



## Physical characterization of commercial polyolefinic thermoplastic elastomers

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### Abstract

In this work, a systematic study of physical characterization on a series of commercial polyolefinic thermoplastic elastomers (TPEs), is reported. Formulations from different manufacturers, having a wide range of Shore hardness values (from A45 to D51), were examined using simple, inexpensive and standard laboratory methods. From this analysis, the TPE chemical composition and its relationship with hardness and tensile set—the key parameters that define the TPE performance in most of the applications—could be established.

It was found that the strategy followed by the manufacturers to design TPEs is very similar. The EPDMs used for the different formulations look similar in ethylene content and thermal properties. Therefore, the TPE bulk modulus (or hardness) is mainly controlled by the PP content. Nice elastomeric behavior was observed only in grades with a dominant proportion of EPDM, in agreement with the deformation mechanism generally accepted for this type of materials. Grades with higher hardness values—and a dominant proportion of PP—showed a mechanical response corresponding to a toughened thermoplastic, even when these grades are marketed by the producers as “thermoplastic elastomers”. Differently from conventional crosslinked elastomers, where hardness and ability to recover from highly deformed states can be simultaneously controlled by changing the degree of crosslinking, the results of this work indicate that it is very difficult to increase TPE hardness without sacrificing elastomeric properties.

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### 1. Introduction

The name polyolefinic thermoplastic elastomer (TPE) has been coined to refer to a specific family of thermoplastic alloys that offers the main advantages of two

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types of polymeric materials: elastomeric behavior at room temperature and thermoplastic behavior at processing temperatures. This dual behavior is obtained because the morphology consists of small rubber particles dispersed in a continuous thermoplastic matrix.

TPEs with hetero-phase morphology are usually prepared by dynamic vulcanization of blends of polypropylenes (PP) and ethylene-propylene (EPM) or ethylene-propylene-diene (EPDM) rubbers, with the required amounts of specific additives. The dynamic vulcanization process is aimed at selectively crosslinking the dispersed rubber phase, without an extensive propagation of the crosslinking reaction into the PP phase. Specially designed chemical systems are used for this purpose [1–4]. Nevertheless, some EPDM-PP copolymer may be obtained via the crosslinking reaction at the PP-rubber interphase. This brings additional advantages to the system [5] by improving PP-rubber adhesion. The PP/rubber weight ratio can be varied in a wide range to adjust several TPE properties like hardness, tensile modulus, elongation at break, compression set, brittleness temperature, oil resistance, and others.

As above-mentioned, the PP-rubber adhesion can be increased by crosslinking reaction, if some PP-rubber graft is formed [2–4]. Benefits to be gained from adequate grafting are improvements in compression set, oil resistance, and processing characteristics [6], reductions of particle size domains [7], improvement of low-temperature impact strength [2,7], and a reduction of the amount of dispersed rubber needed to improve impact strength [3]. PP crystallization at the PP-rubber interface can also improve the thermoplastic-rubber adhesion, creating additional links between the phases that may contribute to a more effective transmission of stresses. The rubber particles can affect the PP crystallization, either by a nucleation effect or by co-crystallization of the rubber with the PP [3,8–10]; semicrystalline rubbers have been used with this aim. Even while rubber crystallinity has been shown to affect PP-EPDM miscibility [11,12], it has been reported to increase hardness, scratch resistance, modulus, ultimate tensile stress, and toughness [5,13].

Fillers, plasticizers and oils are usually added to the TPE formulations. Carbon black is often used to increase hardness, ultimate tensile modulus and tensile set [6]. Some ester-type plasticizers can also be included to improve properties at low temperature or to lower the final product  $T_g$  [6,14]. Large amounts of oil are included in the formulations. The oil acts mainly as processing aid [1]. Besides a significant improvement in processability, it has been shown to render softer final products, either by plasticizing or by diluting the crosslinked rubber [6,14].

Even while many conventional crosslinked elastomers show properties that cannot be achieved by TPEs, the thermoplastic nature of these alloys allows the use

of much easier, safer and cheaper processing methods, previously developed for regular thermoplastic polyolefins. Most of the studies published in the open literature have been devoted to studying the effects of one or a few variables on a few model TPE systems, to establish composition- or structure-properties relationships. As these materials have become commercially available, it is desirable to systematically examine the ways used by some TPE producers to offer products that, being essentially a rubber-thermoplastic polymer blend, can show wide ranges of properties.

This study presents the application of simple, inexpensive standard laboratory methods to examine in detail the formulations, structure and properties of a set of commercial TPEs, including grades with crosslinked and non-crosslinked rubber phases. The grades examined are produced by several traditional TPE manufacturers as DSM, Mitsubishi Monsanto Co. So.F.TER S.p.A and Advanced Elastomer Systems. Special attention is paid to the relationship between TPE chemical composition and mechanical properties such as hardness and tensile set, because these are the properties usually specified to choose the grade to be used for a specific purpose. The main effects of the oil content included in the formulations on thermal and mechanical properties are also analyzed. Solvent resistance is required only for a few special applications; however, as an acceptable combination of softness and solvent swelling resistance can only be obtained with fully crosslinked or traditional elastomers, the swelling behavior is not examined in this study.

