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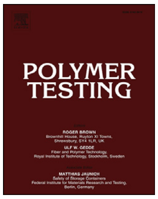

Analysis Method

Smart numerical method for calculation of simple general infrared parameter identifying binary rubber blends

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A B S T R A C T

In the present work, binary blends of carbon black-filled cured rubber, composed of natural rubber (NR) and styrene butadiene rubber (SBR) at three different blend ratios, were subjected to Fourier Transform Infrared (FT-IR) spectroscopic study in attenuated total reflection (ATR) mode. The objective was to use the infrared spectra obtained to calculate a simple general infrared blend parameter (P_{IR}), a characteristic of the NR-SBR blend. The calculation for determining P_{IR} required finding the exact infrared (IR) peak heights for NR and SBR, at 1375 and 699 cm^{-1}, respectively. To obtain the exact peak heights, each of the spectra originally obtained from the IR spectrophotometer was modified using a newly developed numerical algorithmic method of baseline creation on and subsequent subtraction from the original spectrum. A very good baseline fit was achieved using this method. As a result, the numerical calculation of P_{IR} for the NR-SBR blend was possible.

1. Introduction

The end of life tyre (ELT) is a non-reusable tyre in its original form, originating primarily from wear during its use. However, it can find outlet in smart reusing applications. To do this effectively, the blend ratio of rubbers with which the tyre is composed of, needs to be determined. This can be done by using the concept of material reverse engineering of rubber products [1,2], which uses specific tools and analytical techniques to identify the materials which were used to produce a particular vulcanized rubber compound from a combination of raw rubber and other chemicals.

Studies show that the most frequent means used for reverse engineering of rubber compounds are derivative thermogravimetric analysis (DTGA) [3–5] and IR. [6,7] It is known that simultaneous use of DTGA and Py (pyrolysis) FT-IR can quantitatively predict the binary blend composition of compounded and cured rubber product. [6,7] However, in the case of a ternary or higher order blend, where the maximum decomposition temperatures of any two components overlap in DTGA, advanced numerical data study is necessary to identify the constituent compounds [6].

Most of the commonly encountered rubber products are composites that not only contain a blend of various rubbers but also compounding ingredients such as reinforcing and non-reinforcing fillers, antioxidants, process oils, stabilisers, accelerators, curing process activators and, usually, sulphur as the curing agent [8,9].

Usually, rubber tyres used in automobile and aviation industries, contain high quantity of carbon black filler as a reinforcing compounding ingredient, incorporated into the rubber matrix. FT-IR studies of such carbon black containing rubber compounds are best performed in the ATR mode. [10] Usually, a high-refractive-index prism, such as germanium (Ge), is required to analyze black rubber with carbon black filler content. The depth of penetration (dp) for Ge is around 0.7 μm at 1000 cm^{-1}, compared to 2.0 for zinc selenide (ZnSe); this is due to the higher refractive index of the germanium. It's lower penetration depth makes Ge ideal for carbon black rubbers. [11,12] Even in the ATR mode, the absorbance spectra of carbon black containing rubbers and other samples containing carbon black show a baseline that slopes upwardswith decreasing wavenumber. This is because, when using the ATR technique, carbon black displays absorption over the entire region of wavenumber from 4000 to 400 cm^{-1}, with the effect becoming greater with deeper light penetration at the long wavelength (low wavenumber) end. [13] For such a sloping baseline, or for any other uncorrected baseline, the IR spectrum cannot be quantified.

Some earlier works related to IR baseline corrections can be found in the literature: Koch and Weber [14] devised baseline correction of spectra in FT-IR using the method of Bezier, developed to permit the drawing of curves in a manner that allows full control

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of the line curvatures by the user. Ruckstuhl et al. [15] devised a method that used techniques of robust local regression to estimate baselines in spectra that consisted of sharp features superimposed upon a continuous, slowly varying baseline. In another work, Phillips and Hamilton [16] created a new method for baseline estimation and correction in FT-IR absorption spectra in gaseous phase, based on a maximum entropy approach. However, these discoveries do not eliminate the possibility of finding yet another method to perform baseline correction. In a rare work, Lee et al. [6] first corrected the FT-IR baselines and then calibrated the binary blends of NR-SBR, NR-BR, and SBR-BR, using a number of different blend ratios for each of the blends. The aim was to use these calibrations to find unknown ratios of rubber blends. Absorbance ratios were plotted against the percentage content of SBR, BR, and SBR in binary blends of NR-SBR, NR-BR, and SBR-BR, respectively, by preparing various blend ratios of the two rubbers in each case. This yielded exponential curves that were further used to determine the amount of SBR, BR and SBR in unknown compounds; this was done by fitting generalized equations to the curves. The authors of the present manuscript judged the work to be an excellent initial attempt, but not without its shortcomings. Firstly, there was no mention of the nature of the corrected baseline meant to eliminate the matrix effect. Moreover, Lee et al. used an exponential smooth fitting for all curves that was much too generalized In fact, the authors of the present paper verified the equation of Lee et al. for an NR-SBR blend using self-prepared, known blends, and found large errors. Finally, it is quite unnecessary to follow such a generalized scheme when a mathematical route is available to calculate the IR blend parameter, which completely identifies a binary rubber blend.

