

CONTINUOUS RUBBER RECYCLING USING A CO-ROTATING TWIN-SCREW EXTRUDER.

Introduction

MARIS company has been producing co-rotating twin-screw extruders since 1962, when it was established, and has always been engaged in the research of new applications for its products. Starting from PVC compounding, it entered, in addition to the traditional fields of masterbatches and compounds, the food sector and the adhesives one. In 1998 it started to overlook vulcanizable rubber compounding.

Maris experience in rubber compounding allowed their technicians to realize an innovative idea: to devulcanize the rubber using a co-rotating twin-screw extruder, with a completely thermo-mechanical process, which does not require the use of chemical agents.

This project that Maris Technological Center is carrying on and that could be of great interest for rubber industry, concerns the development of a process for rubber devulcanization. A completely thermo-mechanical process, based on the co-rotating twin-screw extruder, that allows to start from vulcanized rubber (e.g. scraps or post consume, traditionally considered as waste), and to obtain a recycled material with properties similar to crude rubber. This new raw material can be used in blend (20-50%) with virgin rubber, or even pure, for less demanding applications. The production costs reduction offered by such a solution is evident: less virgin rubber is needed and waste disposal costs are avoided.

Rubber devulcanization

The research performed at Maris technological centre has allowed to exploit the mechanical features of the twin-screw extruder also to devulcanize a cured rubber compound.

The main feature that distinguishes an elastomer from a plastomer is the cross-linking between polymer chains, which is fundamental to confer its peculiar mechanical properties (elasticity), but which also causes the loss of the material's thermoplastic behaviour, making it very difficult to recycle.

This is the reason why the traditional destination of rubber coming from scraps, post consumer products or waste products, is thermo-valorisation, grinding – to obtain powders used as fillers – or thermal cracking, to obtain hydrocarbons and carbon black. But devulcanization would allow rubber to be used as a raw material again.

Devulcanize cured rubber means to selectively break the cross-links between polymer chains, preserving, as much as possible, chemical bonds along the chains. This operation restores the thermoplastic behaviour of the material, allowing it to be processed again.

Several advantages are introduced by such a process, which allows to re-use the regenerated rubber, in blend with virgin one. From the economic point of view the benefit is double: it allows to reduce the amount of virgin rubber in the product, and to eliminate disposal costs for waste products and scraps. Of course several benefits can also be seen from the environmental point of view.

Different ways are reported in literature to attain this task, using physical methods, such as ultrasounds, microwaves, or thermo-mechanical stress, or chemical methods, making use of devulcanization agents in surge tanks. Plants for rubber devulcanization by means of chemical processes, the first to be developed, disappeared from Europe after the 70s', because economic reasons reduced the interest for rubber recycling, but also because they were time consuming and hazardous for the environment. Nowadays the interest for rubber devulcanization is increasing again, due to its renewed economic appeal, and to the increased sensibility to environmental aspects. But actually just few industrial applications exist.

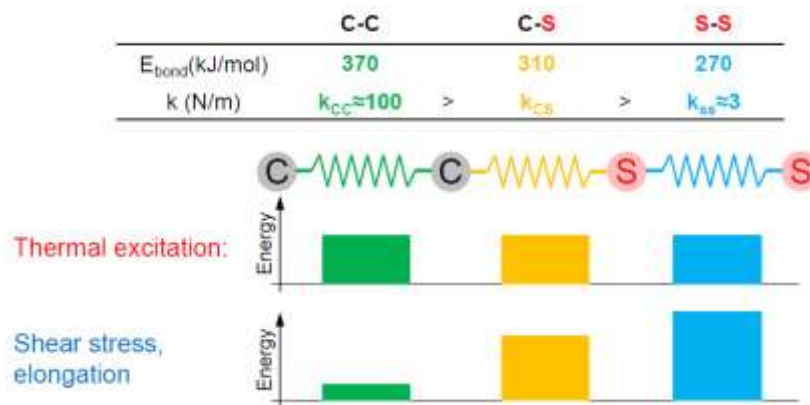


Figure 1: repartition of energy between polymer chain (C-C) bonds and crosslink (S-S) bonds, during a thermal and a mechanical excitation.