## 2. Experimental

### 2.1. Materials

The materials used for this study were a series of commercial TPEs covering a wide range of hardness, starting from A45 up to D51 in the Shore scale. Five samples of the TPE produced by DSM under the commercial name of Sarlink were studied. These are marketed as Sarlink 3140, 4155, 4175, 3190 and 4149D. We also studied TPE samples made by other manufacturers; these included Santoprene 103-40 (Mitsubishi Monsanto Co), Forflex A90 (So.F.TER S.p.A) and Vyram 9201-85 (Advanced Elastomer Systems). It is believed that all these materials were prepared by dynamic vulcanization of PP and EPDM, with the only exception of Forflex, which is a physical blend of PP and non- or weakly crosslinked EPDM. An isotactic PP homopolymer, provided by Petroquímica Cuyo, was used as a reference to compare parameters that characterize thermal transitions (glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and degree of crystallinity) with those of the PP-rich phase in the commercial blends.

Table 1  
List of materials/manufacturers used in this study

Sample ID	Commercial name	Manufacturer	Shore hardness
Sar-40	Sarlink 3140	DSM	A 45
Sar-55	Sarlink 4155	DSM	A 57
Sar-75	Sarlink 4175	DSM	A 74
Vyr-75	Vyram 9201-75	AES <sup>a</sup>	A 75
For-90	Forflex A90	So.F.TER S.p.A	A 90
Sar-90	Sarlink 3190	DSM	A 92
Stp-D40	Santoprene 103-40	MMCo <sup>b</sup>	D 49
Sar-D49	Sarlink 4149	DSM	D 51

Shore hardness data provided by the manufacturers.

<sup>a</sup> AES: Advanced Elastomers Systems.

<sup>b</sup> MMCo: Mitsubishi-Monsanto Co.

Table 1 summarizes the materials studied, ordered by increasing hardness, based on the data of Shore hardness provided by the manufacturers.

## 2.2. Samples preparation

A specially designed jacketed Soxhlet extraction system was used to remove selectively some of the components of the TPE formulations. This system operates keeping the samples at the solvent boiling temperature. To extract the processing oil, we used toluene as a solvent. At toluene boiling temperature, only the oil (and eventually some non-crosslinked EPDM chains) can be dissolved. The amount of oil extracted was monitored by recording the weight changes of the samples. After 2–4 days of extraction, the amount of extracted oil virtually leveled off. We refer to this procedure as oil- or toluene-extraction. The non-crosslinked PP was extracted from the TPEs by using a solvent with higher boiling temperature (xylene), after completing the oil extraction. The weight of the extracted PP leveled off after approximately 4 h of extraction. We refer to this procedure as PP- or xylene-extraction.

All the specimens used for DMA and tensile tests were compression-molded between hot plates. Antioxidant (Santnox from Ciba-Geigy, 1000 ppm) was added to the oil-extracted materials to prevent chemical degradation during the molding stage. All samples were dried in a vacuum oven at 40 °C for 48 h before molding, to prevent the presence of humidity or traces of solvent. Samples were molded using a hot press, applying a pressure of 0.5 MPa at 210 °C, for approximately 5 min. Then, the samples were quenched in cold water.

## 2.3. Experimental techniques

The thermal transitions for the original and oil-extracted samples were measured by differential scanning calorimetry (DSC) using a Perkin–Elmer Pyris II DSC instrument. Runs were performed between –100 and

250 °C using heating and cooling rates of 10 °C/min. Glass transition temperatures were determined as the onset of the transition of the second heating step. Melting and crystallization temperatures were informed as the peak maximum obtained from the second heating/cooling step, respectively.

The thermal degradation of the TPEs was monitored by thermo gravimetric analysis (TGA), using a Mettler-Toledo instrument. Sarlink samples were run from 50 to 650 °C at 10 °C/min, under nitrogen atmosphere. Forflex A90, Santoprene 103-40 and Vyram 9201-75 grades were first run from 50 to 500 °C at 10 °C/min (under nitrogen atmosphere), and then from 500 to 850 °C at 20 °C/min (under air atmosphere). Data from the TGA instrument are shown as the differential of the weight loss with respect to the temperature (DTG curves). As the commercial blends are composed by chemically different materials (oil, polymers, fillers) that decompose at different temperature ranges, the DTG curves consist of a series of well defined but superposed peaks. DTG peaks were decomposed using Labcal 3.1 software. Log-normal functions were used to fit the DTG peaks [15], without constraining the numerical values allowed for the functions parameters.

The oscillatory mechanical response of the original and oil-extracted samples was measured as a function of temperature, in a dynamic mechanical analyzer (DMA) Perkin–Elmer DMA 7e instrument. It was operated at 1 Hz, using a heating rate of 10 °C/min. Three-points bending geometry (span of 20 mm), and specimens of 25 mm length, 5 mm depth and 1 mm thickness, were used. The levels of strain applied were always in the linear elastic response range.

