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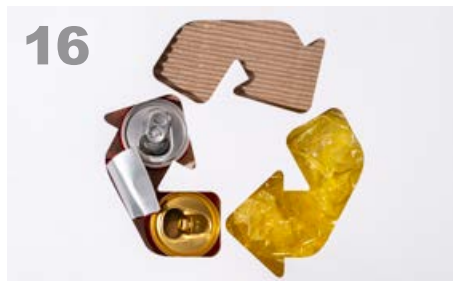


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Welcome



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EDITORIAL

Polymer products play a pivotal role in conserving biological resources, serving as replacements for traditional materials such as wood, metals, and ceramics—resources that can be both energy-intensive and environmentally damaging to obtain and process. Despite the clear advantages polymers offer, especially when accompanied by effective recycling and waste management, discussions on their detrimental impacts—chief among them plastic pollution—still dominate many headlines.

In this edition of ARA Information, several articles illustrate the duality of polymers' influence on society and the environment. For example, one study, Measurement of Antioxidants in Polymer Production Process Using High-Performance Liquid Chromatography (HPLC), delves into the importance of precise analytical methods in safeguarding polymer quality. Meanwhile, an examination of OCS Inspection Systems in the Cable Industry sheds light on cutting-edge control mechanisms that enhance product reliability. In another piece titled Raman Spectroscopy for Reaction Advancement Monitoring, the focus shifts to how advanced spectroscopic techniques can fine-tune manufacturing processes.

Attention to polymer performance also extends to rubber applications, as seen in Measuring Cut & Chip Wear of Rubbers by Instrumented Chip and Cut Analyzer (ICCA), highlighting the necessity for robust testing methods to extend product life. Additionally, the article Plastic Solid Waste Identification System Based on Near Infrared Spectroscopy in Combination with Support Vector Machine showcases how artificial intelligence and spectral analysis tools converge to address plastic sorting challenges.

Beyond production and quality, the know-how surrounding sustainable practices comes to the fore in Recycling Techniques of PET – Comminution of Plastic Beverage Bottles. This approach underlines the significance of PET recycling in reducing environmental burdens.

Finally, environmental protection is prominently featured in two notable contributions. The article Characterization of Biodegradable Polymers Using HPLC and GPC underscores how innovative analytical methods can pave the way for more eco-friendly materials, while Determination of Heavy Metals in Polyethylene and Polypropylene After Xylene Treatment by EDXRF demonstrates the meticulous investigations required to ensure that even traditional plastics pose minimal risks to both human health and the natural environment.

Together, these works underscore how rigorous research, advanced analytical techniques, and informed waste management strategies are crucial in tipping the balance toward a greener future for polymer science. When thoughtfully developed and responsibly handled, polymer products can genuinely support global sustainability goals. We invite our readers to consider these perspectives as we collectively seek to harmonize the undeniable benefits of polymer technology with its potential ecological challenges.



MEASUREMENT OF ANTIOXIDANTS in Polymer Production Process Using High-Performance Liquid Chromatography (HPLC)



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Summary: This article investigates the measurement of antioxidants utilized in the production, focusing on methodologies involving High-Performance Liquid Chromatography (HPLC) as per standard methods. Antioxidants are critical in enhancing the thermal stability and longevity of polyethylene products. This study outlines the types of antioxidants commonly used, the HPLC techniques employed for their quantification, and the implications of these measurements for quality control in polymer manufacturing. Results indicate that precise measurement of antioxidant levels is essential for optimizing polymer performance and ensuring product reliability. In addition, there are comparison between three type of well-known HPLC detectors results.

Introduction

Polymers are integral to modern life, utilized in applications ranging from packaging and automotive components to medical devices and electronics. However, their susceptibility to oxidative degradation poses significant challenges. Exposure to heat, light, and oxygen can lead to a decline in mechanical properties, discoloration, and overall performance deterioration.

To reduce oxidative degradation, various antioxidants are incorporated into polymer formulations. These compounds stabilize the polymer matrix by scavenging free radicals and preventing chain scission. The accurate measurement of these antioxidants is essential for ensuring that polymer products meet industry standards and perform reliably over their intended lifespan.



Types of Antioxidants Used in Polymer Production

Antioxidants can be classified into two main categories: primary and secondary antioxidants.

Primary Antioxidants

These compounds directly scavenge free radicals:

1. **Hindered Phenols:** Compounds such as Irganox 1010 (Pentaerythritol Tetrakis(-3,5)-3di-tert-butyl-4-hydroxyphenyl)propionate)) are widely used due to their effectiveness in stabilizing polymers against thermal oxidation.
2. **Aromatic Amines:** Compounds like N,N'-diphenyl-p-phenylenediamine (DPPD) provide protection against oxidative degradation.

Secondary Antioxidants

These compounds enhance the effectiveness of primary antioxidants:

1. **Phosphites:** Such as Irgafos 168 (Tris(-2,4di-tert-butylphenyl) phosphite) regenerate primary antioxidants and provide additional protection against oxidation.
2. **Thioester Compounds:** These include Dilauryl Thiodipropionate (DLTDP) which can trap free radicals.

As environmental concerns regarding plastic waste



grow, there is an increasing emphasis on sustainability within the polymer industry. The use of biodegradable additives or bio-based polymers could be explored as alternatives to traditional synthetic antioxidants.

Recycling Challenges

The presence of additives like antioxidants can complicate recycling processes. Understanding how these compounds behave during recycling will be essential for developing effective recycling strategies that minimize environmental impact while maintaining product quality.



Material and Methods

ISS Antioxidant analyzer based on HPLC system developed by ARA Scientific Company is used for determination of antioxidant in polymer including: quaternary high pressure gradient pump with vacuum degasser, high precision sample injection system with dilution technique, reverses phase C18 column and also GPC column, Column Oven, Reagent organizer, and different type of HPLC detector based on application, such as UV/Vis, MS, RI, ELSD, PDA and FLD.

1. Chromatographic Conditions:

Sample volume: 5 μ l
Eluent: THF
Flow rate: 0.3 mL/min
Column temp.: 40 $^{\circ}$ C
UV Detector WL: (210 nm)
MS Detector:
Ionization: APCI
Capillary temp.: 180 $^{\circ}$ C
Vaporizer temp.: 450 $^{\circ}$ C
Source voltage: 6000 V
Sheath gas flow: 80 L/min

2. Calibration Standards:

Calibration curves are prepared using known concentrations of standard antioxidants; run multiple dilutions (e.g., from 10 ppm to 1000 ppm) across several runs to establish linearity.

3. Sample Preparation:

Polymers are typically ground into a fine powder to increase surface area for extraction.

Solvent extraction methods using organic solvents like hexane or acetone are commonly employed.

An extraction procedure is involved stirring the ground polymer sample with a solvent mixture at room temperature for 24 hours.

