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THERMOANALYTICAL METHODS IN THE STUDY OF STRUCTURE/PROPERTIES RELATIONSHIPS OF MODIFIED AND CROSSLINKED LINEAR POLYETHYLENE

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Linear polyethylene is a typical semicrystalline polymer. Its physical and mechanical properties are strongly dependent on the crystallinity (crystalline fraction), and on the size and structure of the crystallites.

Modification of linear polyethylene by the grafting of alkoxysilane groups and by subsequent network formation influences the crystalline properties of the polymer. DSC is eminently suitable to follow these changes. For crosslinked polyethylenes above the crystalline melting point, the modulus of elasticity and the thermal expansion coefficient determined by TMA give useful information on the structure. Comparison of the mechanical properties of grafted and crosslinked samples as a function of the crystallinity allows the separation of structural effects. A close correlation has been found between the structure and properties of modified and subsequently crosslinked polyethylenes.

The crosslinking of polyethylene is of considerable practical importance. It extends the range of use by raising the upper temperature limit of application and improves the mechanical properties of this polymer. There are various possibilities of network formation. High-energy radiation or hydrogen abstraction by primary radicals formed in the thermal decomposition of peroxides results in radicals on the polymer main chain, the combination of which produces interchain bonds. Another way is the modification of polyethylene by the incorporation of chemically reactive groups. Bond formation between these occurs in a subsequent reaction. Unsaturated trialkoxysilanes, for instance, can be grafted onto the polyethylene backbone during melt processing in the presence of a suitable radical initiator, and the crosslinking will be achieved through the hydrolysis and subsequent condensation of the grafted alkoxysilane groups. This technology is highly advantageous in many respects.

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On the other hand, polyethylene is a typical semicrystalline polymer, the physical and mechanical properties of which are determined to a great extent by the crystalline fraction, the size and shape of the crystallites, the texture, etc. It has a two-phase structure (crystallites embedded in the amorphous matrix), the properties of which depend on both the composition and the morphology.

It is well known that melt crystallization, even in the case of a highly regular polymer structure, results in partial crystallinity as a consequence of entanglement, interference of crystal growth and other effects. Modification of polyethylene, however, introduces structural irregularities into the chain and such "defects" are necessarily excluded from the crystallites, reducing the crystalline fraction. Crosslinks, of course, are irregularities too, but they also exert an influence on the crystallization by restriction of the chain mobility. These effects of polyethylene modification and crosslinking are best followed by thermoanalytical methods. Data obtained on crystallinity can in turn be correlated with changes in mechanical properties, thereby revealing the relation between the structure and properties of these materials. The determination of such correlations is of great practical and theoretical importance.

Experimental

Modification of linear polyethylene (Tipelin ME 610, product of Tisza Chemical Works) was carried out during melt extrusion (HAAKE Rheocord Rheomix S 3/4" extruder) with trialkoxy-vinylsilane in the presence of a radical initiator. From the modified polymer, 1 mm thick sheets were compression-molded. The characteristic infrared absorption of the modified polymers at 1080 cm^{-1} (Si-O-C vibration) was measured after chloroform extraction with a Specord 75 IR (Carl Zeiss, Jena) instrument.

Determination of the true concentration values of alkoxysilane groups in the modified polymer encountered difficulties because of calibration problems. It was found, however, that the characteristic absorption and therefore the concentration of the active groups are very nearly proportional to the amount of trialkoxy-vinylsilane reacted (Fig. 1). Because of this, the degree of modification was characterized by these latter data. Crosslinking of the modified polymer was effected by boiling in water. The gel content was determined gravimetrically after extraction with hot xylene.

Figure 2 shows that the whole range of modification and crosslinking studied here is well above the gel point, but the gel content seems to have a limiting value (about 0.9), indicating that crosslink formation is not wholly statistical.

For the thermoanalytical measurements, Mettler DSC 30 and TMA 40 units controlled by a TC 10A processor were used. The DSC measurements were performed at a 10 deg/min heating and cooling rate. Enthalpy changes of melting and crystallization were calculated by the integration routine. Melting and crystallization temperatures determined by the same routine (corresponding to the maxima of the DSC curves) were taken uncorrected.