The mechanical response at higher strains, for the original and oil-extracted samples, was measured using a Universal Instron Machine (model 4467). An extensometer model 2603-080 Instron was used. Standard tensile tests were performed at room temperature, using a crosshead rate of 50 mm/min. Tensile set tests were also performed at room temperature in the same instrument,

using the following protocol: the sample was first strained at 120 mm/min until the pre-set strain level was reached (100%). Then, the specimen was allowed to relax stresses at this strain level, for 10 min. After that, the sample was released from the clamps, and the residual strain measured after 10 min. Specimen geometry (3 mm thickness and 115 mm length) and experimental conditions in all the tests were according to the ASTM D412 procedure.

### 3. Results

#### 3.1. Thermal characterization

Fig. 1 shows the normalized DTG curves for the samples Sar-D49 (D 51 Shore hardness), Sar-90 (A 92 Shore hardness) and Sar-75 (A 75 Shore hardness).

At the range of temperatures between 200 and 500 °C, the thermal decomposition of two components with different kinetic parameters is observed. All the TPEs analyzed presented the same decomposition pattern. The peak observed at the lower temperature interval (250–420 °C) can be associated with the thermal decomposition of the oil. The range of decomposition temperatures agrees very well with those reported in literature for oil and plasticizers commonly used in rubber industry [14]. We also performed DTG runs of the TPE samples after Soxhlet extraction with toluene (where the oil is supposed to be selectively removed), which showed the complete disappearance of that peak. The decomposition peak observed at higher temperatures (420–500 °C) corresponds to the decomposition of polymeric materials (EPDM + PP). The range of temperatures agrees with that observed for EPDM and PP [16]. The weight loss curves showed—for all the samples—a residue that did not decompose under inert atmosphere in

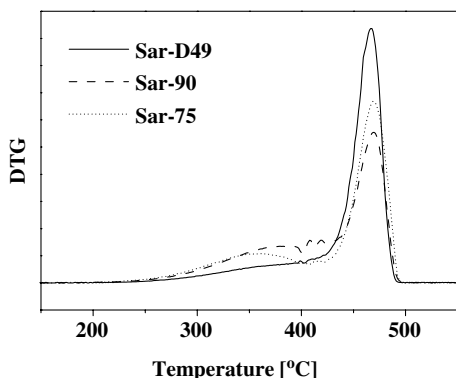


Fig. 1. DTG curves corresponding to the original TPE grades with high (Sar-D49), intermediate (Sar-90) and low (Sar-75) Shore hardness values.

the range of temperature studied (50–500 °C). The residue decomposed partially at higher temperatures (above 600 °C) under oxidant atmosphere. It is well known that mixtures of fillers can be added to these systems to improve mechanical properties and/or to reduce costs. This residue (in the order of 10% for most of the samples) may be well assigned to non-polymeric fillers and is regarded as “filler”.

Fig. 2 shows the DSC scans for materials with low (Sar-40), intermediate (Vyr-75) and high hardness values (Sar-D49).

DSC outputs show characteristics corresponding to two-phase materials, where the thermal transitions of the rubber and thermoplastic phases can be individually observed. In all cases, the low  $T_g$  (around  $-60$  °C) is assigned to the EPDM phase. This transition was affected by the presence of the oil (found in large proportions in most of the formulations), which acts as a plasticizer. The effect of the oil on thermal and mechanical properties will be discussed later.

Some features associated with the possible melting/crystallization of short ethylene crystallizable sequences in the EPDM-rich phase, are also revealed by the DSC traces. Right after the EPDM-rich phase  $T_g$ , a second (weaker) endothermic peak is observed. The peak is broad but clearly observed in those samples with higher EPDM content (see for example the DSC outputs for Sar-40 in Fig. 2). To confirm this idea, the samples were subjected to annealings for 3 h at  $-20$ ,  $-10$  and  $0$  °C. After annealing, the samples were first cooled to  $-100$  °C, and then heated at  $10$  °C/min. DSC scans of the after-annealed Sar-55 sample are shown in Fig. 3.

It is observed that the shape of the melting peak was modified by the annealing processes. Annealing allows enough time for some crystallization, and these peaks can be assigned to melting. These endothermic peaks have been found in commonly used random ethylene-propylene copolymers with ethylene content above 60%, and have been assigned to crystallization of short

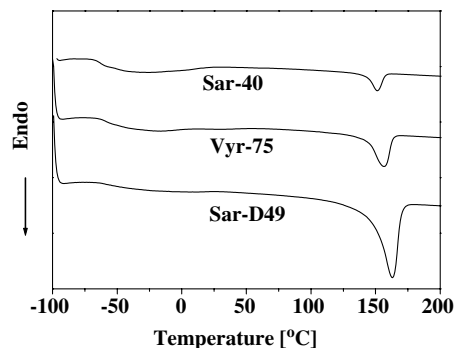


Fig. 2. DSC data for the original Sar-D49, Vyr-75 and Sar-40 grades.

