Dynamic Vulcanization
An Accessible Way to Thermoplastic Elastomers*

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Key Words: thermoplastic elastomer, dynamic vulcanization, TPVs, physical properties, structure

ABSTRACT
Technical and economical reasons relating to the increased performance level, greater productivity, and the economic use of materials and energy are stimulating the industry toward an accelerated increase in the use of thermoplastic elastomers. The thermoplastic elastomers obtained by mixing classical elastomers and plastomers form a class of materials with the largest prospect for commercial application. These materials are obtained by mixing rubbers with thermoplastics and realizing the crosslinking of the elastomer phase during a mixing operation frequently referred to as "dynamic vulcanization". Here the parameters of mixing and the vulcanization operation as well as the properties of the resulting thermoplastic elastomers for non-polar polymers are reviewed.

INTRODUCTION
Thermoplastic elastomers, or TPEs, are a classification of polymer-based flexible materials which combine the physical characteristics of elastomers (high elastic behaviour at ambient temperature) with ease of processing associated with thermoplastics. The two main ways, essentially dissimilar, to obtain TPEs are: synthesis of block copolymers having blocks of different chemical natures and possessing dissimilar physical characteristics, and compounding in order to obtain elastoplastic materials starting from polymers having thermoplastic and elastic properties. Offering an answer of high technical and economical efficiency to the present needs of the polymer processing industry, the production and use of TPEs are forecast to show a steady growth, from around 890 million USD in 1989 to close to 1250 million USD by 1994; the growth rate over this period is estimated at 6-20% (different for various TPE types, with the greatest potential for high performance grades), superior to all other high tonnage polymers [1, 2].

Mixing of rubbers with resins and thermoplastics results in composite materials with new properties, different from the starting materials, with an extended range of utilization. Using various polymers, the characteristics of such composites can be varied between large limits, obtaining new materials with a balance of properties which cannot be obtained with existing single polymers. For many years, such composite materials have been obtained by traditional technology used in rubber processing and their properties are well known [3, 4]. By mixing rubbers with thermoplastics under given circumstances, materials with elastoplastic behaviour can be obtained; at high temperature they can be processed in the molten state and, after cooling, in the temperature range of service, they behave as elastomers [5]. At the present time, such materials are produced and used at commercial scale starting from non-polar elastomers and non-polar plastomers, or from polar elastomers and polar plastomers, or from pairs of dissimilar polarity. The use of the curing agents and accomplishing the curing during mixing stage—so called "dynamic

vulcanization—results in a new class of elastoplastic composite materials with superior performances [6] for which the term Thermoplastic Vulcanizates Alloys—TPVs—is frequently used. The realization of some partly crosslinked compounds obtained during the mixing process was claimed in patent literature as early as in 1962 [7] using recipes based on halobutyl rubber, polyethylene and curing resin. During the last two decades, production of elastoplastic composite materials by dynamic vulcanization has been developed starting from ethylene-propylene rubber and polyolefins [6, 8-10], butyl rubber and polyethylene [11] using plastomers with rigid or flexible backbone and various grades of unsaturation [12-17] with unsaturated elastomers [15, 16, 18] vulcanized with peroxide [12, 14, 18-20], sulfur and accelerators [15-17], phenolic resins [21], bis-imides [13], etc.

**DISCUSSION**

Obtaining and Processing of TPVs

The process of obtaining TPVs has been presented many times [6, 22-25]. Mixing can be realized in an inner mixer (Banbury or Intermix), in a mixing extruder with two screws, and even on an open mill at temperatures exceeding 10-80 °C the melting temperature of the plastomer, in high shear circumstances. The kinetics of the dynamic vulcanization was investigated using a Brabender Plastograph [24]. As illustrated in Figure 1, by addition of the elastomer and plastomer, the torque value reaches a high level, then it decreases as a result of the melting of the plastomer. Shortly after plastomer melting, the curing group is added and the torque value increases again as a result of the increase of viscosity accompanying the progress of the vulcanization process. After crosslinking of the elastomer phase, a new decrease in the viscosity may appear as a result of mechano-chemical destruction of the crosslinked elastomer; carrying on the mixing 2-3 min after vulcanization maximum may be advisable in order to improve the dispersion of the vulcanized phase in the thermoplastic matrix. Then, the molten material is discharged on the mill and a 2 mm sheet is taken off. For the purpose of obtaining a TPV with superior characteristics, reprocessing in an inner mixer followed by sheeting on a cool mill is recommended [6].

