers in UHMWPE. The total degree of crystallinity, as determined by the enthalpy of crystallization, increases with filler concentrations up to 40-50% and then gradually decreases.<sup>16</sup> This decrease is caused by filler aggregation which decreases its nucleation ability.

### 10.3 NUCLEATION

Many papers have been presented on the nucleation process.<sup>7,10,20,23,31,32,35-39</sup> However, the mechanism involved is still disputed.<sup>38</sup> The most important properties of a nucleating agent are its free surface and its ability to organize molecules in conformation which facilitates rapid crystallization. Nucleating agents include various organic materials and inorganic materials, including fillers. Modification of the filler surface may enhance its nucleating abilities. Nucleation provides the benefit of faster processes and better mechanical properties in the final products.

One essential principle of crystallization is expressed by the Lauritzen and Hoffman theory:<sup>20</sup>

$$K = K_0 N \exp\left(-\frac{n\Delta G_n}{k_B T}\right) \exp\left(-\frac{nK_g}{T\Delta T}\right) \quad [10.2]$$

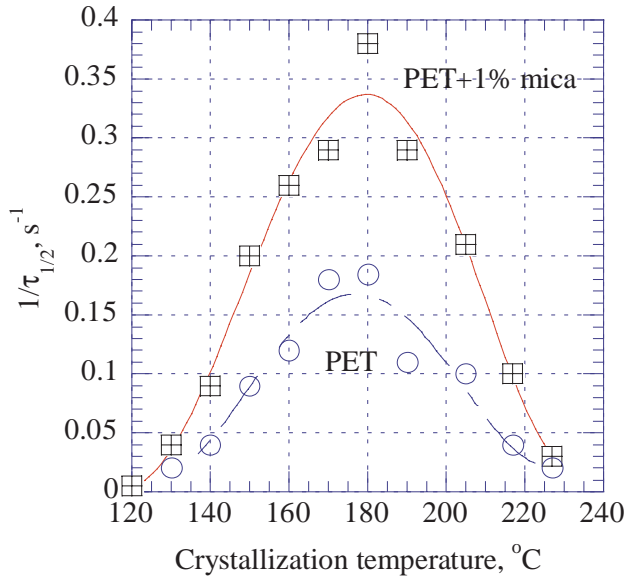


Figure 10.7. Crystallization rate vs. temperature. [Data from Okamoto M, Shinoda Y, Okuyama T, Yamaguchi A, Sekura T, *J. Mat. Sci. Lett.*, **15**, No.13, 1996, 1178-9.]

$$K_g = \frac{4b_0\gamma_eT_m^0}{k_B\Delta h_f}$$

- where:
- K coefficient of Avrami equation see Eq 10.1
  - K<sub>0</sub> constant accounting for geometric parameters of polymer chain and crystalline lamella
  - N concentration of germ nuclei per unit volume
  - n coefficient of Avrami equation see Eq 10.1
  - ΔG<sub>η</sub> free enthalpy of activation governing short distance diffusion of crystallizing elements
  - k<sub>B</sub> Boltzmann constant
  - T isothermal crystallization temperature
  - ΔT = T<sub>m</sub><sup>0</sup> - T, degree of supercooling
  - T<sub>m</sub><sup>0</sup> equilibrium melting temperature
  - b<sub>0</sub> parameter of unit cell
  - γ interfacial free energy for lateral surface
  - γ<sub>e</sub> interfacial free energy for folding surface
  - Δh<sub>f</sub> enthalpy of fusion per unit volume of structural unit

This equation stresses the importance that diffusion of the crystallizing species has on the crystallization rate, concentration of nuclei, the molecular arrangement, and the required degree of supercooling. Figure 10.2 shows that the rate of crystallization is increased in the presence of silica. This is an effect of nucleation. The filler surface also lowers the free enthalpy barrier which promotes the formation of nuclei.

