Supervision of Ethylene Propylene Diene M-Class (EPDM) Rubber Vulcanization and Recovery Processes Using Attenuated Total Reflection Fourier Transform Infrared (ATR FT-IR) Spectroscopy and Multivariate Analysis

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Abstract
Ethylene propylene diene monomer (EPDM) rubber is widely used in a diverse type of applications, such as the automotive, industrial and construction sectors among others. Due to its appealing features, the consumption of vulcanized EPDM rubber is growing significantly. However, environmental issues are forcing the application of devulcanization processes to facilitate recovery, which has led rubber manufacturers to implement strict quality controls. Consequently, it is important to develop methods for supervising the vulcanizing and recovery processes of such products. This paper deals with the supervision process of EPDM compounds by means of Fourier transform mid-infrared (FT-IR) spectroscopy and suitable multivariate statistical methods. An expedited and nondestructive classification approach was applied to a sufficient number of EPDM samples with different applied processes, that is, with and without application of vulcanizing agents, vulcanized samples, and microwave treated samples. First the FT-IR spectra of the samples is acquired and next it is processed by applying suitable feature extraction methods, i.e., principal component analysis and canonical variate analysis to obtain the latent variables to be used for classifying test EPDM samples. Finally, the $k$ nearest neighbor algorithm was used in the classification stage. Experimental results prove the accuracy of the proposed method and the potential of FT-IR spectroscopy in this area, since the classification accuracy can be as high as 100%.

Keywords
Infrared spectroscopy, multivariate methods, ethylene propylene diene M-class rubber, EPDM, vulcanization, recovery, microwave treatment

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Introduction
Ethylene propylene diene M-class (EPDM) is a copolymer of ethylene and propylene with an average molecular weight of between 30 000 and 150 000 depending on the ethylene–propylene–diene proportion and polymerization variables, where the M-class indicates a type of rubber containing a saturated chain of polymethylene, according to the ASTM D-1418 and ISO-1629 standards. Therefore, EPDM rubber is a synthetic thermosetting material used in a wide variety of applications such as in the automotive sector (radiator hoses, wire harnesses, window and door seals, etc.), heat, ventilation and air conditioning applications (pressure tubing, seals grommets, and gaskets, among others), industrial applications (electrical insulations, water hoses, tubing, belts, vibrators, etc.) or in the construction sector (roofing systems, profiles, cable insulation, etc.). The worldwide EPDM market is growing significantly, particularly in the Asia-Pacific region, which is currently the main consumer of EPDM. However, raw virgin polymers offer poor mechanical properties, so in that condition they have very few technological applications, if any. Therefore it is necessary to apply a chemical vulcanization treatment process, which, by...
modifying the inner structure of the polymer, allows their mechanical properties to be improved due to the development of bridges or crosslinks among individual polymer chains, thus increasing the resistance to deformation. Hence, the vulcanization process modifies the raw material by increasing its elasticity and decreasing its initial plasticity.

Different chemical products added to the elastomer during the vulcanization process can be divided into reagents and inert products. Curatives are reagents added during the compounding process to produce the crosslinking of the long-chain polymer. The most commonly applied vulcanizing agents are sulfur jointly with accelerators and ZnO. A less frequently applied vulcanizing system consists of using peroxide crosslinking agents in combination with co-agents, which increase the yield of crosslinks.

Environmental concerns, such as soil contamination, waste accumulation, or air pollution, related to an increase in the worldwide consumption of polymers is encouraging both industry and research institutions to develop new recycling and waste recovery methods. In addition, the disposal of EPDM production waste adds extra costs to rubber manufacturers; therefore, replacement of virgin material by recovered EPDM with suitable properties can contribute to reducing production costs. Due to its special crosslinked-on-heating structure, EPDM is unable to soften with an increase of temperature. Thus, compared to thermoplastics, thermosets are difficult to recover or reprocess since the three-dimensional crosslinked structure must be broken. To this end, there are two main alternatives, i.e., to break the main chain’s carbon–carbon chemical bonds or to break the sulfur crosslinks when cured with sulfur, although the latter alternative, known as devulcanization, is usually preferred since the polymer backbone remains undamaged. The devulcanization recovery process aims at reversing the polymer attributes obtained due to the vulcanization process. This can be done by applying different methods, including chemical, mechanical, thermal, biological, ultrasound, or microwave treatments to break the bonds, while preserving the carbon–carbon chemical bonds in the main chain.