The idea of using the co-rotating twin-screw extruder for rubber devulcanization is based on the following principle: unlike thermal excitation, which causes a non-selective break of cross-links and polymer chain bonds, during a mechanical strain the energy is mainly concentrated in crosslink bonds (typically sulfur-sulfur bonds), because of their lower elastic constant (see fig. 1). Crosslink bonds are therefore in principle selectively broken; but in order to obtain their stretching, a high strain is required, because at lower strains the elasticity is dominated by entropic effects. The effectiveness of the co-rotating twin screw extruder to achieve this task is due to its ability to exert high shear and elongational strain on the material. Of course also the synergic action of thermal energy has an important role in this transformation.

The cleanliness of this process has to be underlined: being a purely thermo-mechanical process, all the problems related to the management of chemical agents are avoided.

During its development, the devulcanization of different kinds of rubber have been tested in Maris Technological Center: NR, IR, EPDM, NBR, SBR. Rubber from technical items has been processed, or from tyres as well. Of course scraps from tyres are much more difficult to process, due to their complex structure, made by different kinds of rubber, metallic and textile parts.

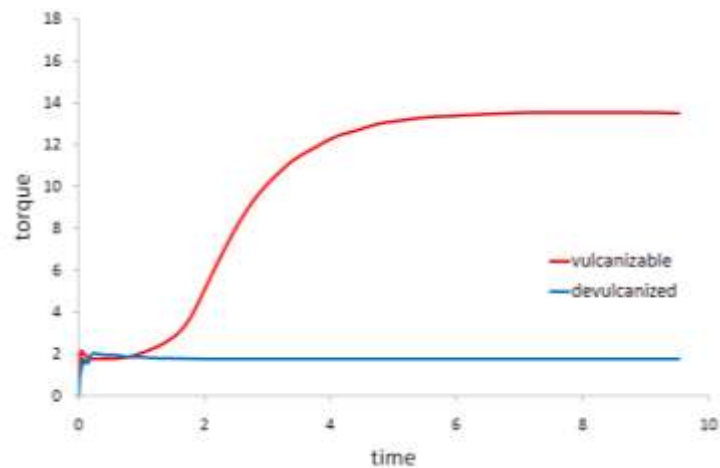


Figure 2: Rheometer test performed on a processed (devulcanized) SBR sample (blue line) and a raw (vulcanizable) sample (red line)

An immediate simple way to characterize the reclaimed rubber obtained with this process is a rheometric measure. In figure 2 the rheometric test performed on a reclaimed (devulcanized) SBR sample is compared to the one performed on a raw (vulcanizable) SBR compound. The latter shows the typical increase of torque with time due to the crosslinking reaction, while the low torque value of the former sample suggests a significant degree of devulcanization. Moreover its flatness demonstrates that curing agents are either not present in the compound, or at least not in an active form.

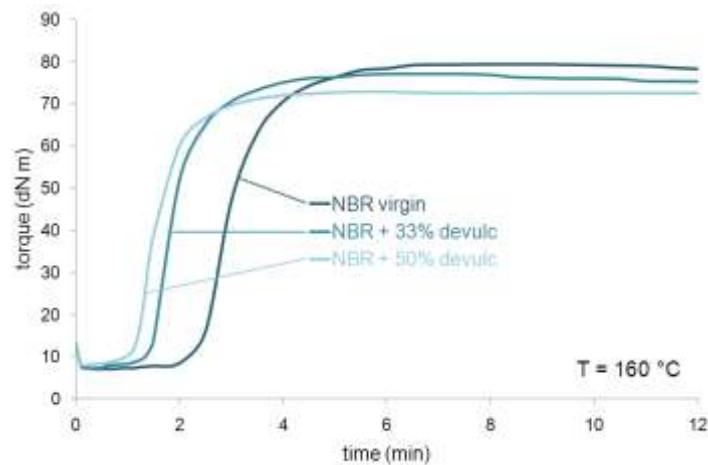


Figure 3: Rheometer test performed (at 160°C) on virgin NBR, and on two blends with reclaimed rubber (33% and 50%).