Figure 10.7 shows how nucleation can be applied to industrial processes. An addition of 1 % mica to PET increases its crystallization rate by a factor of 2. Similar results were obtained with small additions of talc.<sup>37</sup>

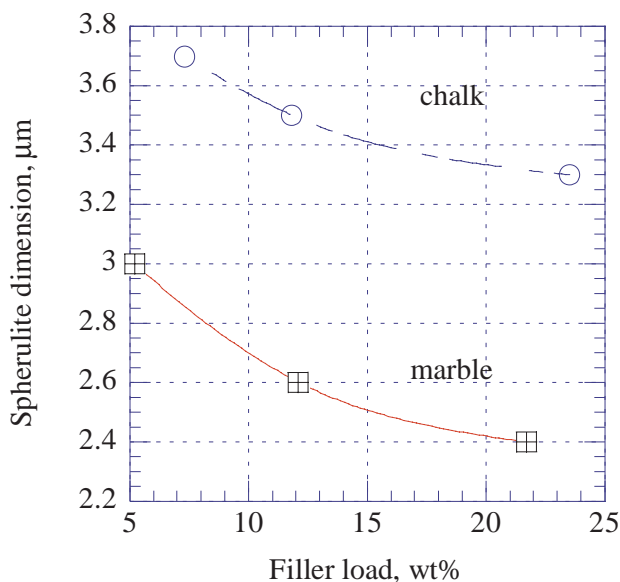


Figure 10.8. Effect of chalk and marble on the size of spherulites in HDPE. [Data from Minkova L, Magagnini P L, *Polym. Degradat. Stabil.*, **42**, No.1, 1993, 107-15.]

Attempts to add fillers to polymer blends produced interesting results.<sup>32</sup> Carbon black was added to a polymer blend containing polycarbonate and polypropylene. Carbon black is known to act as a nucleating agent in polypropylene, however, no increase in the temperature of crystallization was observed. Morphological studies showed that carbon black was preferentially located in the polycarbonate phase therefore it did not affect the nucleation of polypropylene.

Nucleating agents not only shorten the time of crystallization but also improve the mechanical properties of materials. Polypropylene processed with a nucleating agent (2%  $\text{CaCO}_3$ ) had its impact strength and modulus increased by 50%.<sup>31</sup>

## 10.4 CRYSTAL SIZE

Figure 10.8 shows the effect of fillers on the dimensions of spherulites. The size of HDPE spherulites crystallized without a filler was  $3.9\text{ }\mu\text{m}$ . As filler was added and increased in concentration, the size of the spherulites became progressively smaller.<sup>7</sup>

Figure 10.9 shows the kinetics of spherulite growth in polypropylene containing different amounts of  $\text{CaCO}_3$ . Polypropylene with no filler grew spherulites of a large size over a long period of time. The addition of  $\text{CaCO}_3$  reduced the ultimate size of the spherulite and also shortened the time to reach an equilibrium size.<sup>25</sup>

Temperature also has an effect on crystallite size. PVDF containing carbon black had crystallites with mean dimensions of 22.4, 20.1, and  $16.2\text{ }\mu\text{m}$  when specimens were respectively, slowly cooled, air cooled, and quenched.<sup>24</sup>



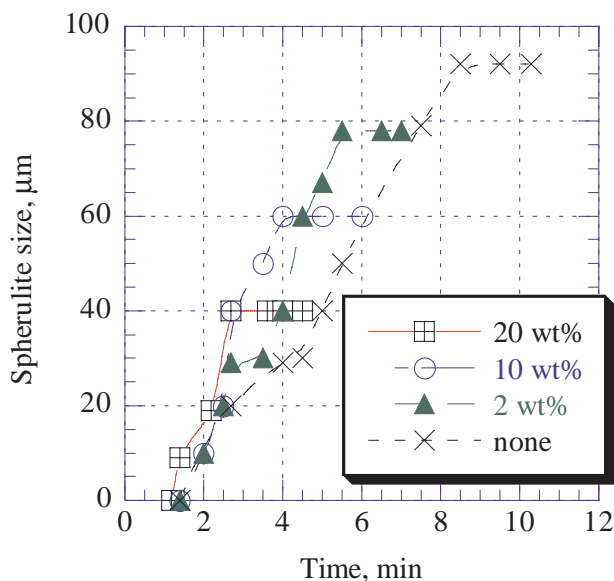


Figure 10.9. Isothermal crystallization of PP containing different concentrations of  $\text{CaCO}_3$ . [Adapted, by permission, from Khare A, Mitra A, Radhakrishnan S, *J. Mat. Sci.*, **31**, No.21, 1996, 5691-5.]

