



MATERIALS AND DEVICES SERIES 9

ELECTRICAL DEGRADATION AND BREAKDOWN IN POLYMERS

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Editor

may consist of a series of crystalline units, roughly cube shaped of side ~ 10 nm with molecules aligned along the fibril axis, intimately connected by many inter-crystalline links. The fibrils themselves may only be weakly bonded and may themselves be aligned more accurately by plastic deformation after solidification (i.e. by drawing).

1.3.4 Crosslinking

Crosslinking a linear polymer prior to crystallisation may cause a normally semi-crystalline polymer to lose its crystallinity. The most common method of crosslinking is to trigger a thermally-activated catalyst by raising the temperature. Since this temperature must be well above the melting temperature if crosslinking is to take place in a reasonably short time, this form of crosslinking always takes place when the polymer is in its liquid state, i.e. in the *amorphous* melt phase. If the temperature is raised very quickly then it may be possible for the crosslinking to start before the lamellae structure has completely dispersed and this level of structure may be retained, at least in part. Because the degree of molecular rearrangement is severely restricted by the crosslinks, it seems likely that the lamellae will not be able to attain a full spherulitic structure in the solid state. Under these conditions in polyethylene, ordered lamellae micro-domains¹⁵, spherulitic precursor lamellae sheaves^{16,17}, or extended lamellae structures¹⁸ (slow cooled HDPE) may be the only form of crystalline arrangement possible. However spherulites are sometimes observed in compression-moulded thin-film specimens^{19,15} which have been crosslinked in this way. In such specimens the temperature throughout the bulk of the material may be raised very quickly from the melting point to that required for the initiation of crosslinking and macro-structural rearrangement may also be hindered by the thin section of the film (typically only a few spherulite diameters thick) and by cohesive forces between the polymer and the mould surface.

Not all crosslinking techniques require the use of temperatures in excess of the melting point. For example in the silane-crosslinking process developed for polyethylene power cable insulation, the polymer is cured at approximately 100°C. This is just below the melting point of the more dominant and thicker lamellae ($\sim 105^\circ\text{C}$) and any spherulite formed during moulding would not be destroyed at this temperature. However spherulites are not normally observed in this material and it seems likely that the silane, which is grafted at temperatures above the melting point, inhibits the production of long dominant lamellae required for spherulitic growth. Radiation may also be used in crosslinking the solid state below the melting point. At lower doses this form of crosslinking does not destroy the crystallinity and any original spherulitic structure will be retained in these materials provided they are not heated above their melting point.

1.4 Bulk defects and free volume

The usual crystal defects, such as dislocations, may be present in polymer crystals but are difficult to observe since the crystallinity is only partial and

they are not therefore likely to be dominant. Many crystal defects are unique to polymers. For example chain ends may be present within the crystal, it is possible that there may be buried loops (i.e. folding within the crystal), or the regular chain may be interrupted with an incorrect mer (for example a polypropylene unit may occur in a polyethylene chain giving rise to a methyl group in a polyethylene crystallite. Such defects act to increase unit cell dimensions and specific volume and lower the melting point.

The specific volume is also increased by the apparently inevitable presence of microvoids in polymers. These may be formed during manufacture by the evaporation of volatile decomposition products from various chemical reactions such as those used for crosslinking and those associated with antioxidants. They may also be formed from impurities and additives which may decompose, migrate, and outgas from crosslinking inhomogeneities in network polymers^{20,21}, and atmospheric gases which have not diffused out. Since diffusion is the *net* movement of particles down a concentration gradient due to the *random* movement of individual particles, there will always be some (individual) voids which do not leave the polymer during manufacture. For example Stevens *et al.*²² have found, using light scattering techniques, that an epoxy resin they manufactured and de-gassed under extremely stringent conditions still contained 10^{12} – 10^{13} voids m^{-3} with diameters of 2 to 5×10^{-7} m (i.e. about 10^{-7} of the total volume). At the other extreme, voids in the 'halos' of steam-cured crosslinked polyethylene cables may be as large as $4 \mu\text{m}$ and occupy as much as 1% of the total volume²³. Typically microvoids are in the range 10^{-8} – 3×10^{-7} m. They are likely to grow in the presence of mechanical and electrically-caused (e.g. by Maxwell forces) mechanical stresses^{22,24}. The upper size limit of microvoids (i.e. when microvoids become voids) is simply a matter of definition. In practice the large end of the microvoid distribution can be observed using optical microscopic techniques and the prefix *micro* suggests that the borderline might lie at diameters of a *micrometer*. The lower size limit is defined in terms of microvoids which are permanent. Below a few nm ($< \sim 3 \times 10^{-9}$ m) there is likely to be space which continuously appears and disappears due to molecular motion, resulting in *thermal density fluctuations* and which can be measured using laser light scattering²¹ and observed as electrical noise²⁵ in dielectric measurements if the molecules are polar^{26,27}.

1.5 Techniques for characterising crystallinity and morphology

1.5.1 Calculating crystallinity from density measurements

For a semi-crystalline polymer it is possible to estimate the fraction of the solid that is crystalline, i.e. its *crystallinity*, by determining the curve of specific volume with temperature if the dimensions of the unit cell are known (this may be determined by X-ray diffraction). For example at 20°C polyethylene has an orthorhombic unit cell with dimensions $736 \text{ pm} \times 492 \text{ pm} \times 254 \text{ pm} = 9.20 \times 10^{-29} \text{ m}^3$ containing two monomers units and therefore having a relative molecular mass of 56.1. This results in a specific volume for the pure crystalline parts of the polyethylene of $v_x = 0.987 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$. The