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Article

Evaluation of EPDM scrap/ natural fiber vulcanization by solvent swelling analysis

Evaluación de la vulcanización de scrap de EPDM/fibras naturales mediante análisis de hinchamiento por solventes

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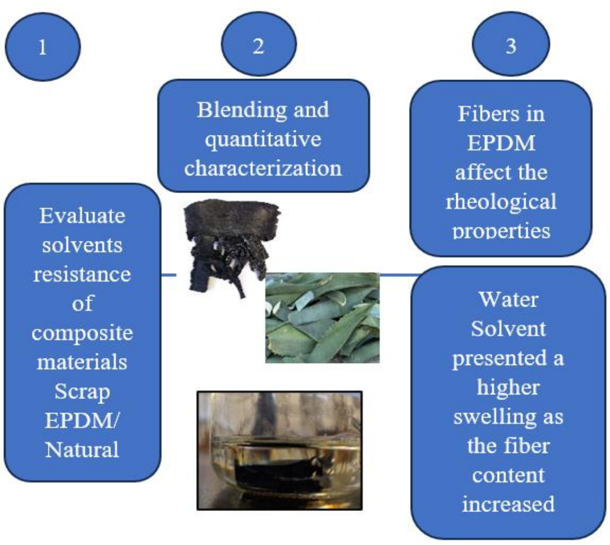
Abstract

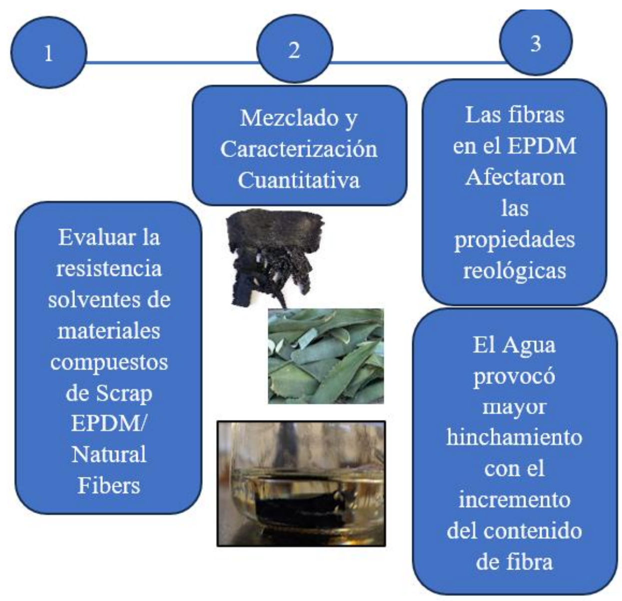
In the rubber industry there is an opportunity to reuse unvulcanized rubber scrap generated during the formulation process, as well as to find alternatives for its use. For this reason, in this work the characterization of EPDM/natural fiber scrap with different proportions is studied through rheological and swelling studies according to the Flory Rehner Equation. The solvents used were distilled water, cyclohexane and toluene at different exposure times. The results found allow us to conclude that the fiber content in EPDM rubber does not affect the scorch time, the maximum vulcanization time. In the case of swelling analysis, the observed changes had a maximum increase of approximately 3% when the fiber content in the composite material increased when they were exposed to water and toluene, this was attributed to the characteristics of the EPDM studied in this work.



EPDM, Flory Rehner, Natural fibers

Resumen

En la industria del caucho existe el área de oportunidad para el reaprovechamiento de scrap de caucho no vulcanizado que se genera durante el proceso de formulado, así como el encontrar alternativas para su uso. Es por ello, que en este trabajo se estudia la caracterización de scrap de EPDM/fibras naturales con diferentes proporciones mediante estudios reológicos y de hinchamiento de acuerdo con la Ecuación de Flory Rehner. Los solventes utilizados fueron agua destilada, ciclohexano y tolueno a diferentes tiempos de exposición. Los resultados encontrados, permiten concluir que el contenido de fibra en el caucho EPDM no afecta en el scorch time, en el tiempo máximo de vulcanizado y que en el caso del estudio hinchamiento los cambios observados tuvieron un incremento máximo del 3% aproximadamente al incrementarse el contenido de fibra en el material compuesto cuando fueron expuestos al agua y al Tolueno, esto se atribuyó a las características del EPDM estudiado en este trabajo.