In experiments conducted to obtain controlled sizes of filler particles formed in a matrix, several polymers were used as the matrix.<sup>15</sup> Copolymers were synthesized from polyethylene oxide (does not interact with  $\text{CaCO}_3$ ) and poly(methacrylic acid) (reacts with *in situ* crystallizing  $\text{CaCO}_3$ ). In the presence of polyethylene oxide, crystals grew to similar sizes as without any polymer. The presence of the poly(methacrylic acid) crystal size of  $\text{CaCO}_3$  was reduced by a factor 5 to 10 depending on the concentration of the filler precursor.

## 10.5 SPHERULITES

Figure 10.10 illustrates the kinetics of spherulite formation with and without fillers.<sup>10</sup> The left half of each photograph shows spherulite growth without a filler. Two attributes of this growth are evident:

- The process of crystallization is slower in filled than unfilled system (the right halves of photographs)
- Spherulites are larger when no filler is present

This helps to confirm that nucleation, crystallization rate, and spherulite size are strongly influenced by the presence of fillers. It is still uncertain what role a filler plays in the mechanism of nucleation.

In one publication,<sup>13</sup> an extensive morphological study was conducted on the effect of  $\text{TiO}_2$  on the morphology of crystallized PP and HDPE. The authors did not find any evidence of a modified morphology around the particles and concluded that spherulites grew until they were stopped by the surface of the filler unless the

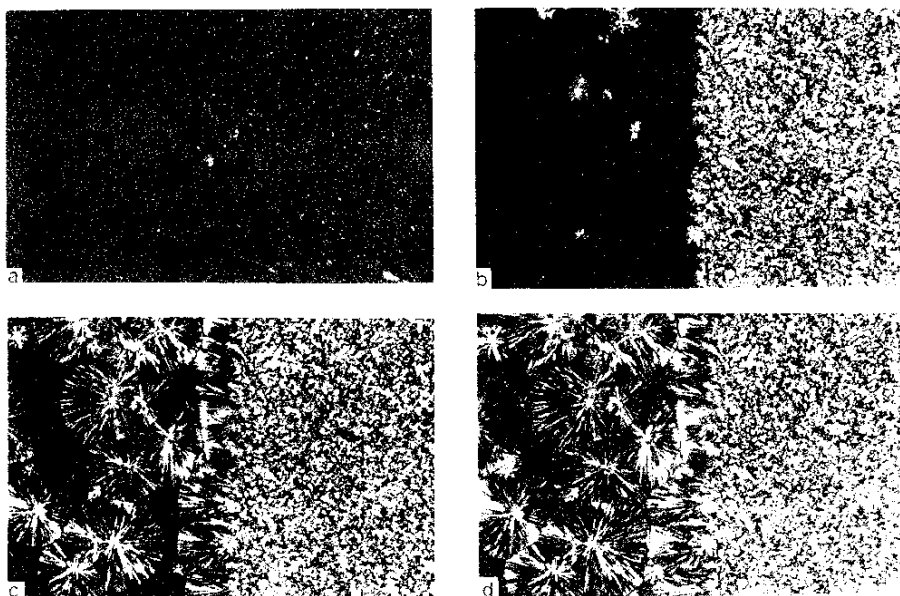


Figure 10.10. Polarization micrographs of PP/talc showing the nucleating effect of talc taken at different times of crystallization. (a) 0.5 min, (b) 7.5, (c) 31, and (d) 38. The left half of photograph is without filler and the right half of the photograph is with 0.5% talc. [Adapted, by permission, from Pukanszky B, Belina K, Rockenbauer A, Maurer F H J, *Composites*, **25**, No.3, 1994, 205-14.]