Due to the high demand and diversity of elastomeric materials, it is highly desirable to develop a fast control tool that can be applied to both the production and recovery processes. Different analytical techniques are currently being applied to control the vulcanization and devulcanization processes. However, analytical techniques often require individualized result interpretation, are often time-consuming, and entail the consumption of chemicals and reagents, thus increasing costs because laboratory-grade facilities and specialized technicians are required.

In contrast, chemometric multivariate analysis methods can be successfully applied to process control from spectral acquisitions in a nondestructive, fast, and even real-time manner. Multivariate methods have been widely applied to determine the composition of polymer blends, since they allow a more exhaustive interpretation of the infrared spectral data which allows determining and weighting the relative proportions of the components in an elastomeric blend.

Infrared (IR) spectroscopy, and specifically Fourier transform mid-infrared (FT-IR) spectroscopy, has been applied to determine the content of vulcanizing antioxidants and accelerators in vulcanized rubber. Fourier transform mid-infrared spectroscopy has been applied to analyze structural changes in vulcanized natural rubber after applying a mechanico-chemical devulcanization process. Tzoganakis and Zhang was proposed that substantial changes in the chemical structure of devulcanized rubber crumb occurred because of the formation of new double bonds and the rupture of carbon–carbon and carbon–sulfur chemical bonds, which are reflected in the FT-IR spectrum of such samples. Therefore, FT-IR spectroscopy can be effectively applied to control such processes.

However, the presence of different components, such as vulcanizing agents and especially variable amounts of carbon black, interferes with the FT-IR spectra. It is a recognized fact that carbon black absorbs infrared radiation, so it has a significant influence on the FT-IR spectrum, thus masking the information and hindering its subsequent interpretation. For this reason, Hirayama and Saron deal with spectral data of samples which are free of carbon black. To this end, previous extraction processes to separate the components in the sample, including the carbon black must be applied. This previous treatment is time-consuming, taking approximately 24 h, and requires the application of chemicals and reagents as well as laboratory-grade facilities and a skilled technician.

This work is focused on the development of a fast and effective method for the direct non-invasive identification and classification of differently processed EPDM samples from the spectral information contained in the FT-IR spectra, without any previous analytical treatment. To this end, a large number of EPDM samples after applying different treatments, i.e., with and without application of vulcanizing agents, vulcanized, and microwave treated EPDM samples, were analyzed by means of FT-IR spectroscopy. It is worth noting that this method does not require any reagent and chemical addition or sample pretreatment; thus its application is fast and simple. However, FT-IR spectroscopy provides a large set of data, which requires to be processed by means of multivariate statistical methods. In this way, the analytically relevant information contained in this large amount of data is concentrated in a reduced number of latent variables, which allow removal of most of the perturbations and noise often present in the raw spectral signal. For this purpose, principal component analysis (PCA) and canonical variate analysis (CVA) featuring extraction algorithms were applied to determine the latent
variables to be used for classifying the input EPDM samples. Finally, the k nearest neighbor (KNN) classification algorithm was applied, which provides the same number of output values (in the range between 0 and 1) as classes dealt with, and assigns an incoming EPDM sample to the class with the highest output.

The main contribution of this paper is found in the supervision of the vulcanization and recovery processes of EPDM compounds from the chemometric analysis of the FT-IR spectra.

Materials and Methods

The Analyzed Samples

The samples analyzed in this work include EPDM, one of the most requested elastomers due to its attractive properties and wide range of applications. This copolymer is often blended with other components, including carbon black, peroxide as vulcanizing agent, oils, plasticizers, and other compounds with diverse functionality. The blending process is carried out by mixing all the components using an internal interpenetrating mixer to integrate all components of the formula, two mills or cylinders which disperse the materials and form the mixture, as well as a cooling tunnel to cool the rubber before packing, so it can be delivered to customers.