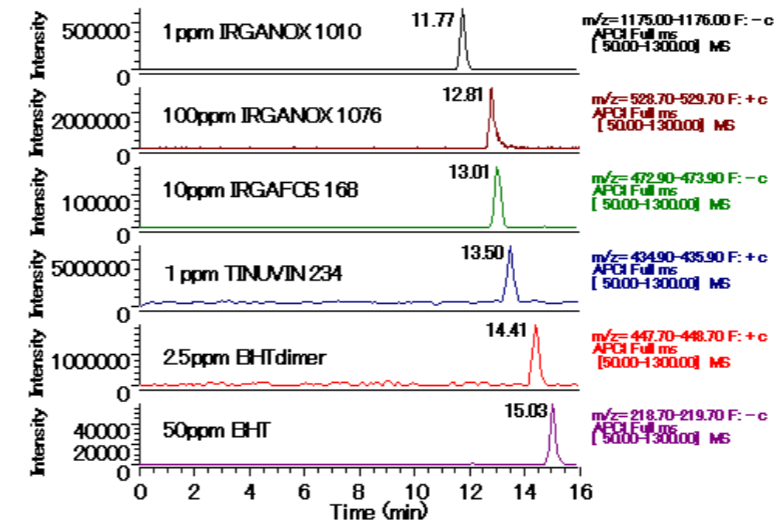


Fig 2. Various additives of polymer in polystyrene were analyzed simultaneously.

The measurement of antioxidants in polymer production using High-Performance Liquid Chromatography (HPLC) is essential not only for optimizing performance but also for ensuring product reliability across various applications. Accurate monitoring enhances product stability while significantly contributing to sustainability efforts aimed at reducing waste associated with degraded materials. As industries increasingly focus on performance alongside environmental impact considerations, ongoing research into effective utilization strategies will remain vital in this domain.



Result and discussion

The HPLC analysis revealed varying type of antioxidants in different polymeric samples. Also by selecting the best system and applying the suitable conditions, optimal results will be achieved with minimal peaks overlap and the simplest sample preparation.

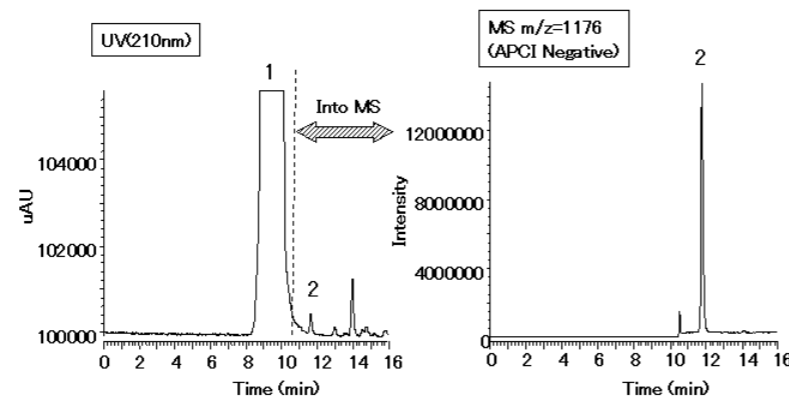


Fig 1. determination of Antioxidant (IRGANOX® 1010) in Polystyrene. Only a low molecule weight domain can be poured into a mass spectrometer (MS) by using GPC mode. Therefore, it is not necessary to pretreat.

Reference:

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MEASURING CUT & CHIP WEAR of Rubbers by Instrumented Chip and Cut Analyzer (ICCA)



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Abstract:

THE CREATION OF cut and chip (CC) resistant rubber products made of rubber blends necessitates a thorough comprehension and precise estimation of the CC behavior of every individual rubber component in the blend under a variety of severe circumstances. This study uses an Instrumented Chip and Cut Analyzer (ICCA, Coesfeld GmbH) to compare cut and chip (CC) examinations of rubber blends under severe circumstances. The results show that the CC effects

depend on temperature changes on the damaged specimen's surface and applied normal pressures (90 - 200 N). The study also reveals notable variations in the used rubbers, with temperature and CC damage reaching their maximum at critical values of the influencing normal load. The emergence of strain-induced crystallization (SIC) in the NR following cyclic impacts is briefly described. The findings provide a compelling explanation for why NR or NR-blends are empirically preferred in practice for reducing CC wear.

Introduction:

Cut and chip (CC) wear, shown in Fig. 1., is a common issue in rubber products like tires, conveyor belts, and rubber tracks, which detaches or breaks away from the treads during difficult road conditions. Tire wear is the primary source of microparticle (MP) emissions into the environment, as tires contain over %50 rubber polymers. Complex physical processes, such as the formation of crack-like flaws and their spread, contribute to rubber wear, causing rubber particles or even tiny pieces to break apart. Strong tensile strains are created due to frictional processes between the hard road surface and soft rubber, accelerating the spread of cracks. High-severity CC wear results in larger separated rubber fragments.



Fig 1. The Cut & Chip wear phenomena of a truck tire tread (A), a rubber track (B) and a conveyor belt (C).

A reliable laboratory forecast of CC behavior is crucial, as field product testing is expensive. A rubber ranking list of CC laboratory tests and the matching tire's CC field protocol show a strong correlation. Traditional lab CC test procedures with small revolving rubber wheels use basic instruments that cannot be applied sufficiently and reproducibly. The Instrumented Chip and Cut Analyzer (ICCA) was established as an innovative testing method and has been successfully incorporated into the rubber industry. The photograph of the ICCA is shown in Fig. 2.



Fig 2. A photograph of the ICCA (left) and a detailed view into the isolated chamber (right).

The composition of rubber blends and rubber polymers significantly affects the CC behavior across various normal pressures. The wear resistance trends for rubber made of butadiene rubber (BR), styrene-butadiene rubber (SBR), or natural rubber (NR) are BR > SBR > NR in low normal forces (70-130 N), corresponding to low tearing energy. However, when applied normal pressures are strong (130-150 N), the tearing energies show reverse wear resistance behaviors. The study focuses on blends of NR, SBR, and NR/SBR (50:50), which show great promise for CC wear



resistance. The materials were exposed to a wide range of applied normal stresses and temperature development during the CC wear process. NR is an essential part of highly dynamically loaded rubber goods that are subjected to CC conditions because it combines a high tensile strength, a remarkable resistance to crack formation, and a very big elastic strain. Conversely, non-crystallizable SBR is the most often used synthetic polymer and is frequently substituted for natural rubber in comparable applications. Regarding the specified application and their resistance to CC wear, both candidates show great promise.

Experimental:

This study examines the characteristics of non-oil extended cold emulsion copolymerized styrene-butadiene rubber (SBR) and natural rubber (NR). The compounds were prepared using a two-step mixing process, starting with the virgin rubber being masticated for one minute at rotor speed 35 rpm to create the masterbatch. Carbon black was added and mixed for five more minutes at rotor speed 45 rpm until the mixture reached a maximum temperature of 150 °C. The final batch was prepared by mixing the masterbatch for one minute at a rotor speed of 30 rpm and at an initial temperature of 70 °C. The entire curing system was added, and the mixture was mixed until it reached 105 °C. The last batch was ground at 60 °C in a double-roll mill.

The curing parameters were measured using a moving die rheometer MDR 3000 Basic at 160 °C in accordance with ASTM 6204. The instrumented chip and cut analyzer (ICCA, Coesfeld GmbH) was used for laboratory cyclic impact (CC) testing. The CC damage, determined by a numerical technique, was assessed from a multichannel data acquisition. The CC behaviors of the rubbers, Using the test settings specified in Table 1, were assessed at room temperature and the temperature development on the impacted sample surface was also measured simultaneously throughout the full CC analysis.