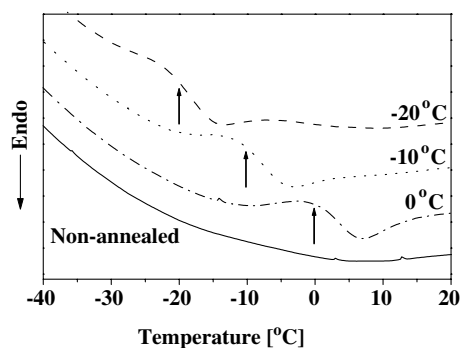


Fig. 3. Effect of the annealing for 3 h, at temperatures above the EPDM  $T_g$ , on the Sar-55 sample: DSC scans after annealing at  $-20^\circ\text{C}$  (dashed line),  $-10^\circ\text{C}$  (dotted line) and  $0^\circ\text{C}$  (dashed-dotted line). The non-annealed Sar-55 is plotted as solid line.

ethylene sequences [17]. This experiment makes evident the common use of semicrystalline EPDM rubber with ethylene content above 60% in most of the TPE formulations.

Finally, we assigned the peaks observed at higher temperatures (above  $100^\circ\text{C}$ ) in the DSC scans of Fig. 2, to melting of PP chains in the thermoplastic phase. The  $T_g$  associated with the corresponding PP amorphous phase is not observable by DSC but in some cases can be detected by DMA, as will be shown later.

### 3.2. Compositional analysis

The analysis of TPE compositions was carried out from DTG, DSC and solvent extraction results. The DTG runs presented in Fig. 1 shows clearly different relative amounts of oil and polymeric phase (EPDM + PP) for each TPE grade. From these curves, the quantification of these components can be precisely carried out by decomposing the DTG trace in its constituent peaks [15], and by calculating the areas under them, as detailed

in the experimental part. We used two log-normal functions to represent the oil and (EPDM + PP) peaks, founding very good agreement between the summation of the individual decomposed peaks (obtained by curve-fitting) and the experimental DTG data. Oil/polymer (EPDM + PP) weight ratios were calculated from the areas under the decomposed peaks. As was above-mentioned, a residue that decomposes at high temperature (that we refer to as “filler”) was found in all the samples; the filler weight fractions were quantified from the weight loss curves. Considering the mass of the residue, the mass of the original material and the relative amounts of oil/polymer, the weight percentages of oil, polymer and filler can be calculated. Results from this analysis are summarized in columns 2–4 of Table 2.

The percentages of processing oil and PP determined from the toluene- and xylene-extraction procedures are summarized in columns 5 and 6 of Table 2. The amounts of processing oil determined from the analysis of the DTG curves are in very good agreement with those determined after Soxhlet extraction with toluene. It is observed that—even though both method results agree well—the values from the solvent extraction experiments are slightly but consistently higher than those obtained from the DTG analysis. In the case of For-90, the difference is even larger (about 25%). These differences may be due to small amounts of non-crosslinked EPDM that may leave the samples during the oil extraction. For the For-90 sample, the EPDM is not crosslinked (this grade was not prepared by dynamic vulcanization) and therefore more EPDM can leave the sample during the oil extraction.

The amounts of PP extracted with hot xylene are reported in column 6 of Table 2. To find out whether the PP component was completely removed by the solvent, we run DSCs of the extracted samples. For some samples, small amounts of PP crystals were detected (see Table 2). This may be due to the presence of PP chains grafted on the crosslinked EPDM phase.

Table 2  
Compositional analysis results obtained from DTG, DSC and solvent extraction experiments

Sample ID	DTGA			Soxhlet		DSC
	% Filler	% EPDM + PP	% Oil	% Oil	% PP	% PP
Sar-40	7.6	42.4	50.0	63	7.9	11.5
Sar-55	12.0	41.0	47.0	47.7	14.7	13.6
Sar-75	10.9	48.6	40.5	43.2	16.6 <sup>a</sup>	20.7
Vyr-75	12.9	53.1	34.0	34.8	22.3	26.3
Sar-90	9.7	60.3	30.0	33.2	33.2 <sup>a</sup>	41.0
For-90 <sup>b</sup>	7.0	62.0	31.0	56.4	–	36.1
Stp-D40 <sup>b</sup>	8.7	63.3	28.0	26.5	–	54.6
Sar-D49	5.9	79.1	15.0	19.2	74.81	69.4

<sup>a</sup> Vestiges of PP crystallinity found in the DSC scans after high-temperature solvent extraction.

<sup>b</sup> PP content could not be determined by xylene extraction because the samples lost integrity.

DSC experiments also provide quantitative information about the relative amounts of PP and EPDM in these blends. The amount of PP in the original samples can be estimated by assuming that PP crystallinity is not affected, neither by the oil nor by the EPDM, and that chains crystallize as in pure PP. As will be discussed later, the oil only affects the equilibrium conditions of crystallization, with little effect on the amount of crystals formed. Even though it has been reported that EPDM may change the PP crystalline morphology by acting as nucleus for crystallization [1], we assume that it does not affect the amount of crystals formed. Under these assumptions, we can estimate the amount of PP in the TPE from the areas under the DSC exothermic peaks by using:

$$\% \text{ PP} = \frac{\Delta H_{\text{TPO}}}{\Delta H_{\text{PP}}}, \quad (1)$$

where  $\Delta H_{\text{TPO}}$  is the TPE bulk melting enthalpy, as calculated from the melting peak corresponding to PP crystals in DSC scans, and  $\Delta H_{\text{PP}}$  is the bulk melting enthalpy for pure PP. We obtained  $\Delta H_{\text{PP}} = 87.8 \text{ J/g}$  from the DSC trace of the standard iPP used as reference. Values of PP weight % calculated in this way are included in Table 2 (last column); they can be compared with those obtained from the extraction experiments using hot xylene (column 6—Table 2).