EPDM, Flory Rehner, fibras naturales

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Introduction

Elastomers are unique materials, which makes them highly attractive materials for industrial and technical applications. The properties they possess are ideal for use in coatings, footwear, tyres, gaskets or insulation. In order for them to have these properties, crosslinks, covalent bonds between the vulcanising agent and the atoms of the polymer chain through the vulcanisation reaction, are necessary. The monitoring of the vulcanisation performance can be done by rheological analysis where three main stages are monitored: burn-in time, 90% vulcanisation time (**Ts90**) and overcuring. The latter is observed in the results if the material is further heated.

EPDM is the fastest growing elastomer in production among synthetic rubbers as it has exceptional resistance to oxygen and ozone. It has low moisture adsorption, excellent weather and chemical resistance, good compressive deformation and very good fatigue resistance. The main use of EPDM is in automotive industry applications, such as door seals, window seals, body seals, cooling system circuit hoses and others.

On the other hand, lignocellulosic fibres or fibres of plant origin include fibres from stems, leaves, fruits, wood and cereals. At the end of their useful life, there is a potential source of economic raw material of non-wood origin. As is well known, the source of Tequila is the Agave Tequilana Weber or Azul process in which only the useful part of the agave is the pineapple. Therefore, during the Jima, the leaves are cut, source of fibres that are normally burnt or left to accumulate. Its characterisation and the study of its addition in polymeric materials or for obtaining biofuels have been reported in other works. The aim of this work is to study the effect of the incorporation of natural fibres into EPDM on vulcanisation and its effect on solvent resistance.

Methodology

The materials used for the elaboration of the composites were: Scrap of non-vulcanised EPDM APD70 for applications in the automotive sector and fibres from Blue Agave stalks previously ground and sieved, donated by local producers in the state of Guanajuato, Mexico.

The solvents used for the swelling study were Meyer Cyclohexane, Karal Toluene and Ecopura distilled water, reagent grade.

The fibre concentrations studied were 10, 15 and 20 phr defined on the basis of 100 parts of rubber, in this case EPDM.

For the preparation of the compound, a BRABENDER mixing chamber equipped with a Banbury rotor, operated at a speed of 60 rpm and a temperature of 90°C was used. The mixing process was carried out for 7 minutes.

For the manufacture of the compression vulcanised sheets, a mould with a thickness of 3 mm, a temperature of 180°C and a pressure of 22,000 lbf was used.

The rheological study was carried out on a PROTECH cone and plate rheometer. For the study, 5 g of each unvulcanised sample was used, programming a time of 5 minutes for the test to be carried out.

In the case of the solvent resistance study, the equations used in this study are presented below.
The calculation of the degree of swelling was carried out using the following formula:

(1)

m_s and mr represent the weight of the swollen and initial rubber sample.

The measurement of the volume fraction of polymer in the swollen sample () was carried out using three times 24, 48 and 72 h. using ASTM D6814-02 as a reference.

(2)

Where m_s and mr are the weight of the swollen and initial rubber sample, ρ_s and ρ_r are the densities of the solvent and rubber, respectively.
The crosslink density of the vulcanised samples was determined by the Flory-Rehner Equation:

$$\upsilon_x = -\frac{[\ln(1-\upsilon_r)+\upsilon_r+\chi\upsilon_r^2]}{\left[V_1(\upsilon_r^{\frac{1}{3}}-\upsilon_r)/2\right]} \qquad (3)$$

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Where V1 is the molar volume of the solvent, y χ el polymer-solvent interaction parameter or Flory-Huggins solubility parameter.