Table 1. Used rubber compound formulas

Samples	Composition in phr		CB	ZnO	Stearic acid	6ppd ^{a)}	sulfur	TBBS ^{b)}
	NR	SBR						
NR	100	–	50	2	1	1	2	1
SBR	–	100	50	2	1	1	2	1
NR/SBR	50	50	50	2	1	1	2	1

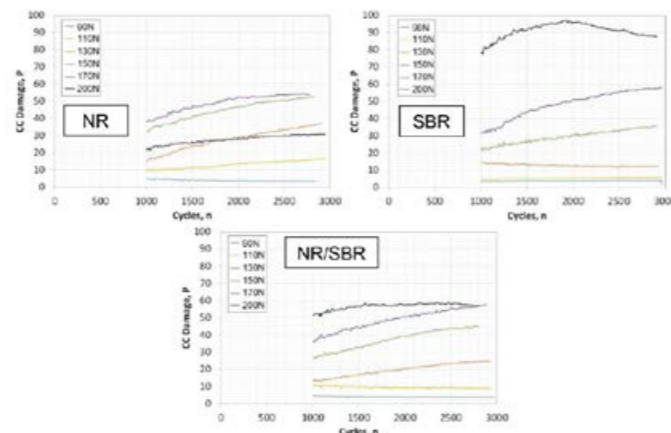
a) N-(1,3-dimethylbutyl)-N'-phenyl-P-phenylenediamine.

b) N-Tertiarybutyl-2-benzothiazole sulfenamide.

Results and Discussion:

The development of the CC damage parameters, P , dependant on the impacting cycles, n , are shown in Fig. 3. The number of locally cut and chipped places from the sample surface increases as cycle numbers rise, indicating an increasing trend in CC damage.

Fig 3. P versus n for all the analysed rubbers. The results are mean values for three test specimens each loading condition.



The CC damage parameters (P) are determined by the impacting cycles, with a maximum value observed for the greatest applied normal force ($F_N = 200$ N) for both NR/SBR blend and pure SBR rubber. This indicates an increasing trend in CC damage. The blend NR/SBR's CC behavior falls between pure NR and SBR, with strain-induced crystallization (SIC) of NR under high strain levels causing the reversion of CC damage in NR and the decrease in NR/SBR.

The temperature development of NR-based materials during a CC process is influenced by the beginning of SIC, with higher NR content promoting this SIC effect. At high typical impact forces, the temperature drops dramatically once the SIC process starts. Recent research on cyclic impact loadings of filled and unfilled natural rubbers using synchrotron wide-angle X-ray scattering (WAXS) and thermography has clarified the effects of cyclic impact loadings. Thermal equilibration to the surroundings is the result of spontaneous heating or cooling following loading/unloading impact.

There are three distinct areas of stress-strain behavior: below the beginning of SIC, the specimen is continually heated by energy dissipated during each loading cycle. A final equilibrium temperature is reached after a particular number of cycles, at which point the amount of heat lost to the surroundings matches the mechanical energy that has been dissipated.

Stronger heating of the sample occurs after beginning of SIC due to the heat of crystallization, and cooling occurs after subsequent unloading when the same amount of energy is released for the dissolution of crystallites. Rubber loses its entropy-elastic properties and becomes more energy-elastic without additional heating when the degree of crystallinity increases significantly due to large deformations. The CC behavior of the blend NR/SBR lies between the characteristics of pristine NR and SBR.

The CC behavior of the blend NR/SBR lies in between the characteristics of pristine NR and SBR is shown in Fig. 4.

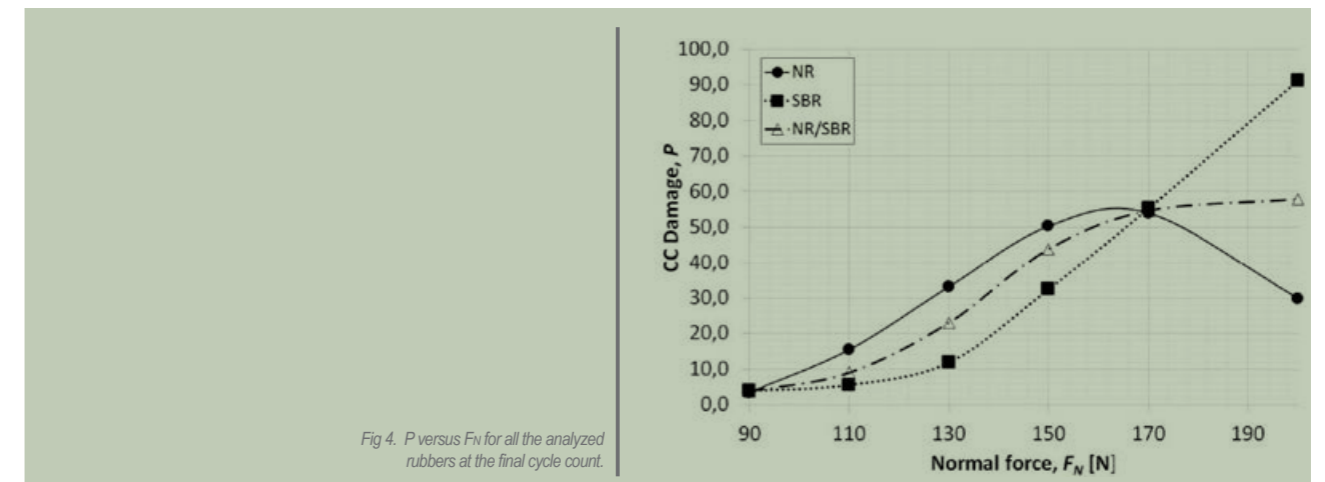


Fig 4. P versus F_N for all the analyzed rubbers at the final cycle count.

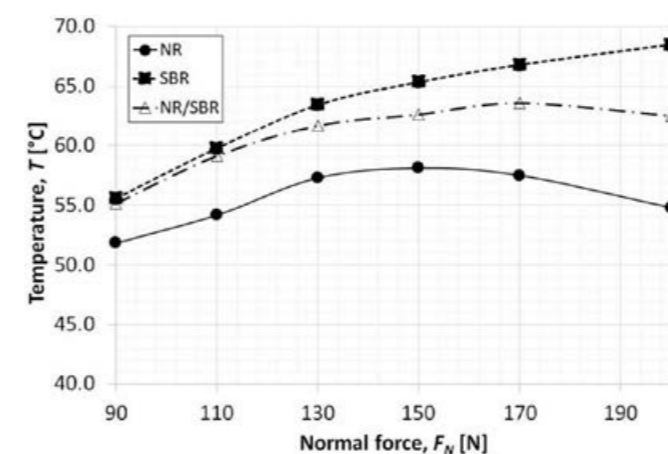


Fig. 5 shows the measurements of the temperature, T , development over the range of applied normal forces, F_N , as approximation from the last final 100 cycles, whereas the data represent the average values from 3 replicates.

Following the last cycle count of ICCA testing, the jagged surfaces of rubber specimens reveal variations in the degree and characteristics of damage for the polymers under investigation. SBR materials undergo a systematic 'cut and chip' fracture process, while NR-based rubber exhibits cracks with unique angles.

Fig 5. T versus F_N for all the analyzed rubbers at the final cycle count.