Once blended with virgin rubber, and with the proper amount of curing agents, a vulcanizable material is obtained again. This is demonstrated in figure 3, where the rheometric curves of virgin NBR and of two blends with, respectively, 33% and 50% of devulcanized NBR are shown. The small differences in the rheometric behaviour can be easily compensated by small variations of the formulation.

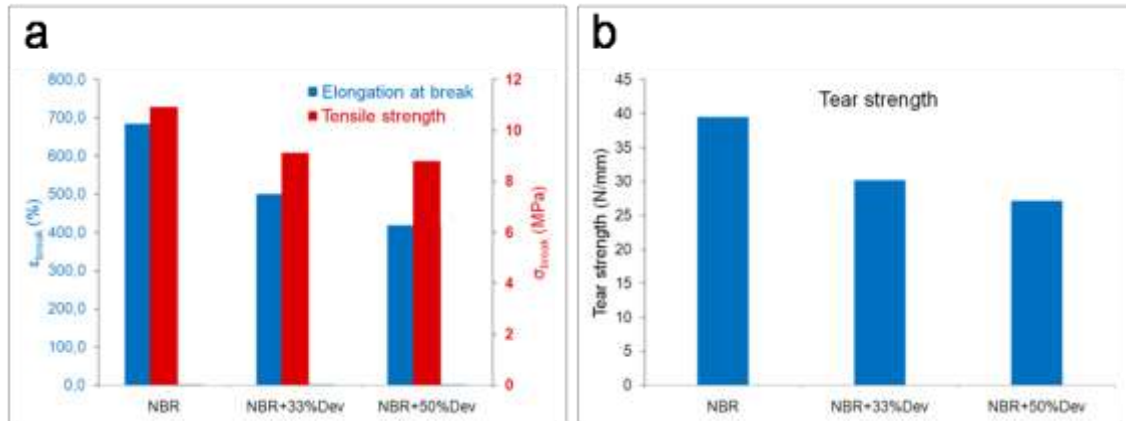


Figure 4: elongation at break, tensile strength (a), and tear strength (b) of specimens made of NBR, virgin and blended with reclaimed (33% and 50%)

Some basic mechanical properties of the obtained blends, once cured, are shown in figure 4, where virgin and blended NBR are compared in terms of elongation at break, tensile strength, and tear strength. A small loss in mechanical properties is compatible with a partial degradation of the reclaimed fraction. This phenomenon is limited, anyway it should be taken into consideration that curing agents and additives have not been completely reintegrated for these samples.

The same procedure has been performed for other kinds of rubber: we show here for comparison some results obtained with polyisoprene. The devulcanization of this rubber allows to obtain a very good reclaimed material, which blended with virgin one (using a 40/60 ratio in the example discussed) gives a compound which, once re-cured, manifests the excellent mechanical properties shown in table 1. From the comparison with the original virgin material, one can notice that the loss of properties is nearly negligible.

Table 1: Mechanical properties of polyisoprene samples: the virgin rubber is compared to a blend prepared with virgin (60%) and devulcanized (40%) material.

	Polyisoprene	
	Virgin	Blend (60/40)
Modulus at 100% (M Pa)	0.95	0.90
Modulus at 300% (M Pa)	1.78	1.75
Tensile strength (M Pa)	22.91	19.94
Elongation at break (%)	891	835
IRHD Hardness	67.1	62.2
Elastic Yield	48.4	42.8

The behaviour of the devulcanized material, in terms of rheological properties during re-vulcanization and mechanical performance of the final blend, is of course important, but we became aware of the necessity to go beyond, and to perform a deeper investigation on the effects of our thermo-mechanical reclaiming process on the chemical structure of the rubber. We asked ourselves, in particular, what are the chemical modifications induced by the process: which chemical bonds are broken, and whether new bonds are formed, for example by oxidation. In order to investigate these issues, different techniques have been used, such as the extraction with solvent, and the ¹³C-NMR. These analysis have been performed by a rubber specialized laboratory.