The presence of different components and especially variable amounts of carbon black notably interferes with the information provided by the FT-IR spectra, whose effect is aggravated by the single-reflection diamond crystal used by the spectrophotometer available to acquire the spectral data.

This work deals with a total of 195 EPDM rubber samples provided by SPC-JEVSA SLU (Castellbisbal, Spain), specialized in manufacturing custom rubber compounds. These samples are distributed into four classes as summarized in Table 1.

Class NVA is composed of raw samples in which EPDM polymer is the basic component. NVA samples also contain plasticizer additives and carbon black, which acts as a reinforcing element to provide the final vulcanizing abrasion resistance, resilience, and high strength. Samples in class VA also incorporate peroxide as vulcanizing agent. Samples in class V have been vulcanized by means of a press using a mold for plates of 2 mm thickness and cured during 8 min at 185 °C to allow the crosslinking among polymer chains. Finally, class M consists of EPDM samples which have been treated in a domestic 2450 MHz Thor TM-17.2B microwave oven. Vulcanized EPDM samples of approximately 1 g confined in a porcelain capsule were placed in the turntable glass plate for 2 min at a power of 700 W with a consequent weight loss of about 0.7%.

Figure 1 shows the attenuated total reflection Fourier transform infrared (ATR FT-IR) spectra of a sample of each one of the four analyzed classes, that is NVA, VA, V, and M. The transmittance axis has been extended in the 20–50% range to boost the amplitude of the characteristic bands of this type of polymers since, as explained, the presence of the carbon black interferes the FT-IR spectra.

Figure 1 shows the common characteristic bands for the four spectra. They correspond to the bands of saturated C–H bounds, that is C–H symmetric and asymmetric stretching vibration (2916 and 2849 cm\(^{-1}\), respectively), CH\(_2\) scissoring vibration (1453 cm\(^{-1}\)), CH\(_3\) bending vibration (1374 cm\(^{-1}\)), and -(CH\(_2\)–CH\(_2\))- backbone (719 cm\(^{-1}\)).\(^1\)\(^2\) Despite the great similarity among the four spectra, subtle spectral differences can be detected, so with subsequent mathematical data processing it is expected to perform a correct classification of the samples according to the different considered classes or processing types. Therefore, for this purpose the mathematical methods detailed in next sections will be applied to process the spectral data.

Figure 2 shows the aspect of the samples dealt with in this work.

FT-IR Spectral Data Acquisition

Spectra from the analyzed samples have been acquired by means of a Perkin Elmer Spectrum One FT-IR spectrometer. This spectrometer includes a LiTaO detector and a 45° ATR top-plate module with a clamping element to ensure a suitable contact between the solid polymeric sample and the single-reflection diamond crystal. The spectra of the raw polymeric samples spectra were acquired at room temperature (25 ± 1 °C) over the wavenumber range 4000–650 cm\(^{-1}\) with 1 cm\(^{-1}\) resolution. An ATR cuvette was used for this purpose and four scans were averaged to minimize random noise effects. In addition, three readings were taken in different areas of each polymeric sample to reduce possible inhomogeneity effects in the samples, which were also averaged. The ATR FT-IR spectra provide information about the analyzed samples and therefore they include the characteristic spectral bands of the constitutive polymers in the EPDM rubber samples. All ATR FT-IR spectra were processed via smoothing and baseline correction operations.

**Table 1.** EPDM rubber samples dealt with in this work.

| Class                                         | Number of samples |
|-----------------------------------------------|-------------------|
| Samples without vulcanizing agents (NVA)      | 48                |
| Samples with vulcanizing agents (VA)          | 49                |
| Vulcanized samples (V)                        | 49                |
| Microwave treated samples (M)                 | 49                |

EPDM: ethylene propylene diene monomer.
The spectra of 195 EPDM samples have been acquired in this study. These spectra are expressed in transmittance mode and further transformed by applying the first and second derivatives with respect to the wavenumber. It was done by applying the Savitzky–Golay algorithm using five left-sided and five right-sided points. The raw spectrum of each EPDM sample comprises 3351 data points, \( x \) being the wavenumber and \( y \) the transmittance. Therefore, three matrixes were obtained, that is, the raw spectra matrix and the first and second derivative matrixes, whose dimensions are \( 195 \times 3351 \), \( 195 \times 3341 \), and \( 195 \times 3331 \), respectively. Due to their large size, it is highly necessary to analyze such matrixes by applying suitable multivariate statistical methods.