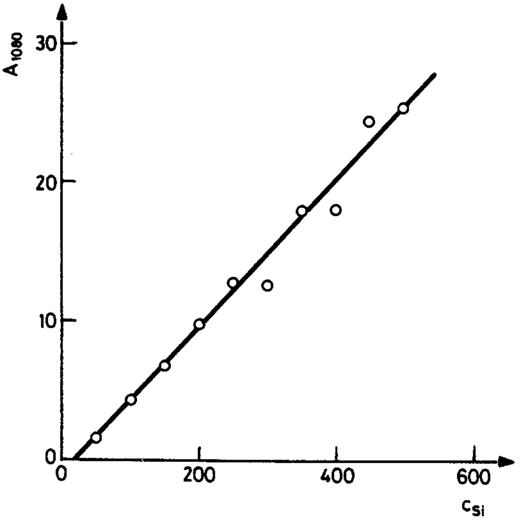

Fig. 1 Absorbance of the modified polyethylene at 1080 cm^{-1} as a function of the trialkoxyvinylsilane concentration used (in arbitrary units)

Thermomechanical measurements were made above the crystalline melting point of the samples. Thermal expension coefficients in the range 160-170° and elastic moduli at 170° were determined with a periodically changing stress of 4.20 ± 10% KPa.

Mechanical properties were measured at room temperature with an FPZ 10 (Heckert) universal testing instrument at 100 mm/min cross-head speed and 55 mm gauge length.

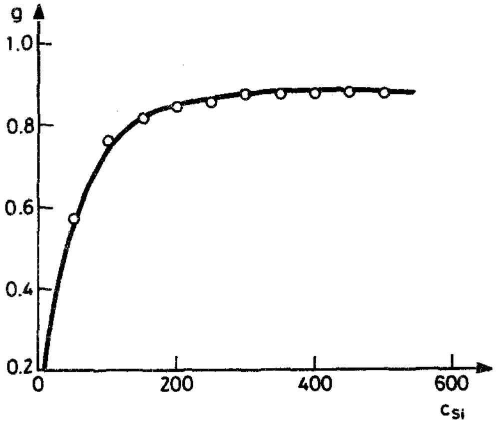

Fig. 2 Gel content of the modified and crosslinked samples as a function of the modifier concentration

Results and discussion

The linear polyethylene used in this study was a copolymer with low 1-hexene content and relatively high density ($d = 0.961$ g/cm^3). The crystalline melting point of the unmodified polymer was 134°. The theoretical upper limit of the equilibrium melting point for wholly regular polyethylene is 146-147°, while the equilibrium melting temperature obtained from experimental data is 141.4° [1]. The depression of the melting point caused by the irregularities can be given as a function of a probability factor p:

$$1/T_m - 1/T_m^{\circ} = -(R/\Delta H_m^o)\log p$$

where $p = 1$ for the ideally regular polymer, while for low concentrations of comonomers or other irregularities it is proportional to the molar fraction of ethylene units [2]. This gives an approximately hyperbolic dependence of the melting point on the degree of modification in this range. Our melting temperature data (Fig. 3) are consistent with this qualitative picture. According to another interpretation, the melting point depression is caused by the diminishing size of the crystals in contact with the amorphous phase, with respect to the infinite crystal [3]. We have no crystallite size (lamellar thickness) data, however, to check this assumption.

As a function of modification, the crystallization temperatures change strictly parallel to the crystalline melting points (Fig. 3). The average difference $Tm - Tc$ is 13.4 deg. We conclude that an increasing degree of modification causes no change in the crystallization mechanism.

The enthalpy change associated with the melting transition is 293 J/g, extrapolated for the ideal case of wholly crystalline regular polyethylene [4]. For our unmodified polymer, $\Delta Hm = 227$ and $\Delta Hc = 231$ J/g were determined from the heating and cooling DSC runs, corresponding to about 78 per cent crystallinity. The enthalpy of melting of the modified polymer

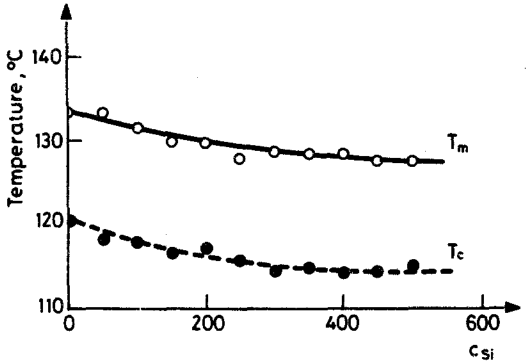

Fig. 3 Peak temperatures of melting (T_m) and of crystallization (T_c) for modified, non crosslinked polyethylene