**Industrial plants for TPV production working in batches, continuously or in a mixed system are described in the literature [10, 22-24]. As an example, Figure 2 shows a simplified scheme of a mixed system plant [24] including an inner mixer working batch by batch, succeeded by an extruder and a granulator working continuously.**

**Figure 1:** Variation of torque in Brabender Plastograph (mean curve) during mixing of EPDM (1), polypropylene (2) and their mixture with ratio 5:2 (3), and of the compound (4) with the following recipe (mass parts): 100 EPDM, 40 PP, 2 stearic acid, 0.5 MBT, 1 TMTD, 2 sulfur, initial temperature 180 °C, rotor speed 90 rpm.

**Figure 2:** A simplified scheme of a technological line for TPV production: 1-Intermix mixer; 2-feeder; 3-extruder; 4-cooling bath; 5-air dryer; 6-granulator.
Table 1, based on literature data [6], presents the main characteristics of the composite materials based on EPDM + PP obtained by the classical method (mixing followed by vulcanization) against a TPV obtained by dynamic vulcanization starting from the same raw materials; it shows that dynamic vulcanization allows composite materials with superior levels of modulus and tensile strength to be obtained.

Table 1: Main properties of some composite materials obtained by traditional method and by dynamic vulcanization.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Traditional method</th>
<th>Dynamic vulcanization</th>
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<tbody>
<tr>
<td></td>
<td>1:0 2:1</td>
<td>EPDM:PP</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>7.1 9.2</td>
<td>11.2 14.2 15.1 16.5</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>285 175</td>
<td>180 215 170 175</td>
</tr>
<tr>
<td>Elongation set, %</td>
<td>12 17</td>
<td>12 22 20 27</td>
</tr>
<tr>
<td>Modulus at 100% elongation, MPa</td>
<td>3.0 6.7</td>
<td>- 10.3 12.8 13.8</td>
</tr>
<tr>
<td>Compression set (72 h at 100°C, 20% strain), %</td>
<td>58 63</td>
<td>- 52 52</td>
</tr>
<tr>
<td>Crosslinking degree, 1/Q (m-xylene)</td>
<td>0.33 0.44</td>
<td>0.51 0.52 0.53 0.53</td>
</tr>
</tbody>
</table>

Recipe, mass parts: 100 EPDM, 120 carbon black ISAF, 100 paraffinic oil, 5 zinc oxide, 2 stearic acid, 1 TMTD, 0.5 MBT, 2 sulfur

TPVs can be processed using machines for plastics processing, with technical characteristics specific for the plastomer included as raw material in the structure of the thermoplastic elastomer [22, 25, 26] for extrusion, calendering, injection and vacuum forming. Figure 3 shows an example for variation of the viscosity of a family of TPVs with temperature and shear rate [25, 26]; these data indicate the important point that such materials must be processed by applying high shear rates in order to enhance their potential performances.

TPVs exhibit a non-Newtonian flow behaviour [5, 26] and their melt viscosity exceeds the viscosity of the plastomer participating in composite material [5, 22, 26]. In order to ensure a satisfactory flow accompanied by a low die swell, such materials should be processed ensuring a shear rate of the order $10^2 \text{s}^{-1}$ and a temperature exceeding by 20-60°C the melting temperature of the corresponding thermoplastic material.

In the same context, Figure 4 illustrates (data excerpted from [24]) the influence of the temperature used during the mixing/vulcanization process and the temperature used during injection moulding on the tensile strength and on the elongation at break of the materials obtained by dynamic vulcanization of a compound EPDM + PP with a 5:2 ratio.

![Figure 3](image-url)  
Figure 3: Variation of the viscosity against temperature (a) and shear rate (b) for a TPV (Santoprene) with various shore hardness: 73A (1); 80A (2); 87A (3); 40D (4).
types of plastomers (for the following examples only non-polar polymers will be retained) the main factors influencing the properties of TPVs have been stated [28].