It is extremely complex to obtain reliable information to perform control of the vulcanization and devulcanization processes directly from the raw spectral data due to the combination of the huge number of variables per sample, that is 3351, and the inherent complexity of the problem. Therefore, it is highly desirable to process such an amount of spectral data in an expeditious and fast manner by using suitable multivariate statistical methods, which are especially conceived to deal with this type of problems. All the applied multivariate methods have been programmed by the authors of this work using the Matlab (The Mathworks Inc.) package.

**Applied Multivariate Algorithms**

In classification problems the whole collection of samples is split into two sets, that is the calibration and prediction sets. This strategy allows evaluating the performance of the classification models by using a sample set different than that used to train the model. Whereas the calibration samples are used to calibrate or train the classification model, the samples in the prediction set are used to evaluate the accuracy of the classification model when identifying a set of samples different than that used to train the model.\(^{27}\)

The large number of wavenumbers or measured variables in each transmittance spectrum of the EPDM samples forces the use of suitable feature extraction algorithms, which concentrate the useful information contained in the
measured variables of the raw spectral data in a reduced set of latent variables.\textsuperscript{17,26,28} The goal of such algorithms is to remove most of the noise often included in the measured variables because it interferes with the useful information. Therefore, by applying combinations the measured variables (transmittances at different wavenumbers), feature extraction algorithms calculate the new or latent variables.

Feature Extraction Algorithms. Feature extraction algorithms can be broadly classified into unsupervised and supervised methods. Unlike unsupervised algorithms, supervised feature extraction methods require the intervention of a human expert to select the class labels of the calibration samples that assign each sample to a determined class. Therefore supervised algorithms are often preferred since they allow enhancing discrimination among different classes.\textsuperscript{27}

Principal Component Analysis. Principal component analysis (PCA) is amongst the most applied unsupervised feature extraction algorithms.\textsuperscript{28,30,31} However, PCA suffers from the inherent limitations of unsupervised algorithms. The orthogonal latent variables provided by the PCA, known as principal components (PCs), are obtained through linear combinations of the original variables (wavenumbers of the FT-IR spectrum). Each PC accounts for a portion of the total variance, so the PCA returns the latent variables sorted in descending variance order, that is, the first PC explains the highest variance whereas the last one accounts for the lowest variance. Principal component analysis returns as many PCs as original variables in the problem, although it is a good practice to only retain a reduced number of PCs, those explaining a sufficient percentage of the total variance.

Canonical Variate Analysis. Canonical variate analysis (CVA) is a multiclass supervised classification method specially conceived to stress the separation among classes.\textsuperscript{17} The non-orthogonal latent variables calculated by the CVA, known as canonical variates (CVs) maximize inter-class separation and minimize intra-class dispersion. Canonical variate analysis provides a number of CVs equal to the number of classes defined in the problem minus one. A major drawback of the CVA is that it requires dealing with problems in which the number of original or measured variables is lower than the number of samples. Fourier transform mid-infrared spectra provide more than 3000 wavenumbers, the original variables, and therefore the number of samples dealt with is clearly lower than the number of variables. In such cases it is often suggested a previous application of the PCA algorithm in order to reduce the number of variables dealt with to fulfill the requirements of the CVA algorithm.\textsuperscript{17,25,27,28}

Once the reduced set of latent variables is calculated, the classification algorithm can be applied. To this end the KNN algorithm is suggested in this paper because is amongst the simpler, accurate and widely accepted classifiers.\textsuperscript{27} It provides as many normalized outputs within the interval [0, 1] as classes defined in the problem. The output values indicate the membership degree of the test sample to each class, so the test sample is classified into the class whose output value is higher than 0.5. To calculate the normalized output membership degree values, the KNN algorithm is based on the weighted vote of the $k$ nearest neighbors of the calibration samples data set, whose class is known. The KNN algorithm assigns the test sample to the most voted class. To this end, scores $k$ and $k - 1$ are assigned to the nearest and second nearest neighbor’s classes, respectively, and so on until reaching a unity score. Once summed up and normalized all the scores of each class, the test sample is assigned to the most voted class.