Conclusion:

This study examines the cut and chip (CC) behavior of rubber materials using NR, SBR, and a hybrid of NR/SBR (50/50) over a range of normal forces to simulate low to high severity conditions on rubber products in the field. The mechanical behavior is investigated, and the impact of strain-induced crystallization (SiC) under high-severity conditions is discussed. The research revealed that CC damage increases at low normal forces and persists for SBR until high normal force levels are reached. Nevertheless, NR exhibits a substantial resistance to CC damage in high-severity conditions, which are primarily encountered in the field in the context of typical rubber product applications such as tires, rubber tracks, or conveyor belts. The study also illustrated the Instrumented Chip and Cut Analyzer (ICCA)'s ability to forecast comparable CC conditions in a laboratory and in the field for rubber products while operating.

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2. www.coesfeld.com/en/products/detail/elastomers/abrasion-friction/icca-instrumented-chip-and-cut-analyser.html



OCS INSPECTION SYSTEMS IN THE CABLE INDUSTRY: The SSA® – A Unique Global Solution for Detecting Surface Defects & Surface smoothness on Semi-conductive Polymer Tapes



Markus Piepenbrik
Sales manager
OCS optical ControlSystem GmnH

IN THE MODERN CABLE INDUSTRY,

the quality of polymers plays a crucial role in ensuring the performance and reliability of finished products. A significant challenge lies in detecting surface defects, such as pips or agglomerates, which can arise during the extrusion process. These imperfections have a direct negative impact on the mechanical and electrical properties of the finished product. This is where the Surface Smoothness Analyzer (SSA®) from OCS proves invaluable – it is a comprehensive solution that uses innovative technologies that work seamlessly together to enhance production quality to the highest level..



The TCA® – The perfect choice for detecting contaminants in transparent polymer tapes

The OCS Tape Cleanliness Analyzer TCA® is an equal partner to the SSA®, designed for testing transparent polymer tapes. The tape line includes the OCS Measuring Extruder (ME) and the OCS Modular Film Analyzer with Calender (MFA Calender), tailored for the wire and cable industry. The Calender system compresses and cools polymer film evenly, preparing it for high-precision optical analysis.

The Tape Quality Analyzer (TQA100) further enhances the line with a high-resolution camera system that identifies gels, black spots, fibres, and other contaminants as small as 5 µm.

User-Friendliness and Efficiency

The SSA® and all other OCS Film Lines feature a user-friendly touch panel interface, enabling operators to easily monitor and adjust system parameters like tape tension, speed, and equipment settings. The software provides data trend visualization and alarms for quick responses to deviations, ensuring flawless process control.

Its modular design allows easy adaptation to diverse production needs, supporting optional add-ons like the OCS Volume-Based Resistance Measurement (VRM) for inline measurement of conductive polymer tape resistance or the X-Ray Tape Analyzer (XTA100) for detecting metallic contaminants as small as 20µm. Versatile data communication guarantees smooth integration into existing IT infrastructures.

Conclusion: Essentials Tool for Quality Assurance

The OCS Tape Lines represent a ground-breaking solution for the quality control of polymer tapes in the cable

industry. Combining high precision, flexibility, and user-friendliness, they deliver substantial value to companies striving for top-quality standards. Both systems allow for the early detection of defects in the surface structure or the tape itself, seamlessly integrating this data into the production process. This leads to a significant reduction in rejects and rework. In an industry where precision and efficiency are critical, the SSA® and TCA® provide the technology needed to optimize production processes while achieving the highest quality.

The high-precision Instrument for Pellet Inspection – The Pellet Scanner PS800C

Unlock the power of precision with the OCS Pellet Scanner (PS800C), designed to analyze both highly transparent and opaque pellets in free fall. Equipped with two advanced colour line scan cameras, it seamlessly inspects both the front and back of the pellet stream for impurities that cause colour deviations. The PS800C features a state-of-the-art multi-track flap system that effectively sorts out contaminated pellets, ensuring superior product quality. With real-time data transfer, the PS800C helps optimize your production process by eliminating impurities before they reach the final product.

When it comes to detecting metallic contamination in

pellets, the OCS X-Ray Pellet Scanner XP7 is the ultimate way to go.

It efficiently identifies metal defects in both highly transparent and opaque pellets, starting at just 50 µm. Thanks to its cutting-edge X-ray technology, the XP7 analyzes the pellet stream in real-time, detecting metallic particles in the polymer by evaluating differences in X-ray absorption.

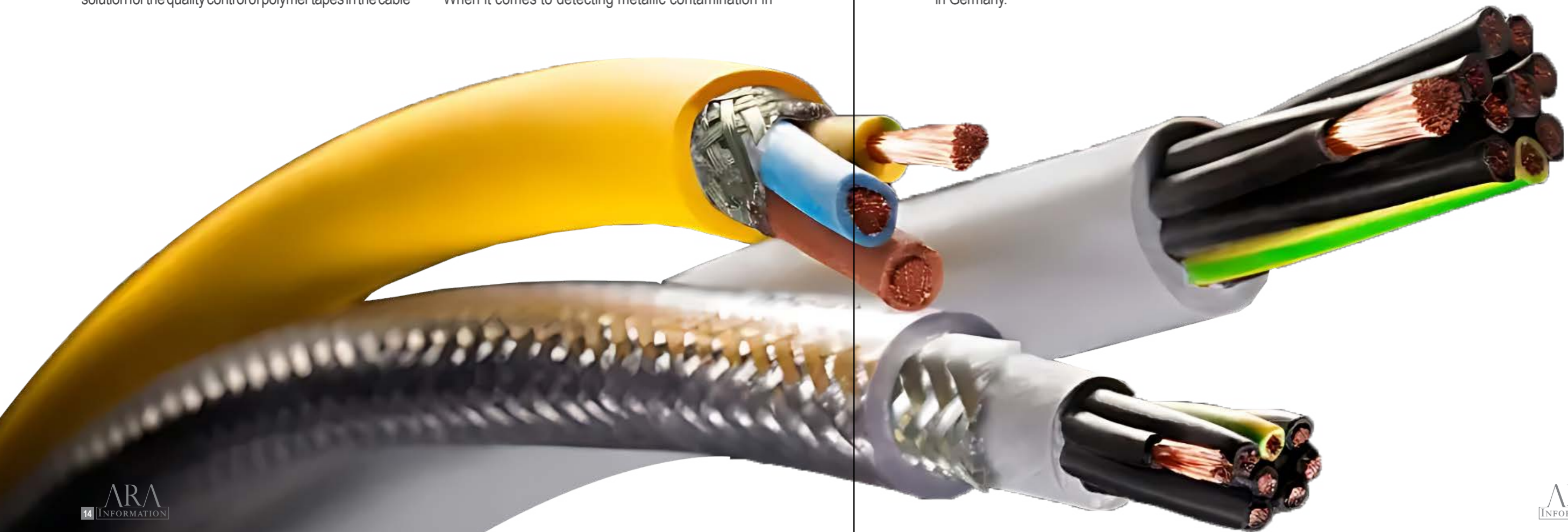
Both pellet scanners are engineered for high material throughputs of up to 1000 kg/h, making them ideal for seamless integration directly into production processes.

The Company

For over 33 years, OCS – Optical Control Systems GmbH has been known for its innovative, customer-specific solutions in quality control and assurance for the polymer and petrochemical industries

OCS has gained international recognition for its customised quality measurement systems and laboratory equipment for raw material production and the polymer processing industry

Our services encompass the development of forward-thinking quality measurement systems, system integration, and the planning, implementation, and commissioning of turnkey laboratories. As the global leader in optical quality inspection systems, we are present in over 35 countries, with more than 120 experts based at our headquarters in Witten. Made in Germany.