![Figure 4: Influence of temperature during mixing and during injection moulding on tensile strength and elongation at break for TPVs based on EPDM + PE (1) and EPDM + PP (2) with ratio 5:2 and a sulfur curing system. Mixes (a, b) moulded at 160°C (1) and 200°C (2) have been obtained by mixing (b, d) at 140°C (1) and 180°C (2).](image)

The nature and ratio of both polymers participating in the system are decisive for the main physical characteristics (Young modulus, modulus at 100% elongation, etc.) and their influence also on final properties (tensile strength, elongation at break, tear strength, etc.) and resilience [10, 29]. For selecting the nature of the elastomer-plastomer pair and their ratio, in order to obtain TPVs with a good balance of properties, three characteristics are decisive: the degree of crystallinity of the plastomer \(W_p\), interfacial tension \(\Delta \gamma_s\) ensuring mutual wetting of the phases, and the size of the chain segment between two successive points of the network \(N_s\) \(N_s = A + B(M_o/z)\) where \(A\) and \(B\) are constants, \(M_o\) is the molar mass of the monomer unit and \(z\) is the number of atoms in the backbone of the monomer unit.

The system elastomer + plastomer in the molten state can be represented as a liquid-liquid emulsion with the stability and degree of dispersion dependent on the interfacial tension [5, 30]. When interfacial tension decreases, the dimensions of the discrete phase tend to decrease. Keeping in mind that the superficial tension \(\gamma\) is correlated with solubility parameter \(\delta\) [31], a proposal was advanced [28] to evaluate the interfacial tension for polymer mixtures based on the difference between solubility parameters of the polymers participating in the system \((\delta_1 - \delta_2)\).

Figure 5 [28] shows the variation of several physical characteristics of TPVs with interfacial tension, indicating a decrease of tensile strength and elongation at break with an increase in interfacial tension, while the permanent set in elongation exhibits a maximum in the region \(\Delta \gamma_s = 5-7\); it results that the optimal balance of properties can be reached in the domain of low values of interfacial tension.

![Figure 5: Variation of TPV properties with function of the starting polymer properties: interfacial tension, \(\Delta \gamma_s\), size of the backbone segment between two successive crosslinking points, \(N_s\), and crystallinity degree of plastomer, \(W_p\).](image)
The utilization of crystalline thermoplastics allows TPVs with physical characteristics of high level, superior to the thermoplastic elastomer obtained using amorphous thermoplastics [29]. For this purpose, not only is the initial crystallinity of the plastomer important but also the modification of the crystallinity following the mixing process implicated in producing and processing of TPVs, as well as the orientation and deformation of the product under stress in service [32]. Figure 5 shows also the influence of the crystallinity (interfacial tension and the size of the network segment being maintained constant) on several important physical characteristics: tensile strength and elongation at break increase while permanent set in elongation decreases when crystallinity of the plastomer participant in structure of TPV increases.

The performance of TPVs is dependent also on the density of the network (network density decreases when value $N_s$ increases) as illustrated in Figure 5. The decrease of the crosslinking density of the elastomer phase is accompanied by a decrease of tensile strength and elongation at break, and permanent set in elongation is unfavourably affected for values $N_s > 600$.

The crosslinking density of the elastomer phase is directly dependent on curing group nature (curing agent, accelerator, activator) which influences the curing rate and final curing degree. As illustrated in Figure 6 [6, 10], the increase of the crosslinking density of the elastomer phase is accompanied by an increase of the tensile strength, and a satisfactory permanent set is reached already at low crosslinking density, without a significant variation during subsequent increase of the curing degree.

A regression analysis applied to experimental results [28] shows that the correlation coefficients and mean square deviation for the equation relating physical characteristics ($\Delta V_s$, $W_p$, $N_s$) and mechanical properties of TPVs are not satisfactory because a series of other important factors (polymer viscosity, mechanochemical processes, interactions at interfaces and others have been neglected. For this reason, the above presented correlations should be considered as a qualitative nature at the present stage of investigation. However, starting only from this rather limited volume of information, by drawing three dimensional diagrams for various limit conditions, it has been found that around 45% of the studied compounds satisfy the request for an elongation at break exceeding 100% and 10% of the obtained TPVs satisfy the condition for a limit elongation exceeding 300% at the same time as for a permanent set in elongation lower than 30%.