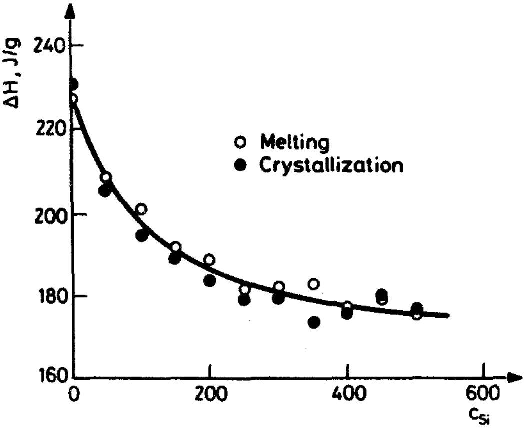

Fig. 4 Enthalpy changes for melting and crystallization of non crosslinked samples

decreases with increasing substitution (Fig. 4), the crystallinity dropping to about 60 per cent. The enthalpy changes of melting and crystallization of a given sample are practically the same, i.e. after a heating/cooling cycle the original crystallinity will be restored for any level of modification. Moreover, it is noteworthy that the crystallinity decreases mostly at low degrees of modification; later, the subsequent decrease is much less expressed. This points again to the probably non-statistical mode of silane grafting.

The modified polymers after crosslinking have values of the melting enthalpy changes which are very similar to those determined for the corresponding non-crosslinked samples. However, there are very significant differences between the melting and crystallization enthalpies, these differences increasing with increasing modification (Fig. 5). Melting and crystallizing of the same samples a second time gives enthalpy change values nearly identical to those obtained during the first crystallization. Obviously, the crosslinking process performed at 100^0 (under the crystalline melting point) leaves the crystalline structure of the samples unchanged. After melting, however, the crystallites can form again only in part, because of the diminished chain mobility connected with network formation.

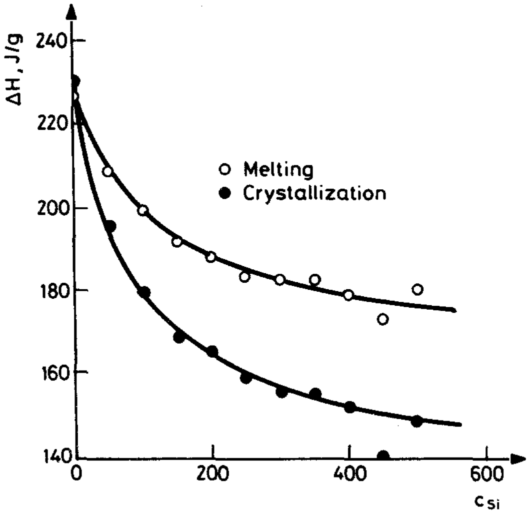

Fig. 5 Melting and crystallization enthalpy changes of crosslinked polyethylene

To separate the effects of network formation from the influences of the crystalline structure, investigations were made on crosslinked polymers above the crystalline melting point, too. With a thermomechanical analyser, the thermal expansion coefficients of the samples were determined and the

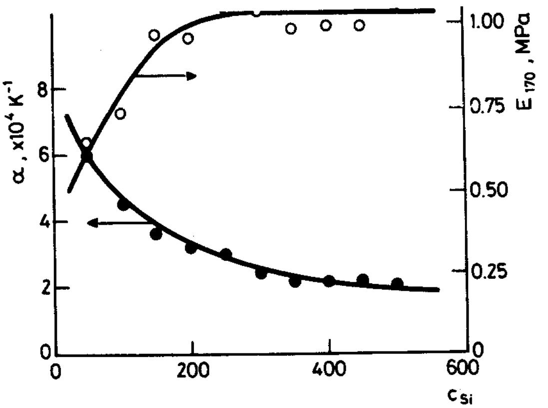

Fig. 6 Thermal expansion coefficients (α) and elastic moduli at 170°C (E_{170}) of crosslinked polyethylene

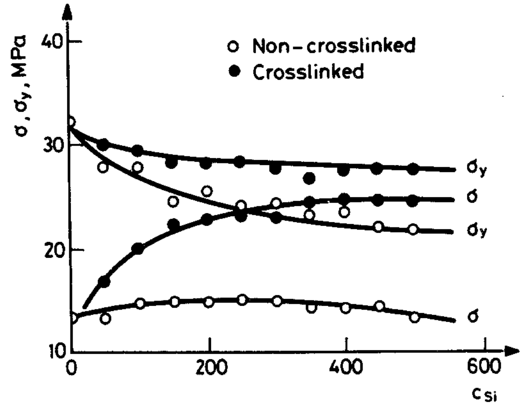

Fig. 7 Yield stress (σ_y) and ultimate nominal strength (σ) of non crosslinked and crosslinked samples

elastic moduli were calculated from the deformation caused by the periodically changing force. Both of these parameters clearly reflect the restricted mobility and growing stiffness of the polymer with increasing substitution and crosslink density (Fig. 6). Again, important changes appear in the domain of low degrees of modification. It must be concluded that the effective number of interchain links is not proportional to the degree of modification.

