2 Dynamic vulcanizates and dynamic vulcanization

2.1 Dynamic vulcanizates as part of TPE

Thermoplastic Elastomers combine rubber elastic and thermoplastic properties. They can be divided into two groups /4/: multi-block copolymers and blends (fig.2.1). The first group are copolymers consisting of an elastomeric and a hard block. Styrene block copolymers (TPE-S) exhibit a wide range of application resulting from the properties such as hardness, grip and rebound. Polyesterester block copolymers (TPE-E) exhibit good mechanical properties until 160°C, resistance to oil and fat as well as high polarity providing the ability to be glued and varnished. Polyurethane/elastomer block copolymer (TPE-U) is a classical TPE showing very good mechanical properties and high resistance to wear. Polyamide/elastomer block copolymers (TPE-A) can be compared to both previous groups with respect to their mechanical properties. Polyethylene/poly (α-olefin) block copolymers exhibit a rather low temperature range of use. TPE blends can be divided in TPE-O with a non-crosslinked rubber phase and TPE-V with a crosslinked rubber phase. Due to their un-crosslinked rubber phase TPE-O are preferably used at lower temperatures without exposition to high mechanical stress. TPE-O are transparent, have a low density and an attractive price. Problematically can be the high shrinking. Partially and fully crosslinked TPE-V are widely used in automotive industry, exhibit low hardness and high application temperature until over 100°C. Dynamic vulcanizates belong to this type of Thermoplastic Elastomers /5/.

![Fig. 2.1 Classification of TPE](image)

2.2 Application trends of dynamic vulcanizates

While at the beginning of the use of TPE-V the aim was to substitute existing applications of elastomers now they are also opening new fields of application. This is explained mainly by their processing potential. The use in automotive industry plays a big role also since lately a lot has been done to improve the thermal reliability and oil resistance as well as to reduce the compression set. Thermoplastic process ability provides more recycling possibilities and their use for fast joints provides an easy way of de-montage. A big advantage is also the possibility to produce parts in one step of extrusion or injection moulding (2-component-injection
moulding) /6/. Major application fields of TPE-V and their development over the years are shown in figure 2.2.

![Graph showing part on market for different application fields from 2000 to 2003](image)

**Fig. 2.2 Divisions of application fields for TPE-V in Germany 2000-2003 /6/**

### 2.3 Dynamic vulcanization

The dynamic vulcanization process was first used by Gessler and Haslett /7/ for the preparation of high impact compositions containing different amounts of partially vulcanized elastomer in an iPP/Polyisobutylene blend. The first crosslinked PP/EPDM blend was produced by Holzer and co-workers /8/. The first TPE-V introduced to the market were derived from Fisher’s/9,10/ discovery of partially crosslinking of the EPDM phase of EPDM/PP by controlling the degree of vulcanization by limiting the amount of peroxide. Further improvement of the thermoplastic process ability of these blends was reached by Coran, Das and Patel /11/ by fully crosslinking of the rubber phase under dynamic shear. They demonstrated the effect of the size of particles and the degree of cure on the materials properties as shown in figure 2.3. Raetzsch et al. /12/ developed a new type of dynamic vulcanizates by means of peroxidic crosslinking of the copolymer phase providing high strength and elasticity as well as colorability.
2.3.1 Morphology development

During dynamic vulcanization generally thermoplastic matrix material as well as a rubber component are blended in an extruder resulting in a so-called, co-continuous blend morphology. By means of a second opening a crosslinking agent can be added into the extruder (see fig. 2.4).

During the crosslinking of the rubber phase the viscosity of the rubber increases causing the blends viscosity ratio to increase, since the viscosity of the thermoplastic matrix remains the same. The shear stress causes rubber phase to fall apart into fine dispersed rubber particles in a thermoplastic matrix. This process is schematically shown in figure 2.5. The formation of the characteristic matrix-particle morphology is essentially influenced by the kinetics of the vulcanization and the resulting crosslinking density of the rubber phase /13,14/.

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**Fig. 2.4** Scheme of extruder profile for dynamic vulcanization
If the crosslinking density of the elastomeric phase is very poor, the rubber phase will be able to undergo large deformation and remains co-continuous. If on the other hand the crosslinking density is too high the rubber phase can only be deformed under shear stress without ripping apart. Therefore an optimum of crosslinking density of $10 \text{ to } 20 \times 10^{-5} \text{ mol/cm}^3$ has been suggested /15-17/.

![Fig. 2.5 Scheme of morphology development of dynamic vulcanizates during the crosslinking](image)

**2.3.2 Curing methods**

The crosslinking of the rubber phase in heterogeneous blends consisting of a thermoplastic and a rubber component takes place by introduction of a crosslinking system during the mixing process. During the crosslinking covalent bonds are formed between network points resisting thermal and chemical stresses. Several crosslinking agents are used for rubber vulcanization. Among them are those who require unsaturated double bonds in the molecules to be crosslinked such as:

- sulfur /18,19/
- phenolic resins /25/

In addition to vulcanization agents accelerators, such as sulfenamines or thiram sulfides, in combination with activators, such as zink oxide or stearic acid, are used to shorten curing times and to prevent thermo-oxidative degradation of the polymer.