filler particle became embedded into spherulites and was not ejected by the forces in the crystallizing material. The results of image analysis are given in Figure 10.11. The majority of clusters contain only one crystal when the polypropylene contained 10%  $\text{TiO}_2$ . The number of multicrystal clusters increased only when more filler (40%) was added. Dispersion is never perfect, so it can be assumed that, with a lower filler content, spherulites are growing at the surface of the filler. The fact that no special morphological feature was detected does not preclude the possibility that the growth of the spherulite is initiated on the crystal surface rather than stopped by it as the authors have indicated. The addition of a larger amount of filler contributes to the formation of agglomerates.<sup>16</sup>

Figure 10.12 proposes a mechanism by which crystalline structure in LDPE is formed. The filler particle is close to the face of the crystal structure.<sup>3</sup> If this mechanism of spherulite formation is accepted, there should be no unusual morphological structures in the material since alignment occurs on a molecular level. The filler acts as a template on which the chain is aligned and this makes further folding much easier. The adhesion between the filler surface and the matrix is not high because of weak hydrogen bonding. This makes detachment easy as observed in many filled materials. In order to form a stronger bonding the material must form additional structures (see transcristallinity below).

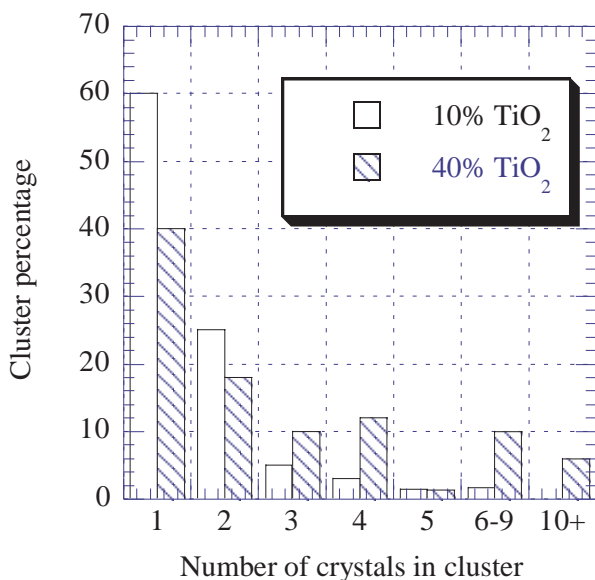


Figure 10.11. Cluster size distribution for TiO<sub>2</sub> particles in injection molded PP. [Data from Burke M, Young R J, Stanford J L, *Plast. Rubb. Comp. Process. Appln.*, **20**, No.3, 1993, 121-35.]

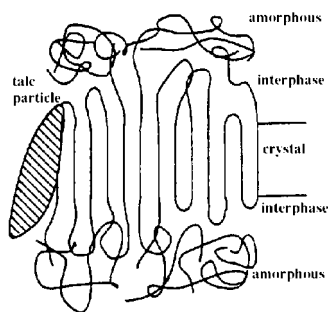


Figure 10.12. Schematic structure of filled and crystallized LDPE. [Adapted, by permission, from Singhal A, Fina L J, *Polymer*, **37**, No.12, 1996, 2335-43.]

The filler affects spherulite size only if cooling rates are low.<sup>16</sup> At a high cooling rate (e.g., 20°C/min), the nucleating role of the filler becomes much less significant.

While the presence of a filler affects the way a matrix crystallizes, the opposite is also true. In studies of *in situ* formation of calcium carbonate in different copolymers, different crystalline forms of calcium carbonate were found.<sup>15</sup> Calcium carbonate crystallized without a polymer had a rhombohedral morphology. When crystallized in the presence of polyethylene oxide its morphology remained rhombohedral because the polymer does not interact with the crystal of calcium carbonate as it

forms. The calcium carbonate crystals which formed in the presence of methacrylic acid copolymer had an elongated structure not found in the other two cases.