Fig. 4 summarizes the information presented in Table 2. We plotted the weight ratio PP/(EPDM + PP) and the weight percentages of oil as a function of the Shore hardness (A-scale, as obtained from the manufacturer), for each one of the formulations studied. Additional experimental data, corresponding to TPEs with Shore hardness values of A 63 and A 71, taken from Ref. [18], were also included. The two formulations with Shore hardness in the D-scale (Stp-D40 and Sar-D49) have been excluded from the plot, but they follow the trend observed.

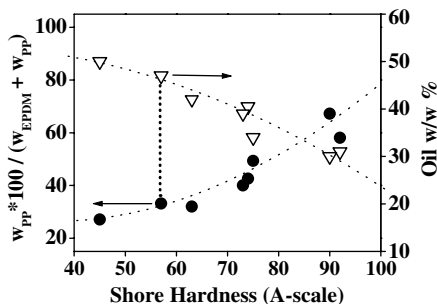


Fig. 4. Oil content and PP/(PP + EPDM) weight ratio as a function of TPE Shore hardness (A-scale). The Shore hardness data were provided by the manufacturer. Data corresponding to Shore hardness values of A 63 and A 71 were taken from Ref. [18].

For all the samples studied, hardness -and therefore modulus- increases with the PP/(EPDM + PP) weight ratio, and this can be expected because Shore hardness is a bulk (average) measurement on a composite structure made up of a very hard continuous PP phase, and a much less hard dispersed EPDM phase. The oil content increases with the EPDM/(EPDM + PP) weight ratio; it indicates that most of the oil is contained in the EPDM phase. The oil/EPDM weight ratio is about 0.65 for most of the TPEs studied.

### 3.3. Mechanical response at small and large deformations

Further insights into the TPEs morphology and the location of the processing oil, can be obtained by measuring their linear viscoelastic response as a function of temperature. Fig. 5A shows the Storage Modulus curves, in the range of temperatures from  $-100$  to  $60^\circ\text{C}$ , for samples with high (Sar-D49, Sar 90), intermediate (Sar-75) and low (Sar-40) hardness values. For comparison purposes, experimental data corresponding to pure iPP (solid line) was also included.

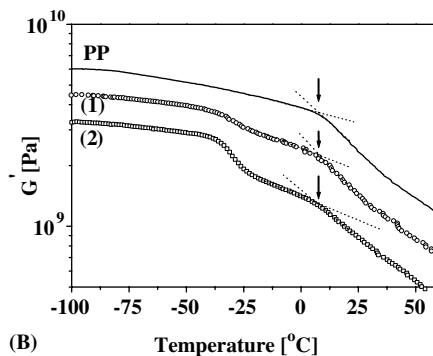
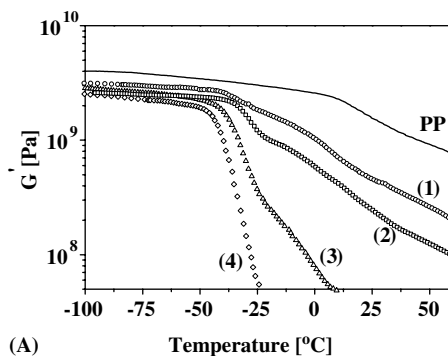


Fig. 5. (A) DMA curves corresponding to the original TPEs: Sar-D49 (1), Sar-90 (2), Sar-75 (3) and Sar-40 (4). The data corresponding to pure PP is also shown as solid line. (B) DMA curves of the toluene-extracted materials: Sar-D49 (1) and Sar-90 (2). Pure PP is shown as solid line. The arrows indicate the  $T_g$  associated to the PP-rich phase.

The iPP data shows one main transition at about 10°C, associated with its  $T_g$ . For the harder TPEs (Sar-D49 and Sar-90)—that contain larger PP weight fractions—two major transitions are observed: One in the vicinity of -40°C, associated to the EPDM-rich phase glass transition temperature, and other one between -10 and 10°C, assigned to the PP-rich phase glass transition temperature. For low hardness grades (Sar-75 and Sar-40),  $G'$  show an abrupt change at the  $T_g$  of the EPDM-rich phase, in a magnitude that reflects the different amounts of EPDM used in each formulation. We found that the magnitude of the  $G'$  slope, above the EPDM  $T_g$ , correlates with the increase in the PP/(PP + EPDM) weight ratio.