PLASTIC SOLID WASTE identification system based on near infrared spectroscopy in combination with support vector machine



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Abstract:

A System for identifying plastic solid waste (PSW) using near-infrared (NIR) reflectance spectroscopy combined with Support Vector Machine (SVM) was introduced. A device was developed to acquire NIR spectra of plastics in the detection platform. Through pre-processing techniques (normalization, first derivative, and smoothing), the repeatability of spectral absorption features was enhanced, aiding in identification. The proposed "principal component analysis (PCA) SVM" method effectively identifies polypropylene (PP), polystyrene (PS), polyethylene (PE), poly (methyl methacrylate) (PMMA), acrylonitrile butadiene styrene (ABS), and polyethylene terephthalate (PET) with an accuracy of 97.5%. This system not only allows clear identification of plastic types and rough discernment of sample shapes but also demonstrates significant potential in industrial recycling by achieving excellent identification results while significantly reducing costs.

Introduction

Plastic solid waste (PSW) grows every year in the world, and the most widely used disposal methods of waste plastic are landfilling, composting or burning, which are neither economical nor environmentally. Therefore, the recycling of PSW has been widely concerned. Contamination in the recycling of different types of plastics can cause serious processing problems, so the classification of plastic is particularly important. Up to now, waste plastic is identified mainly based on the melting temperature, the plastics density and their solubility in different solvents. However, these plastic identification methods are usually subjective, time-consuming and involve a lot of manual work. Therefore, it is necessary to find a method which can correctly real-time identify the plastics with high speed.

Near-Infrared (NIR) analysis technology has been widely applied in plastic detection and identification and it is one of the fastest growing analytical technologies in the world. This technology is accurate, non-polluting and non-destructive, and the measuring is rapid without surface pretreatments. It can be used as a fingerprinting technique to compare various samples, which greatly reduced the time consumed by manual identifying. On the other hand, previously proposed Support Vector Machine (SVM) as a new machine learning methods for regression and classification which could well prevented the occurrence of under-learning and over-learning. And it was suitable for datasets with small numbers of variables, so it always used with principal component analysis (PCA).

In this paper, a PSW identification method with NIR spectroscopy and SVM classification model was developed. Referring to the Computer Numerical Control (CNC), we developed a device that can drive near-infrared optical fiber probe to move in two directions on the detection platform. Furthermore, a software based on SVM to identify the type of PSW and display the identification results graphically was developed. Combining the device with the software, a system based on NIR analysis technology was presented to identify six large-scale applied plastics, i.e. PP, PS, PE, PMMA, ABS and PET. Comparing to the hyper-spectral technology, this method reduced the costs while ensuring high identification accuracy.



Materials and methods

Sample sets

186 samples were prepared as training set and validation set. The training set was used for the establishment of identification model. To ensure the accuracy of modeling data, PP, PS, PE, PMMA, ABS and PET particles were pressed into a uniform round plate (diameter = 100 mm, thickness = 3 mm). The validation set includes these six kinds of PSW as samples, which have different shapes such as film, boxes, and bottles. All samples are transparent or in a bright color.

NIR reflectance spectra

NIR spectra of samples are generated according to vibration of CH, OH and NH bonds in polymer materials. The basis for quantitative analysis of NIR spectra is Beer-Lambert law. The Beer-Lambert law states that absorbance (A) is directly proportional to the thickness of the sample.

$$A = \lg \frac{I_0}{I_1} = \lg \frac{1}{T} = Klc$$

I_0 is the intensity of light incident to the sample, I_1 is the intensity of passing light, K is the molar absorptivity of the absorber, l is the thickness of absorbing medium (optical path), and c is the concentration of absorbing species in the sample. 30 spectra of each kind of plastics were collected, and the average spectra of each plastic are shown in Fig. 1. It is shown that there are obvious differences in the NIR spectral characteristics of different kinds of plastics, this is helpful for the classification of different plastics.

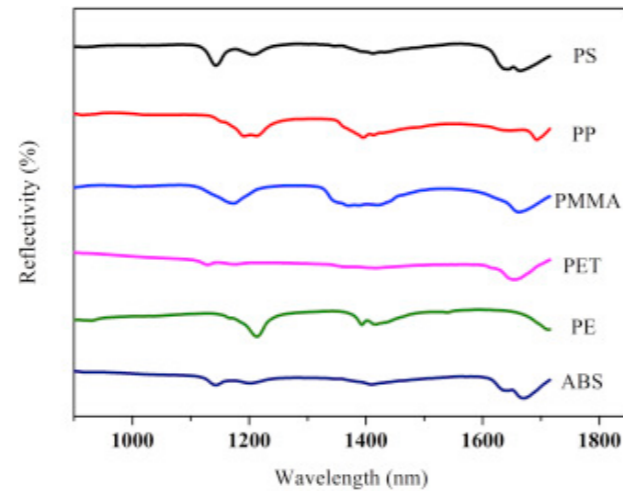


Fig 1. Average spectra of each kind of plastic.

PSW identification system

PSW identification system consists of the device and software. In particular, the most suitable NIR region is 1700–1000 nm, so the NIR optical fiber spectrometer (NIRQUEST 512, Ocean Optics Inc., USA) was chosen as acquisition unit to record NIR spectra. Spectra were collected in diffuse reflectance mode with an optical fiber probe. It took about 0.5 s to record each spectral data of the sample. Two stepper motors were applied in detection device to drive the probe moving in two-dimensions. And in the controlling system, we applied LabVIEW software and data acquisition (DAQ) card. The detection device is shown in Fig. 2, and the red line represents the trajectory of the probe. Considering the feed rate of the stepper motor and the size of spot, we divided the detection platform into 20 × 30

squares, the probe moves to the next square position during the spectral data acquisition interval. Spectral analysis software was programmed through Matlab and LabVIEW.

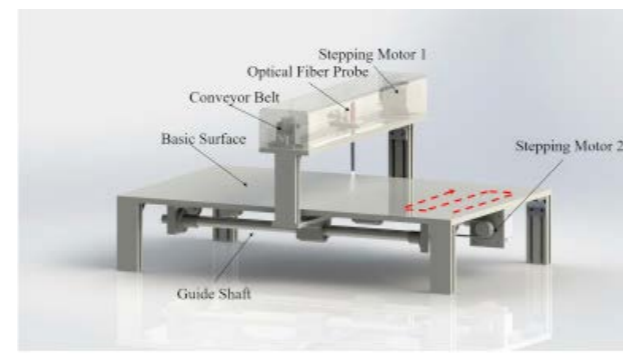


Fig 2. Detection device.

Data analysis

After proper data collection, pre-processing of spectral data was the most important step before chemometric bi-linear modeling which can improve signal-to-noise ratio and improve the multivariate regression, classification model. Here,

normalized, 1st derivative and smooth were applied firstly. After pre-processing, principal component analysis (PCA) was applied to reduce the dimensions of the spectral dataset and make data analysis faster. Success in classification depended on pattern recognition methods, here, SVM was applied to build the classification model. The Radial Basis Function (RBF) was applied as a kernel function to construct a SVM classification model. In order to improve the classification accuracy of the model, the performance of the model has been evaluated using 10-fold cross validation and grid search, two most important parameters of SVM model (cost, gamma) were optimized.