If we consider poly-isoprene (synthetic or natural), the ¹³C-NMR technique can be used to monitor the stress undergone by the polymeric chains during a process. The chemical structure of polyisoprene repeating unit is shown in figure 5, where the two possible (*cis*, *trans*) stereoisomeric configurations of the double carbon-carbon bond can be seen.

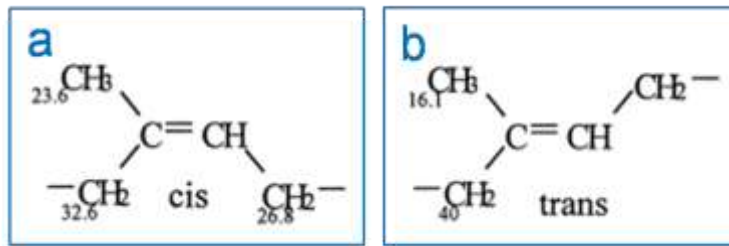


Figure 5: The two possible stereoisomeric configurations of the double C=C bond in the poly-isoprene chain. The *cis* form is the most frequent, both in synthetic and natural polyisoprene

The *cis* isomer is the most frequent, both in natural rubber and in synthetic polyisoprene, which is produced with stereo-selective catalysts. When the polymer chain undergoes a stress, of thermal, mechanical, or chemical nature, a *cis-trans* conversion of the configuration of some of its double bonds can happen. Therefore the variation of the percentage of *trans* form after a process is an index of the stress undergone by the polymer.

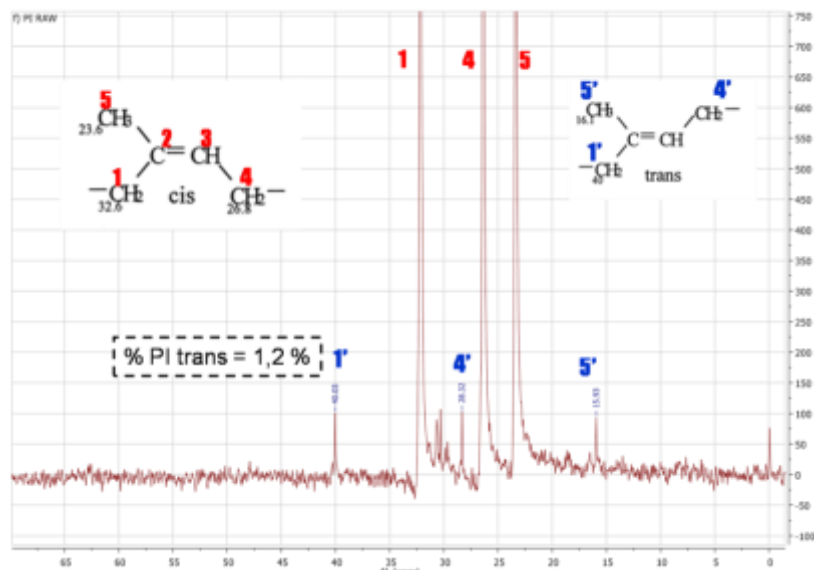


Figure 6: ^{13}C -NMR signals of the allylic carbon atoms of polyisoprene repeating unit, in *cis* configuration (intense signals: 1,4 and 5, red), and *trans* configuration (weaker signals: 1', 4' and 5', blue).

This percentage can be computed from the intensity of the respective ^{13}C -NMR signals of the two configurations, shown in figure 6.

In a sample of raw synthetic polyisoprene the measured percentage of *trans* configuration was 1.2% (see table 2). This parameter increases to 1.9% after compounding, and to 2.5% after vulcanization.

