

Morphology of Coalescence Processes: Secondary Fracture, Cracks and Spherulites

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Summary

Similarity in the shapes of fracture curves and spherulite boundaries makes possible to generalize the respective theories to the case of coalescence of two spreading processes of growth, disturbances or excitations. The geometrical shape of a coalescence curve depends on three parameters: the distance of their spreading centres, the relation of spreading velocities and the time delay of the spreading. According to the character of the process, the shielding effect may take place. In this case, the coalescence curve is composed of two parts which are to be described separately.

Coalescence Processes

Coalescence process is a phenomenon where the final structure (morphology) is a result of two elementary disturbances or structures spreading or growing in all directions from two centers, A and B (Fig.1). Loci of contact of both spreading fronts form a coalescence surface (three-dimensional case) or a coalescence curve (coalescence in a plane). From an analysis of the coalescence formations it is possible to estimate ex post some important parameters of the process.

Typical examples of the coalescence process in polymers are the formation of fracture curves on fracture surfaces and spherulitic growth during crystallization. The general rules of the coalescence process are responsible for the fact that such widely different processes as mentioned above may result in a very similar shape of coalescence curves (Fig.2). This similarity is the obvious reason of several mistakes in literature where the authors tried to prove the existence of spherulites in amorphous polymers, e.g. in the polymethylmethacrylate used for aircraft windows. The knowledge of the character of coalescence process is important not only for the identification of morphology: it makes possible additional deductions concerning the structure, e.g., growth characteristics of particular formations and sometimes even the final properties of the material. In this paper we restrict ourselves to a two-dimensional analysis of the coalescence process (curves on fracture surfaces, the growth of spherulites in a thin layer). A generalization to three dimensions is not difficult (LEDNICKÝ 1977) because of the axial symmetry with respect to the straight line connecting centers A and B.

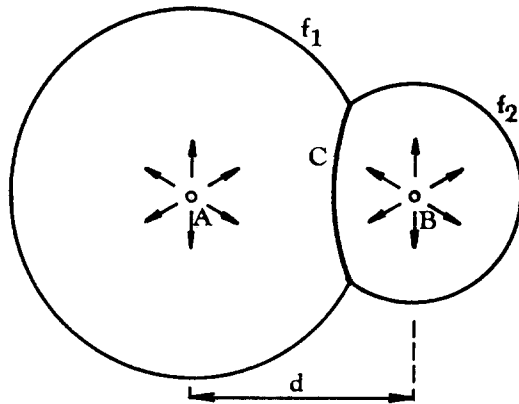


Fig.1. Scheme of the formation of coalescence curves

First papers on coalescence processes dealt with a qualitative explanation of the morphology and formation of fracture curves; only some of the curves were interpreted in mathematical terms (SCHWARZL and STAVERMAN 1956, REGEL 1956, ANDREWS 1959 and 1968) with simplifying assumptions. Classification of all possible kinds of fracture curves was suggested later, after a detailed mathematical description of the process resulting from the interaction of two elementary processes has been developed (LEDNICKÝ and PELZBAUER 1973). The theory enables one to estimate the acceleration of the fracture front from the parameters of consecutive fracture curves (LEDNICKÝ and PELZBAUER 1975). The same mathematical treatment was used for the evaluation of relative growth rate of poly(ethylene oxide) spherulites. The method (LEDNICKÝ 1977) was tested for materials yielding one and/or two types of spherulites growing simultaneously.

Information obtained from the shape of spherulite boundaries proved to be very useful in studying the crystallization process, viz. for the estimation of nucleation kinetics (PAKULA et al. 1979, GALESKI and PIÓRKOWSKA 1980). The possibility of computer evaluation of crystalline polymeric systems (GALESKI 1981, GALESKI and PIÓRKOWSKA 1981 and 1983) has been investigated. An analysis of the spherulite boundary shapes (VARGA 1983) based on the same assumptions as that of the coalescence processes of the secondary fractures (LEDNICKÝ and PELZBAUER 1973) was used to characterize the cylindrical crystallization of polypropylene (VARGA 1983).

Theory

The general quantitative description of the coalescence process (LEDNICKÝ 1977, LEDNICKÝ and PELZBAUER 1973, VARGA 1983) includes its basic characteristics: two growth processes spreading from two centers separated by a distance d (Fig.1), one of which is delayed by time t_0 ; their velocities are constant (but not necessarily the same). Let us assume that by