Result and discussion

Pre-processing

The distance between samples and probe can greatly influence the spectral characteristics due to the dispersion of light source. Fig. 3 shows the change of spectral characteristics of PE samples with increasing distance in wavelength of 1130–1260 nm.

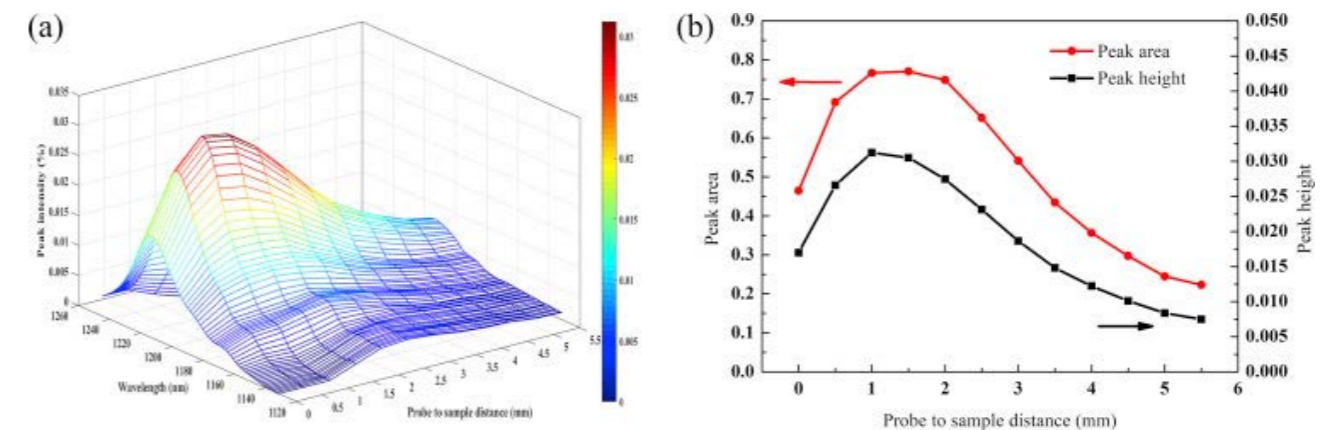


Fig 3. The change of spectral peak influenced by distance, (a) peak shape change of NIR spectra, (b) peak area and peak height change of NIR spectra.

Repeatability of specific absorption features would aid the classification of the different polymers, spectral pre-processing method can improve repeatability of spectral absorption features, Fig. 4 shows the change of spectral repeatability of PE samples after pre-processing (normalized, 1st derivative and smooth). It is show a big promotion of repeatability of spectra.

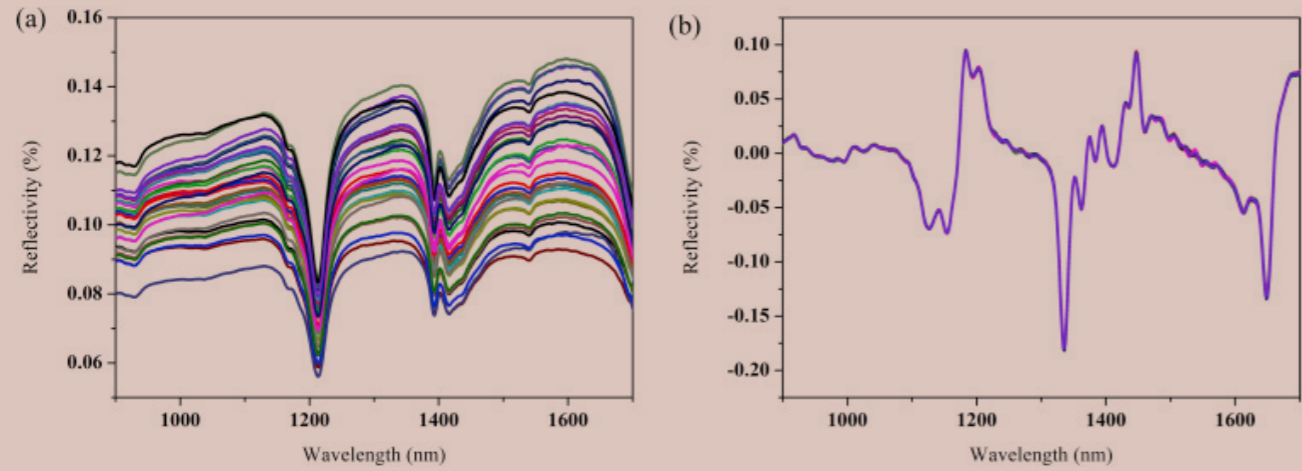


Fig 4. NIR spectra of PE samples: original spectra and spectra after pre-processing, (a) original NIR spectra of PE, (b) NIR spectra of PE after pre-processing.

Classification method

PCA was applied to reduce the dimensions of the spectral dataset, the cumulative contribution rates of the first 10 principal components were shown in Fig. 5. It can be seen that cumulative credibility of the first 7 principal components had reached 99.9%, in which PC1, PC2 and PC3 explained 52.57%, 25.74% and 9.96% of variance. Therefore, the first 7 principal components can fully represent the original spectral data. Applied first three principal components draw the three-dimensional scatter plot to make cluster analysis of different plastics, as shown in Fig. 6, different plastics were separated and accurately clustered.

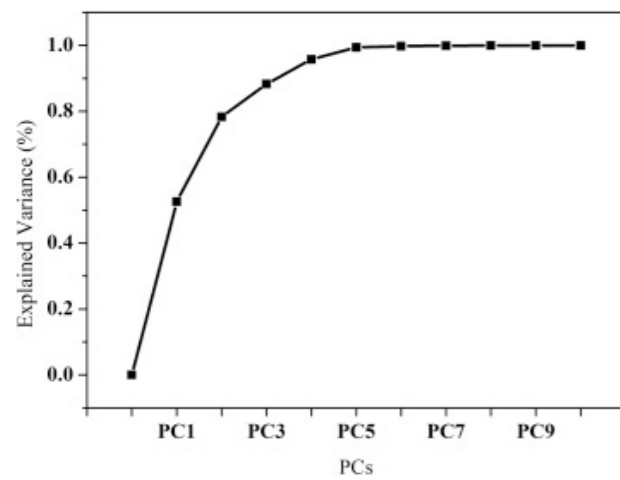


Fig 5. Explained variance plot of the PCA model based on spectra of training set.

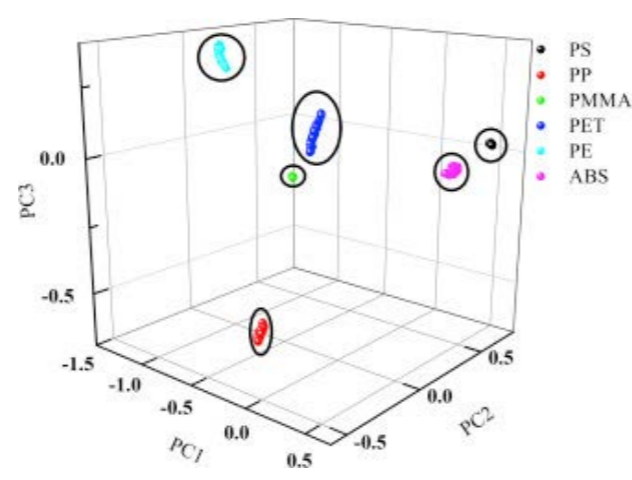


Fig 6. Plot of first three principal components scores for training set.