Figure 3 summarizes the methodology applied in this paper.

Results and Discussion

This section summarizes the results obtained from the analysis of the ATR FT-IR spectral information after application of a preprocessing step, which includes spectra smoothing and baseline correction followed by a calculation of the first and second spectra derivatives with respect to the wavenumber, with or without mean centering or unit variance scaling. Results presented in this section are based on the 195 EPDM rubber samples whose treatment was known...
since they were prepared in the facilities of SPC-JEVSA SLU.

The samples were split into two sets, that is, the calibration set composed of approximately two-thirds of the samples, and the prediction set, composed of the remaining one-third.

The rubber industry cluster is facing a rising request of high quality rubber compounds due to the increasing demand of high quality products for a wide range of applications, including components for the chemical, automotive, aerospace, and energy industries. Manufacturers are pursuing to obtain optimized specific compounds for each application, so there is an imperious need to study and determine the optimal composition or the compounding sequence and temperature to obtain an appropriate dispersion of all constituents. Therefore, it is essential to dispose of non-destructive and fast quality control tools that can be effectively applied to the production and recovering processes.

This paper deals with a classification approach, based on the sequential application of PCA + CVA + KNN since it is well suited for applications related to process supervision aimed to detect whether a specific treatment has been effectively applied to the test sample. Therefore, this classification system allows both the manufacturer and customer determining in a fast, reliable and nondestructive manner the state of the polymer, thus avoiding a previous chemical treatment.

**Table 2.** EPDM rubber samples dealt with in the first study.

| Class                                 | Calibration set | Prediction set | Total samples |
|---------------------------------------|-----------------|----------------|---------------|
| Samples without vulcanizing agents (NVA) | 32              | 16             | 48            |
| Samples with vulcanizing agents (VA)   | 33              | 16             | 49            |
| Vulcanized samples (V)                | 33              | 16             | 49            |
| Total                                 | 98              | 48             | 146           |

**Table 3.** Dimensions of the spectral data matrices.

| Set             | No derivative | First derivative | Second derivative |
|-----------------|---------------|------------------|-------------------|
| Calibration set | 98 x 3351     | 98 x 3341        | 98 x 3331         |
| Prediction set  | 48 x 3351     | 48 x 3341        | 48 x 3331         |

These dimensions are also valid for the mean-centering and unit variance transformed matrices.

**Discrimination of Samples Without and With Vulcanizing Agents and Vulcanized Samples**

A first study aimed to discriminate samples with three different treatments was conducted. For this purpose a total set of 146 samples was analyzed, which are summarized in Table 2. The three classes dealt with are EPDM samples without vulcanizing agents (NVA), with vulcanizing agents

![Figure 4](image-url)
Figure 5. First derivative of the ATR FT-IR spectral data. Dispersion plot of the calibration and prediction sets of the three classes (NVA, VA, V) in the plane of the two CVs arising from the PCA (30 PCs) + CVA.

Figure 6. Second derivative of the ATR FT-IR spectral data. Dispersion plot of the calibration and prediction sets of the three classes (NVA, VA, V) in the plane of the two CVs arising from the PCA (30 PCs) + CVA.