Fig. 5B shows  $G'$  curves for Sar-D49 and Sar-90 after oil extraction. It is observed that the oil affects the TPE thermal transitions, acting as a plasticizer. After oil extraction, the  $T_g$  of both PP- and EPDM-rich phases is shifted at higher temperatures. In absence of oil, these transitions are almost coincident in both grades, and the PP-rich phase  $T_g$  matches that of the pure PP. The same pattern was observed in all the samples.

The mechanical response of the TPEs at higher deformations, in the form of stress–strain curves, is shown through Fig. 6A and B. These curves were measured

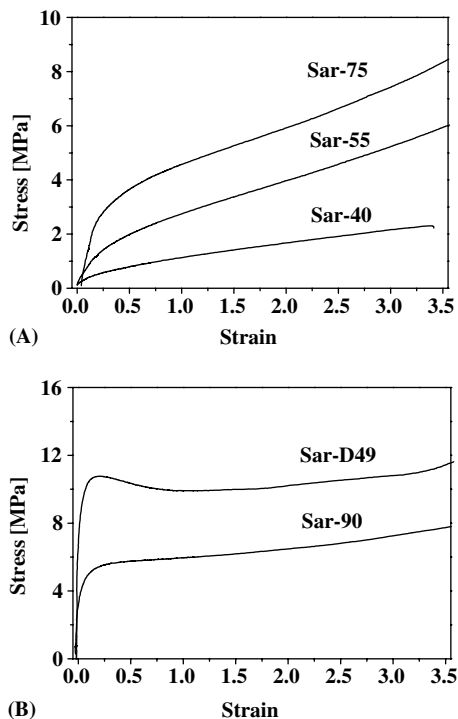


Fig. 6. Stress–strain curves corresponding to the original TPEs. (A) Grades with high proportion of EPDM (Sar-40, Sar-55 and Sar-75). (B) Grades with high proportion of PP (Sar-90 and Sar-D49).

from tensile test at room temperature, using a crosshead rate of 50 mm/min.

We found that the values of the TPEs initial modulus and stress at break, obtained from stress–strain curves, correlate with the PP content in the samples, and consequently with the TPE hardness. It suggests that the TPE hardness can be only varied by increasing the PP/EPDM ratio; the same conclusion can be drawn from Fig. 4.

The mechanical response changes markedly with the TPE composition. Those grades with higher PP content (Sar-D49 and Sar-90) show a behavior closer to a thermoplastic. The stress–strain curves for these grades exhibit yielding and a mechanical behavior similar to pure PP. These formulations should be considered as toughened thermoplastics more than as thermoplastic rubbers. Samples with higher proportion of EPDM (Sar-40, Sar-55 and Sar-75) show the typical elastomeric response, in a similar fashion to pure EPDMs. Equivalent results for similar TPEs with high EPDM content have been explained by Inoue and coworkers [19,20] via finite elements analysis. The authors showed that—even for large deformations—the PP ligament matrix between rubber particles is locally preserved at low stress concentration, and thus prevented from yielding, maintaining an equivalent stress within its elastic limits. In this way, the bulk elastomeric behavior reflects the EPDM-rich phase mechanical response.

Residual strain results for some of the samples analyzed are shown in Fig. 7, plotted against the PP/(PP + EPDM) weight ratio (the figure also includes results for oil-extracted samples that will be discussed in the next section). Residual strains represent structural changes in the sample that cannot be recovered in a short time. The results obtained are consistent with the previous observations. For TPEs with high EPDM content, the PP matrix deformation is very low; for TPEs with higher PP content, the deformation mechanism

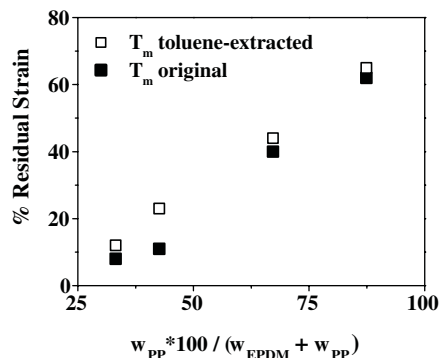


Fig. 7. Residual strains from tensile set experiments as a function of PP/(PP + EPDM) weight ratio, for the original and toluene-extracted TPEs.

keeps changing towards higher local PP matrix deformation, and therefore higher residual strains are measured.

### 3.4. Effect of the oil on thermal and mechanical properties

The analysis of TPE formulations reveal that these materials contain important amounts of oil, in some cases in proportions comparable to those of the main components (see Table 2). One would expect that this oil act as plasticizer, improving the blend processing but also affecting thermal and mechanical properties of the blend and its rate of elastic recovery.

The DMA results of Fig. 5 showed that both glass transitions corresponding to the rubbery and the thermoplastic phases were affected by the presence of the oil. A systematic study of the oil influence on the phase transitions can be performed by DSC. Fig. 8A shows the EPDM-rich phase  $T_g$ s for original and for the oil-extracted materials, obtained from DSC measurements. As observed by DMA, the oil reduces the  $T_g$  of the EPDM-rich phase. Small differences for the EPDM rich phase  $T_g$  after the toluene extraction are found between the different formulations; these differences may be due to EPDM chemical composition, to copolymerization statistics (catalyst and reactor effects) or to slightly different degrees of crosslinking.