The PCA can only show the clustering trend of samples, it is necessary to further establish the classification model. On the basis of PCA, SVM was applied. Due to the big difference between the spectra of different plastics, the accuracy of self-verification was always 100% no matter what parameters were selected in the range of 2–5–25, so the default parameter (cost = 1, gamma = 0.143) was chosen to build the SVM classification model.

Identification result

For validating model accuracy, 120 spectra were collected at different positions of samples in the verification set. The identification result is shown in Table 1. The similarity of NIR spectra of PP and PE caused that several PE samples were mistakenly identified as PP, so the identification accuracy of the model was 97.5% instead of 100%.

Table 1. The identification result of validation sets based on PCA-SVM.

Plastic group	Number of spectra	The number of correctly identified spectra
PS	20	20
PP	20	20
PMMA	20	20
PET	20	20
PE	20	17
ABS	20	20

For the final examination, as shown in Fig. 7a, the validation set samples are put in the detection platform, and the result after identification by the PCA-SVM method is illustrated in Fig. 7b. It shows that each PSW sample could be clearly identified, e.g., PET bottle, PP disposable box cover, PE plate, PMMA spline, PS and ABS circular plate. Shape of samples was also roughly discernible. But the label on PET bottle was unidentified because of the product label interferes with the spectra collection. Considering that the spectral acquisition response is 0.5 s for each pixel, it will consume a lot of time for spectral acquisition if detection platform were separated into too many pixels, that's why the outline of sample was so rough in the identification result.

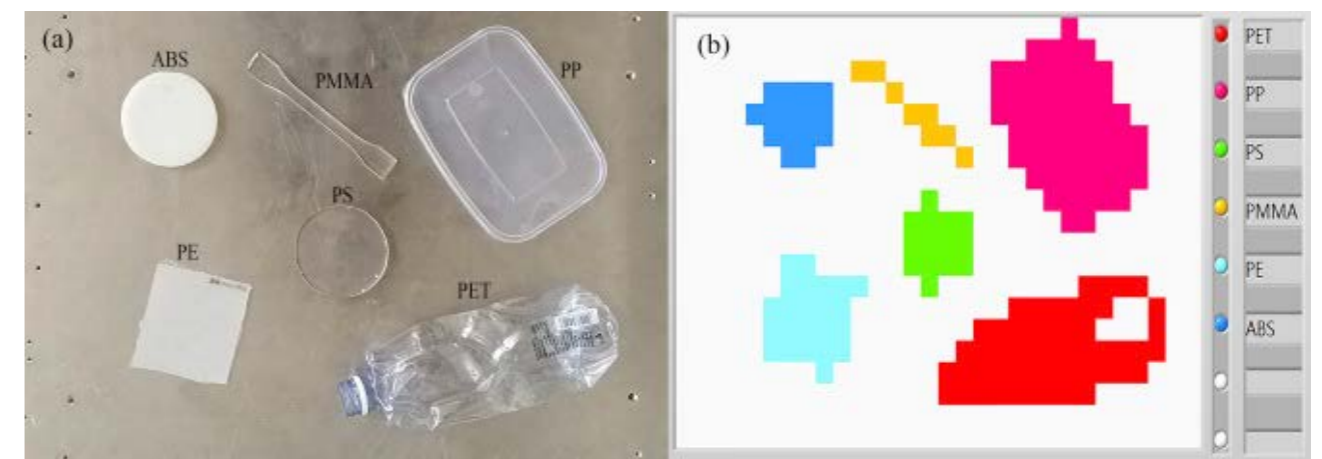


Fig 7. PSW placement and identification results of PSW identification system, (a) PSW placement, (b) PSW identification results.

Conclusion

NIR spectroscopy has been demonstrated as a valuable method for identification of waste plastics. By applying pre-processing methods, repeatability of spectra greatly promoted and the classification is helpful. Combining with PCA-SVM classification model which accuracy was 97.5%, PSW can be absolutely identified by our identification system, and the shape of samples can also be roughly discerned. The label on the sample would not be identified because the NIR spectra was disturbed by the label. Compared to the hyper-spectral imaging technology, this system can achieve similar recognition results while reducing costs considerably. There are some advises for the system improvement.

1. Add multiple NIR probes to the device for improving the efficiency of spectral collection.
2. Improve stability of transmission device, so as to enhance the signal to noise ratio.
3. Establish a NIR database of polymer materials, so that more types of polymer materials can be detected through the system and its application would be wider.

Reference:

Sh. Zhu, H. Chen, M. Wang, X. Guo, Y. Lei, G. Jin, *Advanced Industrial and Engineering Polymer Research*, 2 (2019) 77-81.



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OIL-FREE VICAT SOFTENING TEMPERATURE (VST) TESTER

The Vicat Softening Temperature (VST) measures the temperature at which a material, typically plastic, begins to soften. This test is essential for materials without a distinct melting point. The VST is determined by heating the material and measuring the temperature at which a flat-ended needle with a 1 mm² cross-section penetrates the material to a depth of 1 mm.

Key features include:

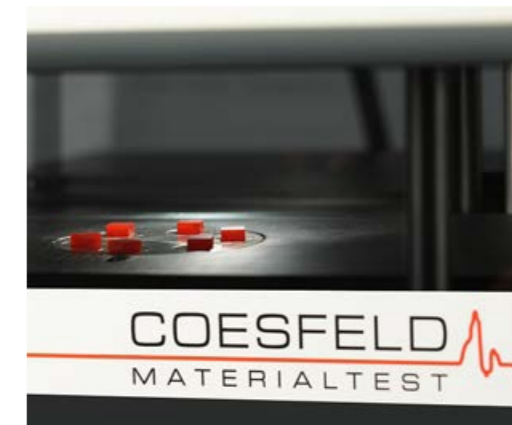
Oil-Free Operation: The measuring procedure is free of oil vapors or powder deposits, as heat transfer occurs directly without additional media.

Automated Process: The procedure is managed entirely via software, with integrated weight sets for methods A and B automatically placed during the measurement sequence.

Efficient Cooling: Integrated air cooling, with optional water cooling, enables fast measurement throughput.

Direct Tempering: Samples are tempered directly, eliminating the need for heat transfer media that may evaporate or release fine dust at higher temperatures.

The Coesfeld Eco VST is a compact, clean, and efficient oil-free measuring device for determining the Vicat softening temperature that complies with international standards and has been industrially tested and established for over 20 years.





ACCELERATED CREEP TESTING, ACT

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Material Creep

POLYMER MATERIALS UNDER CONSTANT STRESS ARE constantly deforming over time. This phenomenon is known as creep. Over long periods of time the creep deformation will reach a degree that the intended use of the polymer becomes impossible and eventually the material will rupture. The time to rupture does increase exponentially with increase of the stress level. Therefore, it is important to know and measure creep and creep rupture time of engineering polymers.

Creep Measurement

Measurement of creep is standardized, e.g. by DIN ISO EN 899 and ASTM D2990. The standards describe tensile and flexural test conditions at which test specimen are subjected to static load under specified environmental conditions. With data of multiple measurements each with different load it is possible to derive an isochrone stress-strain diagram (fig. 1) and fatigue strength diagram (fig. 2). Each point of the diagrams is the result of a single creep test measurement.