Table 4. PCA (30 PCs) + CVA + KNN results summary.

| Spectra transformation | Prediction set | KNN success arte |
|------------------------|----------------|------------------|
|                        |                | $k = 3$          | $k = 4$          | $k = 5$          |
| No derivative          | 48             | 48/48 (100%)     | 48/48 (100%)     | 48/48 (100%)     |
| First derivative       | 48             | 48/48 (100%)     | 48/48 (100%)     | 48/48 (100%)     |
| Second derivative      | 48             | 45/48 (93.8%)    | 45/48 (93.8%)    | 46/48 (95.8%)    |

PCA: principal component analysis; CVA: canonical variate analysis; KNN: $k$ nearest neighbor.
(VA), and vulcanized samples (V). Whereas class NVA has a total of 48 samples, classes VA and V have 49 samples each. As explained, the samples in each class were split into the calibration and prediction sets. Therefore, two-thirds of the total body of samples was randomly assigned to the calibration set whereas the remaining one-third was assigned to the prediction set.

Next, the data matrices were transformed through the mean centering and unit variance scaling. The best results were attained with the mean centering operation, so all results presented in this paper are based on this transformation.

Table 3 summarizes the dimensions of the data matrices dealt with in this section.

A preliminary analysis revealed that with sole application of the PCA algorithm it is not possible to make an accurate discrimination of the three processing types. Therefore, as explained, it is required to apply of PCA + CVA in the feature extraction step because due to the large number of wavenumbers in the spectra, the direct application of the CVA algorithm is not possible. After applying the PCA, it is required to retain a reduced number of latent variables o PCs before applying the CVA algorithm. After selecting the appropriate number of PCs the CVA algorithm is applied, thus obtaining as many CVs as number of classes in the problem minus one, so two CVs are obtained in this case, which are the inputs of the KNN algorithm.

The results obtained from the mean-centered ATR FT-IR spectra by applying the PCA + CVA are displayed in Figures 4 to 6.

Results from Figures 4 to 6 clearly show that results obtained with raw spectral information without applying any derivative or with the first derivative are better than...
Figure 8. First derivative of the ATR FT-IR spectral data. Dispersion plot of the calibration and prediction sets of the four classes (NVA, VA, V, M) in the plane of the three CVs arising from the PCA (50 PCs) + CVA.

Figure 9. Second derivative of the ATR FT-IR spectral data. Dispersion plot of the calibration and prediction sets of the four classes (NVA, VA, V, M) in the plane of the three CVs arising from the PCA (50 PCs) + CVA.
when applying the second derivative. This is corroborated by the classification results provided by the KNN method, which are summarized in Table 4.

**Discrimination of samples without and with vulcanizing agents, vulcanized, and microwave treated samples**

A second study with four treatments, the three of the first study (NVA, VA, V) and microwave-treated samples (M) was also conducted, which was aimed at controlling the process of devulcanization for a possible later recovering. A total set of 195 samples was analyzed, which are summarized in Table 5. The steps followed to correctly classify unknown test samples are the same as in the former section.

Table 6 shows the dimensions of the data matrixes dealt with in this classification problem.

The results obtained by using the mean-centered ATR FT-IR spectral data by applying the PCA + CVA algorithms are presented in Figures 7 to 9.

Results from Figures 7 to 9 clearly show that the better separation among classes is obtained when dealing with spectral information without applying any derivative. This is supported by the classification results provided by the KNN method, which are summarized in Table 7.

**Conclusion**

In this paper, a nondestructive, effective, and fast method is proposed for the direct classification of differently processed EPDM by applying the PCA + CVA + KNN multivariate processing methods to the information provided by FT-IR spectra. To validate the accuracy of the proposed method, two studies were conducted. In the first study, the best results were obtained when dealing with spectral information without applying any derivative or with the first derivative, whereas in the second study the better separation among classes was obtained when dealing with spectral information without applying any derivative. In both classes, a 100% classification success rate was obtained despite the presence of carbon black in the composition of the samples. Therefore, these encouraging results show the potential of this methodology in the supervision and control of the vulcanization and devulcanization processes of EPDM compounds from the chemometric analysis of the FT-IR spectra. Therefore, the proposed classification system may be very useful for both the manufacturer and customer to determine in a fast and nondestructive manner the state of the polymer, thus avoiding a previous chemical treatment.

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**Conflict of Interest**

None declared.

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