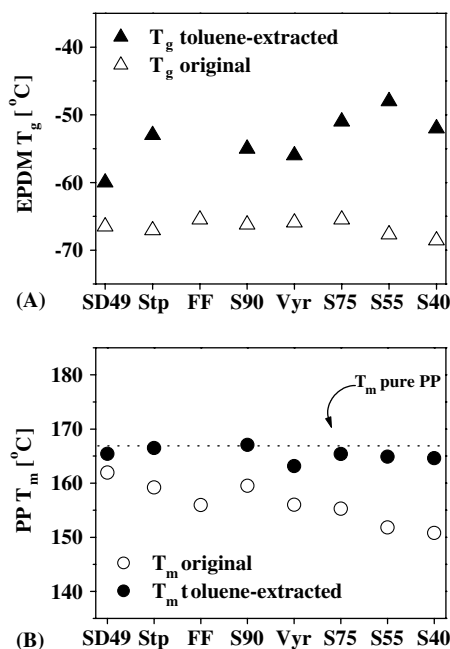


Fig. 8. (A)  $T_g$  of the EPDM-rich phase—obtained from DSC experiments—for the original- and toluene-extracted materials. (B)  $T_m$  of the PP-rich phase—obtained from the maximum of the melting peak in DSC scans—for the original- and toluene-extracted materials.

Fig. 8B shows DSC melting temperatures for the original and for the oil-extracted formulations. The PP melting peak maximum is shifted toward lower temperatures by the presence of increasing amounts of oil. This may be due to the thermodynamic effect of the oil, depressing the melting and crystallization temperatures of the PP, as predicted by the classical Flory-Huggins theory. The  $T_m$  of the PP-rich phase changes more for the softer TPEs (with higher oil content), which can be explained in at least two ways: (a) the effect of higher oil content in the PP amorphous phase and (b) the larger area/volume ratio for the PP phase. To quantify the relative importance of both effects, dilatometry equilibrium melting temperatures have to be measured.

The analysis of the DSC traces revealed that the crystallinity of the PP-rich phase is not affected by the presence of oil. The total heat of crystallization by unit mass of PP-rich phase was—for all samples—the same before and after the oil extraction. It is due to the high mobility of the small oil molecules that allows their fast diffusion away from the forming crystallites.

The thermodynamic compatibility of the oil with the PP and EPDM rich phases is an important issue from the point of view of the TPE application. If the oil were dissolved in the PP too well, then the PP melting temperature would be lowered too much, reducing the service temperature range for the material. On the other hand, good oil-EPDM compatibility is needed to keep all the oil in the TPE system, making it a usable, non-contaminating material.

We end this section with some comments about the influence of the oil on the TPE mechanical properties. DMA and stress-strain data showed an increase in Storage/Young modulus after oil-extraction, in a magnitude that correlates with the amount of oil extracted from the sample. In this case, the oil is expected to reduce the concentration of elastically active chains, which ought to decrease the TPE modulus. The effect is not minor in TPEs with higher oil content (Sar-55, Sar-40), where we found that the TPE modulus decreased up to 10 times in presence of the oil. On the other hand, it may be beneficial in applications that require soft materials. The presence of the oil improves considerably the TPE fluency, particularly in blends with high EPDM content that otherwise would be very difficult to process. The effect of the oil on the TPE strain recovery is shown in Fig. 7, which includes residual strain data for the oil-extracted and original samples, as a function of the PP/(PP + EPDM) ratio. It is observed that the original formulations show a slightly better ability to recover from highly deformed states compared with the oil-extracted materials. The plasticization effect of the oil on the EPDM phase, rendering a faster recovery, may explain the differences observed. From these data, we can conclude that the presence of oil does not markedly affect the TPEs deformation mechanism.



#### 4. Summary and conclusions

The fact that TPEs made by several producers follow the same general correlations simultaneously (see for example Fig. 4) indicates that the strategies used for these manufacturers to design TPE formulations are very similar.

All the EPDMs used in the formulations analyzed behaved following similar patterns. Their diluted  $T_g$  are very close to each other, they are crosslinked while diluted with similar oil contents (the ratio EPDM/Oil is almost constant in all the formulations). They also showed evidence of ethylene content of about 60% [17], as indicated by the endothermic peaks observed in all the formulations right after the EPDM-rich phase  $T_g$ , associated to melting of ethylene units. Therefore, the modulus for the rubber phase ought to be almost the same, and the TPE bulk hardness can only be increased by increasing the PP content.

This is basically the strategy followed by the producers to offer products with a wide range of hardness values. However, grades with a high PP content showed a mechanical response far from the expected elastomeric behavior. It is clearly reflected in their stress–strain curves, similar to that of thermoplastic materials, and in the high values of residual stresses found after application of moderate strain levels, from which a typical elastomeric material is expected to recover nicely. Differently from conventional crosslinked elastomers, where hardness and ability to recover from highly deformed states can be simultaneously controlled by changing the degree of crosslinking, it seems to be difficult to increase TPE hardness without sacrificing elastomeric properties.