In Table 1, the theoretical data used for the calculations of the crosslink density and the EPDM Swell Degree are presented. The theoretical data for the solvent Toluene are also given, as well as the rubber/solvent interaction parameter used.

Box 1

Table 1

Theoretical data used for calculations of crosslink density and Swelling Degree of EPDM and composite materials

Data	EPDM	Tolueno
Density (g/cm^3)	0.86	0.87
Molar volume (cm^3/mol)	-	106.13
Flory Huggins rubber/solvent interaction parameter (χ)	-	0.496

Source: Own elaboration

Results

Table 2 shows the results obtained from the study of the rheological properties of EPDM and composites. The tests were carried out at 180°C to ensure the vulcanisation of the rubber.

Box 2

Table 2

Curing properties of EPDM and composites at 180°C.

Fibre (phr)	M_L (dN.m)	M_H (dN.m)	ΔM (dN.m)	Ts_2 (min)	Ts_{90} (min)
0	5.02	16.51	11.49	0.53	1.81
10	5.33	10.79	5.46	0.44	1.78
15	5.67	10.6	4.93	0.5	1.81
20	4.47	8.65	4.18	0.54	1.77

Source: Own elaboration

For the analysis of these results it is important to mention the meaning of each rheological parameter:

M_H: Maximum torque (dNm), maximum applied force.

M_L: Minimum torque (dNm), minimum applied force.

Ts_2: Scorch time (min), Time that elapses before vulcanisation begins at an elevated temperature. It can also be called induction or burn-in time.

Ts_{90}: Optimal vulcanisation time in minutes. It is the time to reach 90% vulcanisation at the indicated temperature.

From **Table 2**, it can be seen that one of the most important parameters during the study of vulcanisation is the value of **Ts_{90}**. According to the data, by incorporating Agave Fibres in EPDM, the value of the optimum vulcanisation time remains practically without a significant variation. Something very similar in the case of **Ts_2**, **which** indicates that the presence of the fibres is not affecting the speed of the reaction, since in other works, for example with sawdust, the reaction speed increased. The authors mention that the hydrophilic properties of the sawdust influenced this behaviour. In the case of **M_L**, a similar behaviour can be observed, which indicates that the initial viscosity is not affected by the presence of agave fibres, which is unexpected since it has been reported that the addition of fibres promotes an increase in viscosity. The opposite is true for **M_H**, where there is a decrease of approximately 50% with respect to the control EPDM. It is important to mention that the EPDM and the composites studied were not dried during the rheological tests. However, despite being studied in this way, it did not seem to influence the acceleration of vulcanisation significantly.

Box 3

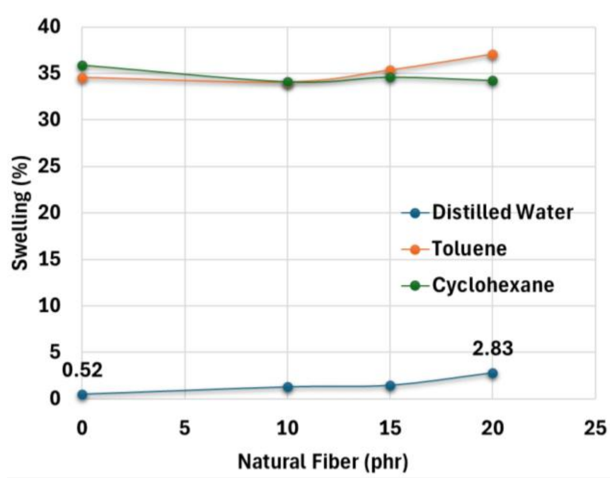

Figure 1

Swelling Degree (%) Vs Natural Fibre Content (phr) as a function of solvent type after 72 hours of treatment.