Our thermo-mechanical devulcanization process causes a further increase to 5% (see table 2): of course the process has exerted a certain stress, with consequent degradation, upon the polymer, but if we compare this result to the one obtained with a thermo-chemical treatment, during which the *trans* percentage increases from 3% to 19% or even 41% (see table 3), we realize that this side-effect is not so intense.

Table 2: Percentages of repeating units in *trans* configuration of raw (synthetic) polyisoprene, and of samples of the same material after the different stages of the process: compounding, vulcanization and de-vulcanization. This data are compared to the ones relative to a thermo-chemical reclaiming process reported in literature.

Maris Thermo – Mechanical Process	% isop. trans
PI raw	1.2
PI compound (not vulcanized)	1.9
PI compound (vulcanized)	2.5
PI de-vulcanized by MARIS	5.0
Thermo – Chemical process (*1)	
NR compound (vulcanized)	3
NR devulcanized with Diphenyldisulphide (2.4 wt%)	19
NR devulcanized with Diphenyldisulphide (10 wt%)	41

*1: Rif.: "Mechanism involved in the recycling of NR and EPDM"; M.a.L. Verbrugen, L. Van Der Does, J.W.M. Noordermeer - RC&T Vol. 72, 731-740.

The ¹³C-NMR technique has been used also to monitor the oxydation undergone by the polymer. Figure 7 shows the chemical shift interval of NMR spectrum where the signals of ketone, aldehyde, or acid groups, typical products of oxydation on an organic molecule, should appear. The absence of signals in this region suggest the absence, or very low level, of oxydation.

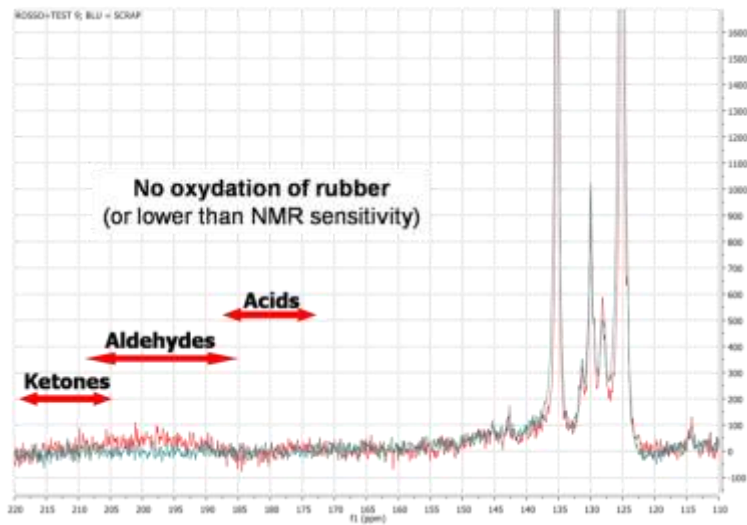


Figure 7: Portion of ^{13}C -NMR spectrum where signals of ketones, aldehydes and acids typically appear. The absence of signals can exclude the occurrence of a significant oxydation during the devulcanization process.

The extraction with solvent (chloroform) technique has been used to estimate the residual crosslinking in polyisoprene after devulcanization. The presence of a swollen part at equilibrium suggests the occurrence of a residual crosslinking, which can be estimated, through Flory-Rhener model, measuring the polymer volume fraction in this swollen part. In this way it has been possible to estimate a yield of 70-80% for the devulcanization process.

Measuring the amount of sol fraction it has been also possible, with the help of the Horikx model, to detect a certain degree of degradation of the polymer chain, also confirmed by a decrease of Mooney viscosity. This is an unavoidable side-effect, but of limited intensity.

Conclusions

The process, developed in these last years, has been tested on different kind of rubber, for different applications, with very interesting and promising results, confirmed by the characterization of the material obtained.

The obtained material can be re-used as a second raw material. Having characteristics similar to the virgin rubber, it can be used as a blend but it can also be used for applications with a lower value compared to that of the first one. In this way the waste expenses are considerably reduced and it also decreases the cost of raw materials required.