At present, actually all systems of non-polar polymers useful in producing TPVs have been investigated, and the largest extent shared the systems based on EPDM + PP, IIR + PP, NR + PP. Table 2 [28] contains the main information concerning the performances of some non-polar TPVs. Their properties are dependent on the characteristics of starting polymers (molecular mass, distribution of molecular mass, crystallinity and others), on compound recipe (polymer ratio, nature and amount of curing group, nature and amount of filler and plasticizer, addition of special components), on the circumstances for producing and processing of TPV. For special purposes,
Table 2: Main physical characteristics of some TPVs obtained from non-polar elastomers and plastomers (elastomer:plastomer = 3:2)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Polypropylene</th>
<th>Polyethylene</th>
<th>Polystyrene</th>
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<tbody>
<tr>
<td></td>
<td>NR</td>
<td>BR</td>
<td>SBR</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>26.4</td>
<td>20.8</td>
<td>21.7</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>290</td>
<td>258</td>
<td>428</td>
</tr>
<tr>
<td>Elongation set, %</td>
<td>24</td>
<td>27</td>
<td>30</td>
</tr>
<tr>
<td>Ay. $10^5$ N.m$^{-1}$</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>$W_p$</td>
<td>0.63</td>
<td>0.63</td>
<td>0.63</td>
</tr>
<tr>
<td>$N_a$</td>
<td>454</td>
<td>416</td>
<td>460</td>
</tr>
</tbody>
</table>

additives with a specific end (antidegradants, ignifugants and flame retarders, etc.) as well as pigments for the desired color may be added. A specific additive in recipes of TPVs is the compatibilizer, a low/high molecular substance specifically added in order to reduce the interfacial tension between the two polymeric phases, leading to an improved dispersion of discrete phase in the matrix (eventually for mutual interdispersion) with significant consequences on physical properties of the composite materials. Bearing in mind that the number of the recipe components is rather high and processing parameters are able to introduce significant variation in properties of the resulting composites, statistical design of experiments and computer assisted optimization are useful tools in TPV development.

Structure of TPVs
The properties of TPVs are determined by the structure of these composite materials. The thermoplasticity is a feature of the elastomer + plastomer compounds in the molten state in the domain of ratio values from 40:60 to 85:15 [5, 33], estimating that in this range, both phases are continuous, interpenetrated. The existence of a continuous phase of plastomer, even for a rather low amount, is due to the fact that, at elevated temperature, its viscosity is 5-10 times lower than elastomer viscosity at the same temperature.

The existence of a two-phase system is an indispensable condition in realization of composite materials with elastoplastic properties and this assertion is confirmed by various methods. Electronic microscopy being the most intuitive and widely used [5, 6, 30, 34]. The obtained images show that as an essential peculiarity, the formation of particles of crosslinked elastomer with microgel aspect (the crosslinking of the elastomer phase takes place during dynamic vulcanization and the subsequent mechanodestruction leads to particles of 0.5-10 µm), phase boundary does not have a sharp appearance on the micrographs and this fact is interpreted as a consequence of mutual interaction of elastomer and plastomer phases.

In an attempt to stimulate the structure of TPV, particles of vulcanized EPDM of various dimensions have been introduced [6,10] in a polypropylene matrix (Figure 7), following the influence on stress-strain behaviour of the resulting composite material. The obtained data reveal that TPV is equivalent to the composite with the smallest dimensions of the vulcanized particles.

Using the radiothermoluminescence technique in investigation of a TPV based on EPDM + PP, a shift of the maximum corresponding to the amorphous phase was observed [35] and this experimental fact was explained as an "elastification" of the plastomer phase while the glass transition temperature of the crosslinked elastomer remained unchanged.