For practical purposes, the mechanical properties of the crosslinked polymer determined by materials testing methods at room temperature are of primary importance. To discover the structure/properties relationships of the studied PE, however, it is instructive to compare the behaviour of the modified but not crosslinked material with that of the crosslinked polymer. In Fig. 7, the yield stress and the ultimate tensile strength are plotted as a function of the modification for the crosslinked and non-crosslinked samples. The ultimate strength is not significantly influenced by the modification in the case of non-crosslinked samples; crosslinking, not unexpectedly, results in a substantial increase in this property. The yield stress decreases with increasing degree of modification, this effect being much more pronounced for non-crosslinked samples than for the crosslinked ones. It is well known that the yield is connected with the disorganization of the crystalline structure (and, eventually, with the formation of a new one). The decrease in yield stress with diminishing crystallinity is quite natural, but the higher yield stress values of the crosslinked samples having similar crystallinity indicate that the yield mechanism changes as a consequence of crosslinking.

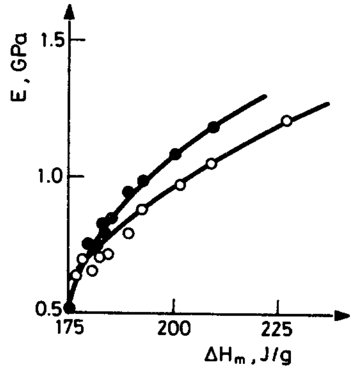

Fig. 8 Elastic modulus as a function of melting enthalpy change (i.e. of crystallinity) for crosslinked (●) and non crosslinked (o) samples

It is informative to compare the mechanical properties of crosslinked and non-crosslinked polymers as a function of crystallinity. Elastic moduli plotted against the melting enthalpy change (Fig. 8) show a similar dependence, albeit the change is somewhat more pronounced in the case of crosslinked samples. The dependence of the yield stress (Fig. 9) allows separation of the two structural factors. The yield stress is a linear function of the crystallinity, as was found for the non-crosslinked polymers. Crosslinked samples with the same crystallinity have higher yield stress values, the difference increasing with increasing crosslink density.

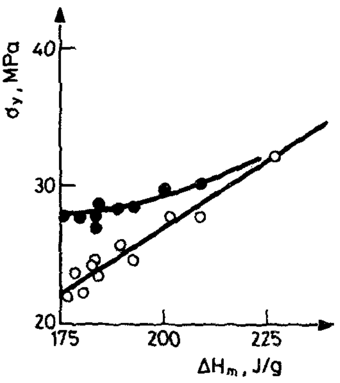

Fig. 9 Yield stress of crosslinked (•) and non crosslinked (o) polyethylene as a function of crystallinity

Conclusions

The properties of crosslinked semicrystalline polymers are determined by both the crystallinity and the network structure. Thermoanalytical methods are informative in the study of such materials. DSC gives important data on the crystalline fraction and, to a lesser extent, on the crystallite structure. Thermomechanical analysis is suitable for the investigation of crosslinked samples above the crystalline melting point. Data obtained by thermoanalytical methods can be correlated with the structural changes caused in the polymer by modification and crosslinking on the one hand and with the changes in the mechanical properties on the other.

References

1 B. Wunderlich, Macromolecular Physics Vol. 3. Academic Press, New York 1980, p. 48.
2 P. J. Flory, Principles of Polymer Chemistry, Cornell, Ithaca 1953, p. 569.
3 D. C. Bassett, Principles of Polymer Morphology, Cambridge University Press, Cambridge 1981, p. 69.
4 B. Wunderlich, Macromolecular Physics Vol. 3. Academic Press, New York 1980, p. 40

Zusammenfassung — Lineares Polyethylen ist ein charakteristisch semikristallines Polymer. Seine physikalischen und mechanischen Eigenschaften hängen sehr stark von der Kristallinität (kristallinen Fraktion) und von der Größe und Struktur der Krsitallite ab.

Eine Modifizierung linearen Polyethylenes durch Propfung von Alkoxysilangruppen und anschließende Vernetzung beeinflußt die Kristalleigenschaften des Polymers. Zu einer Untersuchung dieser Veränderungen ist DSC äußerst gut geeignet. Der mittels TMA ermittelte Elastizitätsmodul und Wärmeausdehnungskoeffizient liefern bei vernetzten Polyethylenen über dem kristallinen Schmelzpunkt nützliche Informationen zur Struktur. Ein Vergleich der mechanischen Eigenschaften modifizierter und vernetzter Proben als Funktion der Kristallinität erlaubt die Herausstellung struktureller Einflüsse. Zwischen Eigenschaften und der Struktur von modifizierten und anschließend vernetzten Poly-ethylenen konnte eine enge Korrelation festgestellt werden.