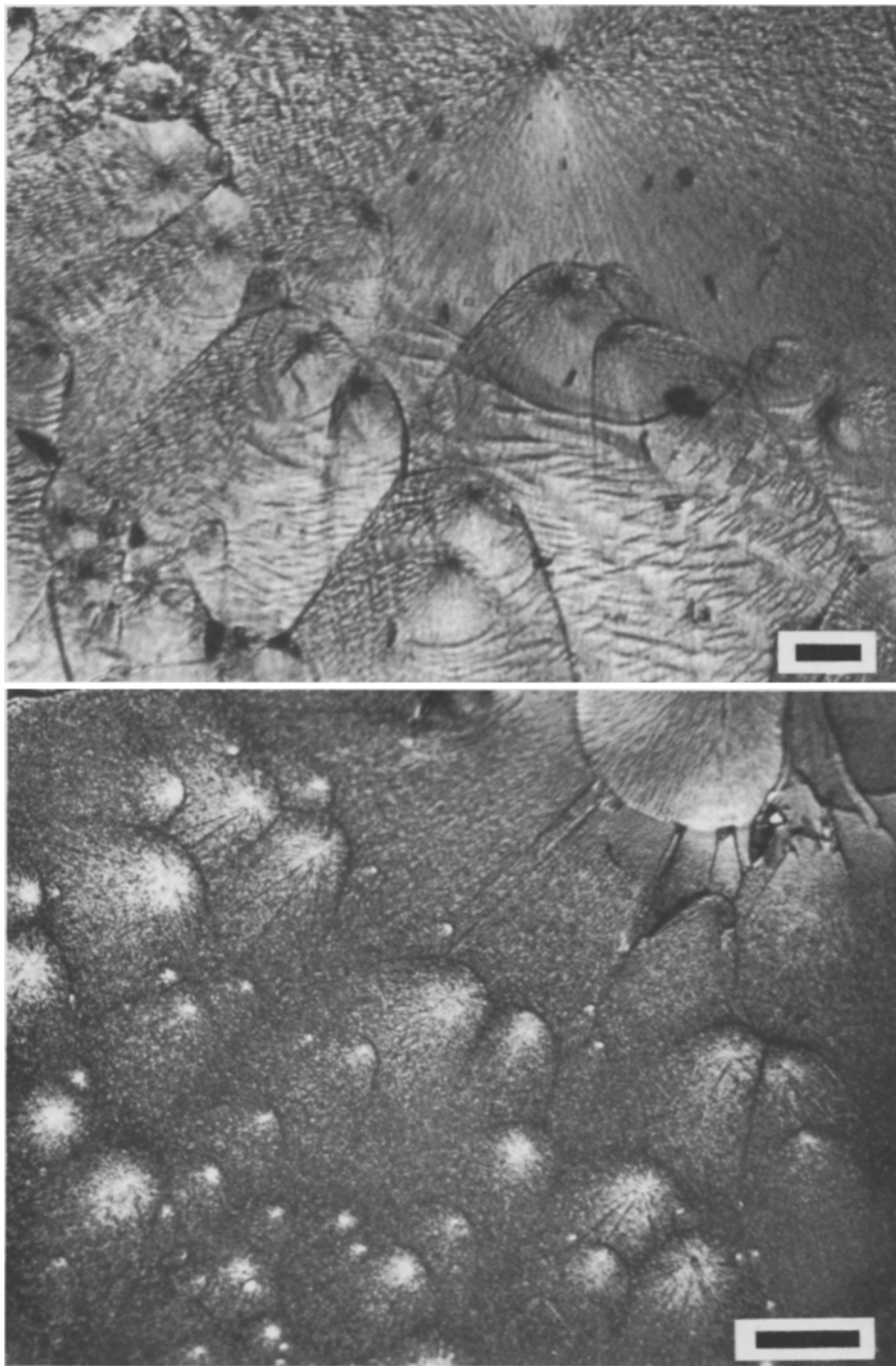


Fig.2. Morphological similarity of different coalescence formations

a spherulites of poly(ethylene oxide) POLYOX WRS 35 (two-dimensional spherulites grown from the melt at room temperature; non-polarized transmitted light); b curves on the fracture surface of poly(methyl methacrylate) (metal-coated surface, reflected light). The bar scale represents 100 μm .

time t the growth front f_1 has spread to the distance

$$r_1 = v_1 \cdot (t + t_0) \quad (1)$$

from the point A while the growth front f_2 has spread to the distance

$$r_2 = v_2 \cdot t \quad (2)$$

from the point B; let

$$a = d - v_1 \cdot t_0$$

be the activation distance (nucleation distance in the case of spherulitic crystallization), i.e. the distance of the front f_1 from center B at the moment t_0 when the front f_2 starts spreading;

$$V = v_1/v_2$$

is the relative growth rate. The coalescence curve C can be then expressed, e.g., in polar coordinates ρ , ϕ in the form

$$\rho^2 \frac{1 - V^2}{a} - 2\rho[V(1 - \frac{a}{d}) + \cos \phi] + a(2 - \frac{a}{d}) = 0 \quad (3)$$

where $\rho \cong r_2$ and $\phi = 0$ defines the direction from center B to center A. Shapes of theoretical coalescence curves are determined by the three parameters V , a , d of equation (3); the curves can be either open or closed (LEDNICKÝ and PELZBAUER 1973) (Fig.3).