## 10.6 TRANSCRYSTALLINITY

The cooling of polymer melt in the presence of a foreign surface which can nucleate crystalline growth inhibits the lateral growth of spherulites. Crystallization occurs in a direction normal to the surface.<sup>38</sup> This is called transcrystallinity. It can im-

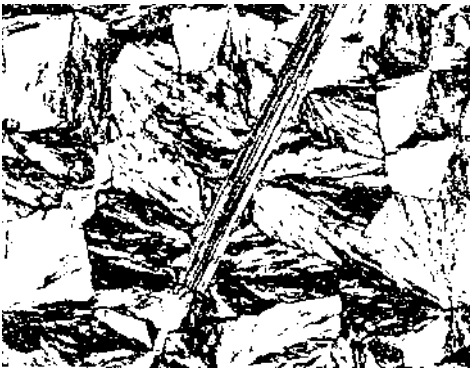


Figure 10.13. Optical micrograph with crossed polars of bamboo fiber in PP matrix (x100). [Adapted, by permission, from Mi Y, Chen X, Guo Q, *J. Appl. Polym. Sci.*, **64**, 1997, 1267-73.]

prove the adhesion and the mechanical properties of composites. Figure 10.13 shows spherulite formation on the surface of a bamboo fiber. There is a nucleation phenomenon on the surface of fibers but the normal three-dimensional growth is hindered. Figure 7.18 shows transcristallinity which occurs due to changes in the conditions of the process.

The strength of the material and the adhesion between fiber and matrix depend on the thickness of the transcristalline layer. Figure 10.14 shows the effect of some process conditions (in this case temperature) on the thickness of the transcristalline layer.<sup>30</sup>

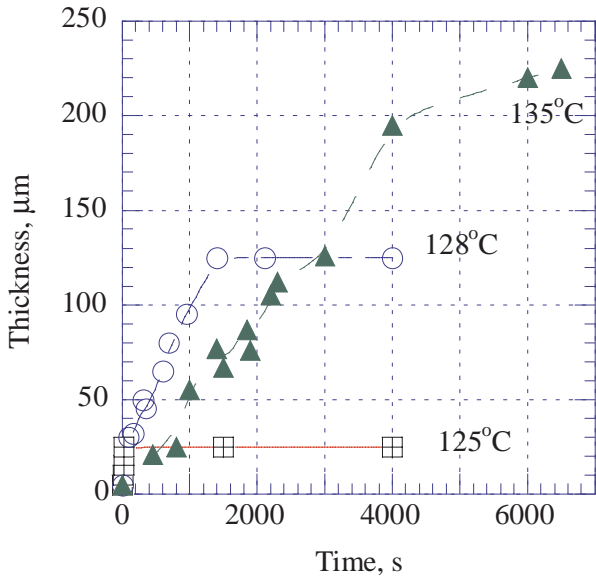


Figure 10.14. The thickness of transcristalline layer versus time at different melt temperatures in cellulose reinforced PP. [Adapted, by permission, from Gatenhom P, Hedenberg P, Karlsson J, Felix J, *Antec '96*. Volume II. Conference proceedings, Indianapolis, 5th-10th May 1996, 2302-4.]

Many process parameters are responsible for transcristallinity.<sup>40-42</sup> The most extensive transcristallinity is observed under rapid pulling of fibers and high cooling rates. Other parameters include the viscosity of the polymer melt, the rate of shear, the fiber/matrix wettability, and the temperature gradient between matrix and fiber.<sup>40</sup> Figure 10.15 shows the effect of interlayer thickness on the fracture en-

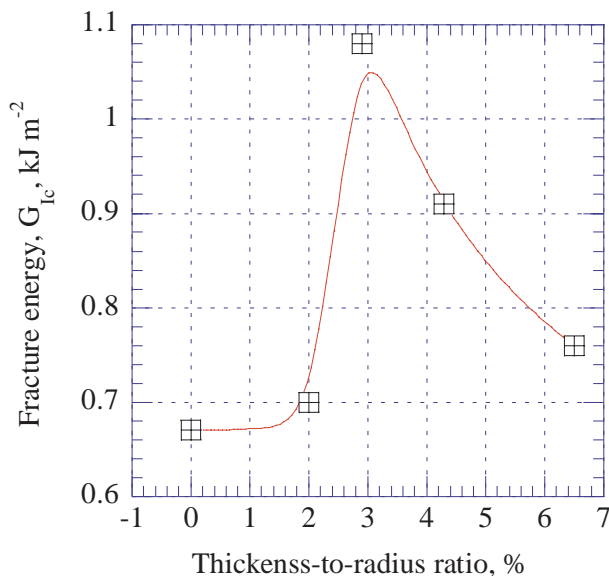


Figure 10.15. Fracture energy vs. interlayer thickness in glass beads-reinforced epoxy. [Adapted, by permission, from Gerard J F, Chabert B, *Macromol. Symp.*, **108**, 1996, 137-46.]