A scheme of the vulcanization process by the classical vulcanization agent sulfur is shown in figure 2.6.
By means of accelerators and activators the sulfur cycle opening (1) occurs providing for an active sulfurizing complex (2). The self destruction of this complex results in an active sulfur oligomer (3), which reacts with the rubber molecules crosslinking them (4). Due to the high vulcanization temperatures thermo-oxidative degradation of the rubber molecules as well as the sulfidic bridges can take place. Maturation (5) is the separation of sulfur from the polysulfidic bridges. Reshuffling the crosslinks may form intramolecular bridges (cyclic structures).

Phenol formaldehyde resins are also used to vulcanize diene elastomers in the absence of sulfur (see fig. 2.7). The crosslinking reaction occurs through the free phenol groups in the presence of stannous or iron chloride as catalysts. Vulcanizates with good mechanical properties and enhanced resistance to moisture and heat are obtained.

Saturated as well as unsaturated rubbers or copolymers can generally be crosslinked by free radicals, induced by:
- irradiation /22/.
- silanes /23/
- peroxides /24,25/

For irradiation crosslinking with high-energy radiations, free radicals are formed on the polymer chain, which couple to form carbon-carbon crosslinks. In this case, the elastomer, that does not contain vulcanizing agents, is heated to 100-150°C, pressed and then, irradiated.

During crosslinking with silanes a polyfunctional network structure is formed, in which the polymer chains are crosslinked via siloxan bridges (Si-O-Si). In case of EPDM two steps are necessary. First unsaturated organosilane molecules are grafted onto a polymer chain, which
was first activated with peroxide. Secondly the crosslinking reaction via hydrolysis and kondensation result in Si-O-Si bridges between the polymer chains.

The mechanism of crosslinking using peroxides is a homolytical one. At the beginning of the vulcanization process, the organic peroxide splits into two radicals. The free radicals formed as a consequence of the decomposition of the peroxide, abstract hydrogen atoms from the elastomer macromolecules, converting them into macroradicals. In the case of an ethylene-propylene copolymer, the radical formed by the decomposition of the peroxide attacks the tertiary carbon atom. The resulting macroradicals react with each other forming carbon - carbon intermolecular bridges. The crosslinking reaction of an EPM with peroxide is shown in figure 2.8.

Simultaneously with these crosslinking processes, side reactions occur, which reduce vulcanization. Thus, peroxides can react with the components of the compound, i.e., antioxidants, plasticizers, extenders, etc., and can be deactivated. Other side reactions can take place on the radical centers formed on the elastomer backbone. These radicals can disproportionate leading to a saturated molecule and an unsaturated one.

Type and amount of ter-monomer, ethylene content and degree of branching of an EPDM influence the peroxide crosslinking efficiency and resulting vulcanizate properties. The effect of type and amount of third monomer on crosslinking efficiency was measured by the maximum torque difference in a rheometer and was rated as dicyclopentadiene (DCPD) > ethylidene norbonene (ENB) >> hexadiene (HD). This result was explained by different steric and chemical environment of the free double bond. Nevertheless the effect of type of third monomer on vulcanizate properties as hardness and compression set was low. High ethylene contents promote tensile properties being not only a result of higher crosslinking efficiency, but also of partial crystallinity of the polymer. High ethylene contents cause a high compression set at low temperatures. The branching level not only lowers the crosslinking efficiency, but also the kinetics of the crosslinking process /26/.

A general problem during crosslinking is posed by thermo-oxidative degradation processes. Polypropylene is depolymerised by free radicals in a so-called „chain - scission” process. The reason for this lays in the different reactivity of secondary and tertiary C-atoms in PE and PP /27/. Therefore only EPMs with an ethylene content above 50 mol% apply for radical crosslinking. During the free radical crosslinking acetophenone is formed providing for a characteristic smell. At elevated temperatures acetophenone is diffusing out of the polymer /28/. When oxygen is present a chain reaction occurs initiated by decomposition of hydroperoxides. However, it was suggested that higher crosslinking levels hinder the penetration of oxygen into the polymer matrix decreasing the oxidation rate protecting the polymer from extended oxidation /29/. The use of coagents such as triallylcyanurate during peroxidic crosslinking in dynamic vulcanization of PP/EPM systems has proven to be successful preventing β-scission for EPM with ethylene contents below 50 wt% /30/. Another
method to prevent chain scission is the use of monomers such as styrene, which reacts with the free radicals. The effect is visible on the torque curve in the internal mixer. If chain scission occurs after the adding of the peroxide the torque is not reaching a stable value but gradually sinking. The addition of styrene prevents this decrease.