Discussion

Most of the observed coalescence formations (LEDNICKÝ and PELZBAUER 1973, LEDNICKÝ 1977, VARGA 1983) are in agreement with the coalescence theory. On the other hand, several shapes not predicted by the theory were observed; closed coalescence curves characterized by a kink at the point where the curve closes during the growth (LEDNICKÝ and PELZBAUER 1973). This effect was studied in the case of spherulitic crystallization (LEDNICKÝ 1984) and the shielding effect was proved to be responsible, caused by the newly-grown spherulite. (The main demonstration of the shielding effect are the optical effects in polarized light, Fig.4.) Shielding may take place in the case of fracture surface curves as well (cf. Fig.5 in LEDNICKÝ and PELZBAUER 1973).

Consequently, the shielding mechanism is to be taken as a general phenomenon and must be considered when evaluating coalescence curves. Mathematical details have been published elsewhere (LEDNICKÝ 1984). The corresponding coalescence curve then must not be considered as resulting from a single coalescence process; its closing part is influenced by two

Fig. 3. Examples of the theoretical shapes of coalescence curves classified according to the respective values of a and d (LEDNICKY and PELZBAUER 1973)
 $1/d \neq 0$ (a,b,d,f); $1/d = 0$ (c,e,g); $a = d$ (a); $0 < a < d$ (b,c);
 $a = 0$ (d,e); $a < 0$ (f,g). Numbers at curves denote the value of parameter V .

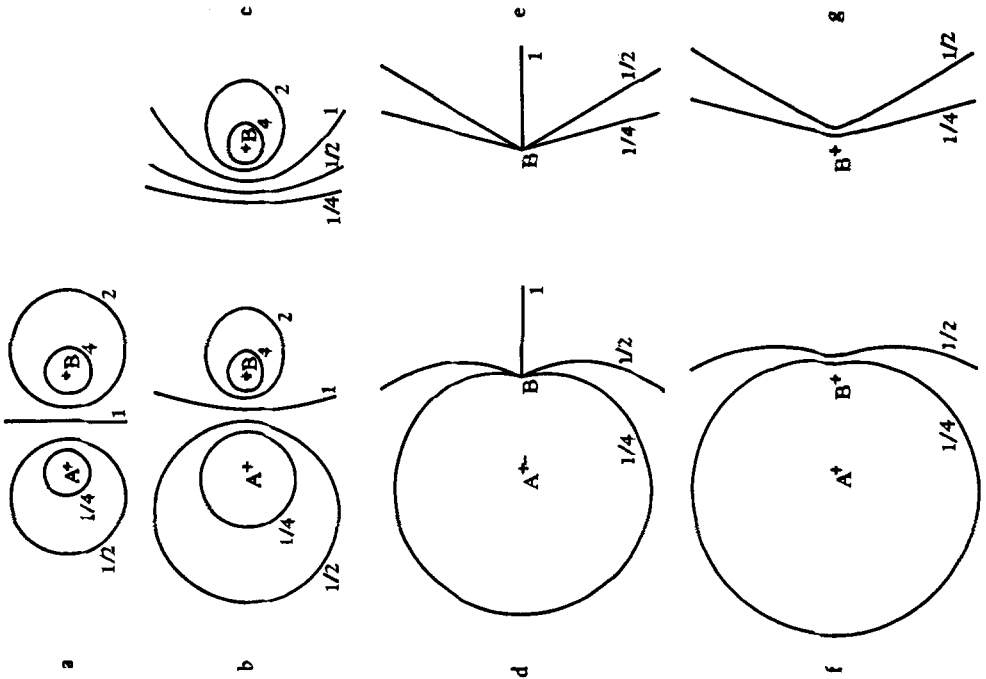
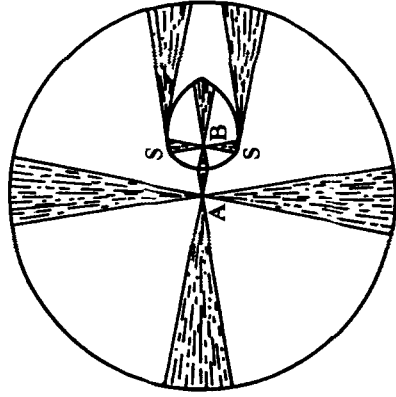


Fig. 4. Scheme of the shielding effect of spherulitic growth



processes starting respectively at points B and S (shielding points - Fig.4).

The existence of coalescence processes is not necessarily restricted to either fracture surface curves and spherulite boundaries or to polymeric materials. They can arise wherever two waves interfere, especially when their velocities of spreading are different. The coalescence process has been used for the measurement of fracture speed by marking the proceeding fracture front by letting it interact with ultrasonic shear waves (cf. KERKHOF 1953 and 1956, GREENWOOD 1972, TAKAHASHI et al. 1978 and 1979, TAKAHASHI and HYODO 1981). Owing to its general validity, further applications can be expected.

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