INTRODUCTION

Polyolefins, like other thermoplastic polymers, soften and finally flow at elevated temperatures. The resistance to thermo-mechanical deformation of polyolefins may be improved by crosslinking, i.e. by converting the initially thermoplastic material into a thermosetting one. The radical crosslinking of polyolefins is very well studied. Peroxide crosslinking and, to a lesser extent, radiation crosslinking are the two main methods of crosslinking industrially employed. Peroxide crosslinking, involving the use of organic peroxides at elevated temperature, is used especially in the cable industry. Radiation crosslinking, involving the polymer treatment with high energy rays, usually accelerated electrons, appears to be restricted to thin finished articles like films, light wiring, heat-shrinkable sleevings and foams. Both methods have production disadvantages in spite of their commercial acceptance.

In the last decade a new crosslinking method has been developed. The process consists, basically, of two distinctly separated steps: grafting and crosslinking. Polyolefins are melt grafted with unsaturated hydrolyzable organosilanes. After shaping, accomplished on line with grafting or coming after that, the finished article is crosslinked in the presence of water. The new method avoids some technological disadvantages of the radiation and peroxide crosslinking and improves certain properties of the crosslinked polyolefins. Therefore, the silane crosslinking technology may be employed in those areas where radical crosslinked polyolefins are used.
already and in areas where they have either gained no entry or made only a minor inroad.

This paper reviews the literature of polyolefin crosslinking by grafting hydrolyzable unsaturated organosilanes. As in a previous review (1) an attempt was made to present the state of the art and future developments of this new crosslinking method.

CHEMISTRY OF THE SILANE CROSSLINKING METHOD

In the first step of the process, polyolefins (PO) are grafted with polyfunctional organosilanes (SI) having the general formula \( R'Si(OR)_3 \), where \( R' \) is a polymerizable group and \( OR \) an easily hydrolyzable functionality. The melt grafting method is employed. This is a relatively simple process which is accomplished in extruders or internal mixers, at 140-240°C, in the presence of a grafting initiator. The grafting of SI onto PO proceeds via a free radical mechanism. The grafting initiator thermally decomposes to free radicals which abstract hydrogen atoms from the PO backbone. The SI is then grafted onto these active sites (figure 1.A).

The silane grafted polyolefins (PO-g-SI) are crosslinkable polymers. In the absence of moisture they are still thermoplastic and can be processed in the same way as normal, uncrosslinked PO. Therefore, crosslinking takes place separately

\[
\text{A.} \quad \text{peroxide} \quad \begin{array}{c}
\text{CH}_2\text{CH}_2^+ + \text{CH}_2=\text{CH} \\
\text{(PE)}
\end{array} \quad \begin{array}{c}
\text{Si(OCH}_3)_2 \\
\text{(VMSI)}
\end{array} \quad \begin{array}{c}
\text{180-240°C} \\

\text{-CH}_2\text{CH}_2\text{Si(OCH}_3)_2 \\
\text{(PE-g-VMSI)}
\end{array}
\]

\[
\text{B.} \quad \begin{array}{c}
\text{RO-Si-OR} \\
\text{OR}
\end{array} \quad \begin{array}{c}
\text{crosslinking} \\
\text{catalyst}
\end{array} \quad \begin{array}{c}
\text{H}_2\text{O} \\
\text{OR}
\end{array} \quad \begin{array}{c}
\text{+ 2 ROH} \\
\text{-Si-}
\end{array} \quad \begin{array}{c}
\text{crosslinkable PE-g-VMSI} \\
\text{-Si-}
\end{array} \quad \begin{array}{c}
\text{crosslinked PE-g-VMSI} \\
\text{-Si-}
\end{array}
\]

Fig. 1. The chemistry of the grafting (A: vinyltrimethoxysilane onto polyethylene) and crosslinking (B) steps.