ergy of epoxy reinforced with glass beads. Large gains in mechanical properties can be obtained by tailoring the properties of the interlayer.<sup>41</sup>

Formation of the transcrystalline structure also depends on the geometry of the chain and the fiber surface. Carbon fibers and polyamides are a good match. This makes the chain arrangement on the surface of the fiber very precise and thus the resultant composite is very strong.<sup>42</sup>

## 10.7 ORIENTATION

Three processes of orientation occur simultaneously during the processing of filled materials. These are: filler particle orientation (see Chapter 7), chain orientation (or conformation change) as related to filler particle, and the direction of crystallite growth.<sup>25,27,43-46</sup> Often orientation is detrimental to the material produced. These processes are very difficult to study. Some information is available but more is needed.

Talc is always an attractive subject of such studies due to its platelet structure. In thermoforming and compression molding processes of three resins (PP, HDPE, and PPS), each containing 20% talc, the talc particles were always parallel to the specimen surface, regardless of the resin used.<sup>27</sup> Crystallites grew in a direction normal to the surface of talc particles and thus were perpendicular to the specimen surface. But in the case of unfilled HDPE, crystallites grew parallel to the specimen surface. There was no difference in crystallite growth direction in the case of polypropylene with and without talc.

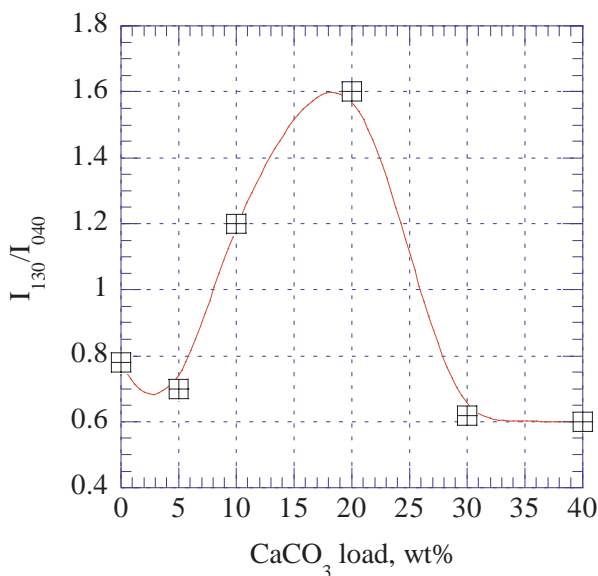


Figure 10.16. The ratio of intensities of the 130 and 040 reflections as a function of  $\text{CaCO}_3$  concentration. [Adapted, by permission, from Khare A, Mitra A, Radhakrishnan S, *J. Mat. Sci.*, **31**, No.21, 1996, 5691-5.]

The orientation of PMMA chains on the surface of alumina was found to be affected by acid-base interactions. Due to these interactions, the *trans* conformation was more common at the interface than the *gauche* conformation which was prevalent in bulk.<sup>43</sup>

In injection molded composites of polypropylene containing short glass fibers, the fiber orientation depended on the flow pattern (which, in turn, is related to mold thickness, the position of the gate, and flow rate).<sup>45</sup> Substantial variation was detected along the thickness of the sample. Crystallites followed a pattern of fiber distribution but they grew in a direction perpendicular to the direction of the fiber and specimen surface. The direction of spherulite growth was different in neat resin where crystallites grew parallel to the surface of the mold (specimen).

Figure 10.16 gives data on orientation of crystallites in polypropylene containing various amounts of  $\text{CaCO}_3$ . Maximum orientation of crystallites is obtained when the concentration of calcium carbonate is in the range of 15-20%.<sup>25</sup>

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