Finally, important amounts of oil were found in all the formulations. The oil content correlates well with the EPDM concentration, which indicates that most of the oil is preferentially located in this phase. The oil affects thermal and mechanical properties of the TPE. It shifts the melting peak corresponding to PP crystals, and the  $T_g$  of the EPDM- and PP-rich phases toward lower temperatures. While the TPEs elastic modulus is decreased, the ability of the TPE to shrink back from highly deformed states is almost not affected. Thus, the main motivation for including the oil in the studied formulations is the improvement of TPE processability, particularly critical in grades with higher proportions of crosslinked EPDM.

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#### References

- [1] Yang Y, Chiba T, Saito H, Inoue T. Physical characterization of a polyolefinic thermoplastic elastomer. *Polymer* 1998;39(15):3365–72.
- [2] Inoue T. Selective crosslinking in polymer blends. II. Its effect on impact strength and other mechanical properties of polypropylene/unsaturated elastomer blends. *J Appl Polym Sci* 1994;54(6):723–33.
- [3] Inoue T, Suzuki T. Selective crosslinking reaction in polymer blends. III. The effects of the crosslinking of dispersed EPDM particles on the impact behavior of PP/EPDM blends. *J Appl Polym Sci* 1995;56(9):1113–25.
- [4] Inoue T, Suzuki T. Selective crosslinking reaction in polymer blends. IV. The effects on the impact behavior of PP/EPDM blends. *J Appl Polym Sci* 1996;59(9):1443–50.
- [5] Petrovic ZS, Budinski-Simendic J, Divjakovic V, Skrbic Z. Effect of addition of polyethylene on properties of polypropylene/ethylene–propylene rubber blends. *J Appl Polym Sci* 1996;59(2):301–10.
- [6] Abdou-Sabet S, Puydak RC, Rader CP. Dynamically vulcanized thermoplastic elastomers. *Rubber Chem Technol* 1996;69:476–93.
- [7] Lohse DJ, Datta S, Kresge EN. Graft copolymer compatibilizers for blends of polypropylene and ethylene–propylene copolymers. *Macromolecules* 1991;24(2):561–6.
- [8] Wenig W, Asresahegn M. The influence of rubber–matrix interfaces on the crystallization kinetics of isotactic polypropylene blended with ethylene–propylene–diene terpolymer (EPDM). *Polym Eng Sci* 1993;33(14):877–87.
- [9] Bielinski DM, Slusarski L, Wlochowicz A, Slusarczyk C, Douillard A. Some aspects of isotactic polypropylene crystallization in an ethylene–propylene–diene rubber matrix. *Polym Int* 1997;44(2):161–73.
- [10] D’Orazio L, Mancarella C, Martuscelli E, Sticotti G, Ghisellini R. Thermoplastic elastomers from iPP/EPR blends: crystallization and phase structure development. *J Appl Polym Sci* 1994;53(4):387–404.
- [11] Chen CY, Yunus W, Chiu HW, Kyu T. Phase separation behaviour in blends of isotactic polypropylene and ethylene–propylene–diene terpolymer. *Polymer* 1997;38(17):4433–38.
- [12] Mukhopadhyay P, Das CK. Effect of E/P ratio on the rheology and morphology of crosslinkable polyethylene and EPDM blends. *J Appl Polym Sci* 1990;39(1):49–62.
- [13] Nomura T, Nishio T, Iwanami K, Yokomizo K, Kitano K, Toki S. Characterization of microstructure and fracture behavior of polypropylene/elastomer blends containing small crystal in elastomeric phase. *J Appl Polym Sci* 1995;55(9):1307–15.
- [14] Ellul MD. Plasticization of polyolefin elastomers, semi-crystalline plastics and blends crosslinked in situ during melt mixing. *Rubber Chem Technol* 1998;71:244–76.
- [15] Yang J, Kaliaguine S, Roy C. Improved quantitative determination of elastomers in tire rubber by kinetic simulation of DTG curves. *Rubber Chem Technol* 1992;66:213.
- [16] Sircar AK. Analysis of elastomer vulcanizate composition by TG-DTG techniques. *Rubber Chem Technol* 1991;65:503.

- [17] Pizzoli M, Righetti MC, Vitali M, Ferrari P. Presence of low-melting crystallinity in ethylene–propylene elastomers. *Polymer* 1998;39(6):1445–51.
- [18] Kawabata S, Kitawaki S, Arisawa H, Yamashita Y, Guo X. Deformation mechanism and microstructure of thermoplastic elastomer estimated on the basis of its mechanical behavior under finite deformation. *J Appl Polym Sci, Appl Polym Symp* 1992;50:245–59.
- [19] Kikuchi Y, Fukui T, Okada T, Inoue T. Elastic–plastic analysis of the deformation mechanism of PP-EPDM thermoplastic elastomer. Origin of rubber elasticity. *Polym Eng Sci* 1991;31(14):1029–32.
- [20] Kikuchi Y, Fukui T, Okada T, Inoue T. Origin of rubber elasticity in thermoplastic elastomers consisting of cross-linked rubber particles and ductile matrix. *J Appl Polym Sci, Appl Polym Symp* 1992;50:261–71.