In compounds of polymers realized by physical methods, various structures (usual dispersion, fibrils, lamella, formation of...
Figure 7: Influence of the dimension of vulcanized EPDM particles on tensile strength and elongation at break in composites of EPDM + PP with a ratio 3:2.

In the investigation of TPVs, mechanical and thermo-mechanical methods have been applied [10, 37-39], revealing various types of relaxation processes and allowing the evaluation of the nature and level of the energy involved in the interaction between the system phases.

Applications of TPVs
The possibilities of application of TPVs are conditioned by their performances: superior physical characteristics near or at room temperature, maintenance of their working capability from -50 up to 120-150 °C, low values of permanent set, a remarkable stability against weathering (including ozone action) and various aggressive agents. Table 3 presents the main properties of some commercial TPVs.

Concerning the cost/performance ratio, TPVs are situated in the middle region of the domain of TPE as well as for classical, crosslinkable elastomers (Figure 8).

The possibility of using a rather flexible production technology, the significant reduction (or even avoidance) of waste in processing (by easy, on place recycling) make TPVs very attractive materials in the production of a large range of technical items (including items for cars and other vehicles), insulating materials, sealing profiles, insonorization sheets for civil and industrial building, sport and leisure items, and recently, large possibilities for medical/pharmaceutical use have been revealed [40].

SUMMARY
Thermoplastic elastomers as composite materials are polymer-based flexible materials which combine the physical characteristics of elastomers and easy processability of thermoplastics.

Although these materials have been obtained as early as 1962, the use of the curing agents and accomplishing the curing during mixing stage are of more recent developments on materials such as ethylene-propylene rubbers and polyolefins, butyl rubber and polyethylene.

The nature and ratio of both polymers participating in the system are crucial for the main physical characteristics (young modulus, modulus at 100% elongation, etc.) and their influence on final properties (tensile strength, elongation at break, tear strength, etc.) and resilience.
Table 3: Main characteristics of some commercial TPVs

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Specific mass, g/cm³</th>
<th>Shore Hardness</th>
<th>Modulus at 100% elongation, MPa</th>
<th>Tensile strength, MPa</th>
<th>Elongation at break, %</th>
<th>Elongation set, %</th>
<th>Tear strength, N/mm</th>
<th>Compression set, %</th>
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<td>7</td>
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<td>20</td>
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<tr>
<td>023</td>
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<td>82A</td>
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<td>7.7</td>
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<tr>
<td>019</td>
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<td>92A</td>
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<td>14</td>
<td>300</td>
<td>40</td>
<td>18</td>
<td>75°</td>
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<td>1700</td>
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<td>7</td>
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<td>20</td>
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<tr>
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<td>101-73</td>
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<td>73A</td>
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<td>7.6</td>
<td>375</td>
<td>14</td>
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<td>80A</td>
<td>4.6</td>
<td>9.7</td>
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<td>160</td>
<td>0.97</td>
<td>60A</td>
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<td>5</td>
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<td>10°</td>
<td>-</td>
<td>33°</td>
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<tr>
<td>170</td>
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<td>70A</td>
<td>3</td>
<td>8</td>
<td>500</td>
<td>14°</td>
<td>-</td>
<td>36°</td>
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<tr>
<td>171</td>
<td>0.90</td>
<td>70A</td>
<td>3.8</td>
<td>5</td>
<td>220</td>
<td>17°</td>
<td>-</td>
<td>55°</td>
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<tr>
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<td>45D</td>
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<td>15</td>
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<td>60°</td>
<td>-</td>
<td>66°</td>
</tr>
<tr>
<td>250</td>
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<td>96A</td>
<td>-</td>
<td>14.2</td>
<td>280</td>
<td>32°</td>
<td>-</td>
<td>68°</td>
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<tr>
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<td>50D</td>
<td>11.5</td>
<td>14</td>
<td>280</td>
<td>60°</td>
<td>-</td>
<td>68°</td>
</tr>
</tbody>
</table>

*° at 70°C  ** ° at 100°C  *** after 100% elongation

The data presented from various works indicate that composite materials based on EPDM + PP obtained by dynamic vulcanization have superior levels of modulus and tensile strength.

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REFERENCES