Fernandez-Berridi et al. [7] implemented a method to quantify the results obtained from pyrolysis FT-IR on different blend ratios of NR and SBR by using the “Turbo Quant” software based on the method of partial least square. However, the drawback of this work lies in the difficulty of pyrolyzing unknown blends in a reproducible manner, which is very important for obtaining quantitative results using the calibrated plots. Finally, according to the authors, it was not possible to obtain satisfactory quantitative results for compounded and cured rubber blends containing heavily filled insoluble compounds through non-pyrolytic ATR FT-IR, which is why they had no option but to follow the lengthy pyrolysis path.

The literature survey thus revealed a considerable amount of room for a new method of calibration of heavily compounded carbon black filled binary rubber blends using the non-pyrolytic, easy, effective and very rapid ATR FT-IR approach if such a method can be found. This was the primary motivation of the present work.

In the present work, binary blends of NR and SBR at three different blend ratios and commonly encountered rubber additives, including 50 phr (parts per hundred rubber by weight) carbon black, were compounded, cured and then subjected to a series of FT-IR studies in ATR mode. The aim was to calculate the infrared blend parameter, P_{IR}, a characteristic of the NR-SBR blend, from the obtained IR spectra. In each of the spectra generated by the IR spectrophotometer, study focused on calculating the peak height ratio of NR at wavenumber 1375 cm^{-1} to SBR at 699 cm^{-1}. This naturally required finding the magnitudes of the peak heights, based on some theoretical background. The magnitudes were precisely read from a modified spectrum, which was generated by fitting each of the initially obtained spectra with a created baseline that was then subtracted from the spectrum in question. The dataset of intensity versus wavenumber obtained from the IR spectrophotometer was processed using a completely new algorithm to create and subtract the baseline. It was rigorously applied to find the correct characteristic peak heights of NR and SBR from where the peak height ratios were easily calculated. The calculated peak height ratios of three different blends of NR-SBR were used to determine P_{IR} for NR- SBR blend using the Beer-Lambert law [6]. In effect, this parameter may be confidently used for understanding of the exact composition of various unknown blends of the discussed rubbers.

2. Theoretical background

The theoretical background of the work is divided into two sections. *Section A* explains the new the new algorithm used to generate the modified spectrum, while *Section B* deals with the calculation of P_{IR} for the NR-SBR blend.

2.1. A. Description of the numerical algorithm

Instead of a smooth baseline fitting over the entire range of data, the algorithm focuses on finding a baseline separately for each peak. The peaks of interest in a spectrum may vary across different studies. This led the authors to device a new approach that would be useful to all researchers, regardless of the specifics of their study. It was assumed that at the base of each peak, which mathematically consists of two local minima, the baseline was almost a straight line. Therefore, an array of paired points was separately fitted at the base of all peaks and these points were then joined by straight lines to obtain the new baseline.

The algorithm accepts some initial parameters set by the user, based on which the spectrum is modified accordingly. These parameters are categorically as follows:

1. x1, x2 – range of wavenumber selected from the data
2. k1, k2 – cut-off values for differentiation on the initial dataset and on the regenerated dataset in the negative output respectively.
3 ky – cut-off value for negative area in output

It is necessary to mention here that during an intermediate stage of running the algorithm, a dataset is generated in the negative output. So a cut-off parameter was created for the negative output as well.

The cut-off parameters k1, k2 and ky, on the y-axis, are required to discard small and unwanted peaks. If the user is interested in small peaks, these parameters should be adjusted to lower values.

In the process of creating the modified spectrum, the dataset generated by the IR spectrophotometer is imported and processed using the new algorithm, which is implemented using Wolfram Mathematica. The algorithm takes the following main steps to obtain the final modified dataset in (x, y) (wavenumber, absorbance) from the initial source:

These steps can be more easily understood by following the flowcharts in Fig. 1 and 2, as well as by observing some of the major modifications brought about in the original spectrum to obtain the modified spectrum, as depicted in Fig. 3.

The flowchart of the algorithm is shown in Fig. 1. Also, since the determination of minima by substrings was the most important step in modifying the initial dataset obtained from the FT-IR instrument, the sub-routine for finding the minima is shown in Fig. 2. The other subroutines, such as selection of ranged data, creation of sign vector, conversion of sign vector to string, calculation of output, calculation of negative output, finding minima in negative output, calculation of equations of straight lines and finding basepoint, and subtraction of basepoints are not shown, so as to avoid unnecessary increasing text length.

Important stages in the stepwise modification of the original spectrum to the final one are shown in Fig. 3.