Source: Own elaboration

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Figure 1 shows the change in Swelling Degree (%) Vs Natural Fibre Content (phr) for EPDM and composite materials after 72 hours (considered the equilibrium swelling time of the materials) of exposure to 3 different solvents: Distilled water, Toluene and Cyclohexane. According to the results, it can be observed in general that the solvents to which the materials are more sensitive are the non-polar ones, reaching values of up to 35% swelling, in contrast to the polar solvent in which swelling reached about 3%. These significant differences between the solvents are attributed to the characteristics of EPDM.

In the case of distilled water, the increase is favoured by increasing the phr content of agave fibre in the composite. However, in the case of the solvents Toluene and Cyclohexane, an increase of 3% and a minimal change in the percentage respectively are observed.

Box 4

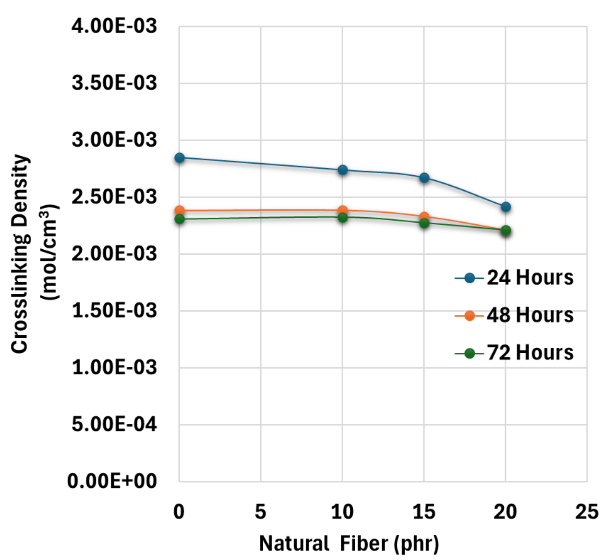

Figure 2
Crosslink density (mol/cm3) Vs Natural Fibre Content (phr) as a function of treatment time studied with Toluene.

Source: Own elaboration

In **Figure 2**, it can be seen that as the exposure time to the solvent toluene increases, there is a decrease in the crosslink density in all the materials analysed, being more important after 24 h, in contrast to the results at 72 h, where a stabilisation of the density is already observed, regardless of the fibre content in the composite.

Analysing these last results, it can be appreciated that the crosslinking density between EPDM and the composites was insignificant, which can be correlated with the rheological results, since no values with important differences were obtained in T_{s2} and T_{s90} , which corroborates that the agave fibres with the characteristics investigated in this work do not affect the kinetics of vulcanisation, a fundamental factor in the performance of EPDM rubber.

Conclusions

The incorporation of fibres in EPDM does not affect the rheological properties of the composite material. Composites exposed to water showed a higher degree of swelling as the fibre content increased. The solvents toluene and cyclohexane showed 3% and no significant differences in the degree of swelling of the materials with respect to EPDM, respectively. The crosslinking density calculated according to the Flory-Rehner equation showed that at least 72 hours were required to reach an equilibrium value.

The presence of agave fibres in the EPDM did not affect the vulcanisation kinetics, however, further material characterisation is needed. Future work will analyse the effect of reactive compatibilising agents during vulcanisation in the EPDM/natural fibres composite material on its rheological properties.

Declarations

Conflict of interest

The authors declare no conflict of interest. They have no known competing financial interests or personal relationships that could have appeared to influence the article reported in this article.

Author contribution

The contributions of each researcher to the points developed in this research were defined based on:

Kantun-Uicab, María Cristina: Contributed to the project idea, research method and technique and the writing of the article.

Estrada-Monje, Anayansi: Contributed the type of research, the approach, and the method.

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Rodríguez-Sánchez, Isis: Contributed to the research method, technique as well as writing the article.

Availability of data and materials

EPDM was donated by a company that is not mentioned due to formulation rights. Blue Agave leaves were donated by local producers in Guanajuato, Mexico. The characterisation of the materials was carried out in the laboratories of CIATEC, León and in the laboratories of UPJR.

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Abbreviations

EPDM	Ethylene-propylene-diene Monomer

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