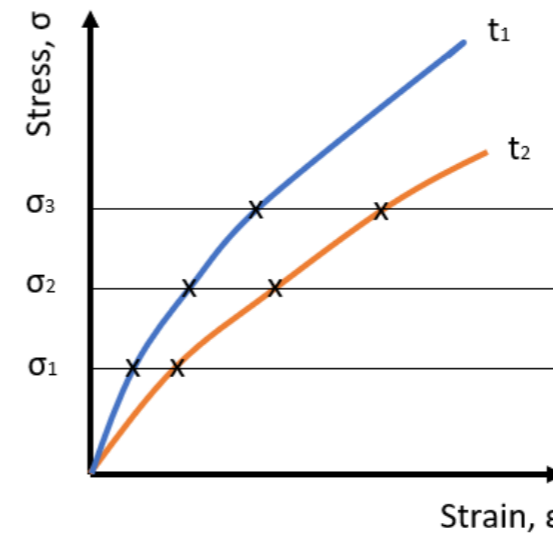


Fig 1: Isochrone stress-strain diagram – strain at constant stress after specific time $t_2 > t_1$

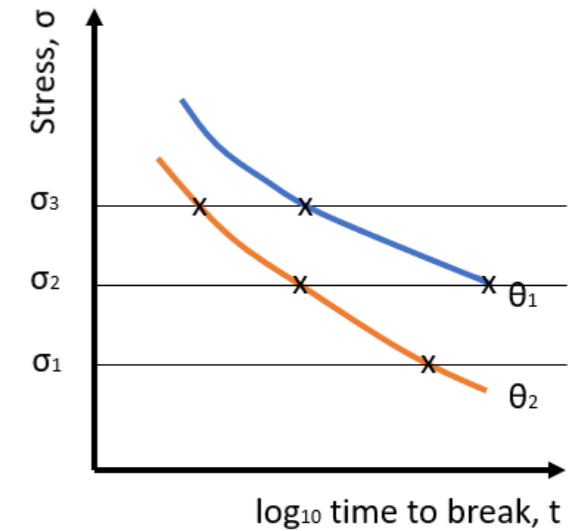


Fig 2: Fatigue strength diagram – Time to rupture at constant stress for different temperature $\theta_2 > \theta_1$

This data is essential to parametrize material models for reliable computer aided product simulation or to define safety limits for the intended use case.

As the test set-up appears relatively simple, e.g. apply constant load to test specimen, the efforts of collecting creep data is often times underestimated. The extrapolation of data is limited and typically not exceeding a factor of 10, compare ISO 1-1104 Acquisition and presentation of comparable multipoint data. Therefore, a typical measuring time of a single test ranges from 1000 to 10.000 hours. Considering that multiple measurements are required to build a single isochrone stress-strain curve or fatigue strength diagram it becomes obvious that obtaining this data is heavily binding test capacities and depending on environmental conditions, generating high energy cost. The measurement of creep, due to its slow progress, is lengthy and costly.

Accelerated Creep Testing

Accelerated creep testing (ACT) enables to predict the long-term (scaling in years) creep based on a series of short-term (scaling in hours) creep measurements. The methods are based on the time-temperature (TTS) and/or (TSS) time-stress superposition. Basic idea of TTS and TSS is to expose specimen at elevated temperature or stress to simulate creep at lower temperature or stress at a longer exposure. The acceleration of creep due to elevated temperature (TTS) can be explained on fundamental polymer physics. Creep that is slowly caused by stress will happen faster at higher temperature. The acceleration of creep due to elevated stress (TSS) is a semi-empiric approach, which is based on the observation that creep at constant stress in a longer period is similar to creep at higher constants stress in a shorter period. A combination of both temperature and stress elevation, e.g. Time temperature stress superposition TTSS, can be used to achieve more data even when temperature or stress limits are reached.

All approaches have in common that a master curve of the long-term creep is constructed by time-shifting measurement data of multiple short-term creep tests. Each of the short-term tests is performed on a new specimen of the same material at different temperature exposure and/or applied stress. Figure 3 illustrates the principle of data evaluation exemplary for TSS.

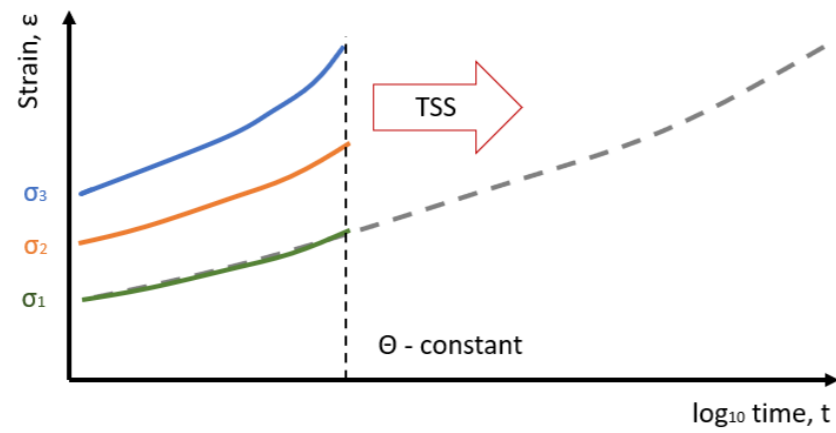


Fig 3: TSS – strain over time at constant temperature extrapolated for σ_1

In combination with the Boltzmann superposition principle, which describes that the total deformation of sequential stress events is equal to the sum of identical single stress events, ACT can be conducted on a single specimen and in a single course of measurement sequence. This approach is saving even more time and resources. The stepped isothermal method SIM is based on the TSS and the stepped isostress method SSM is based on the TSS.

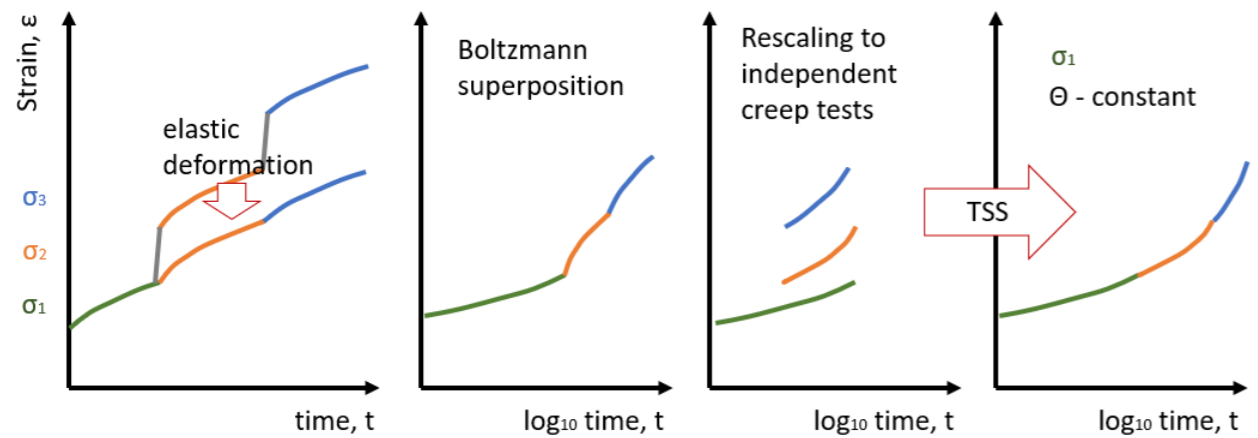
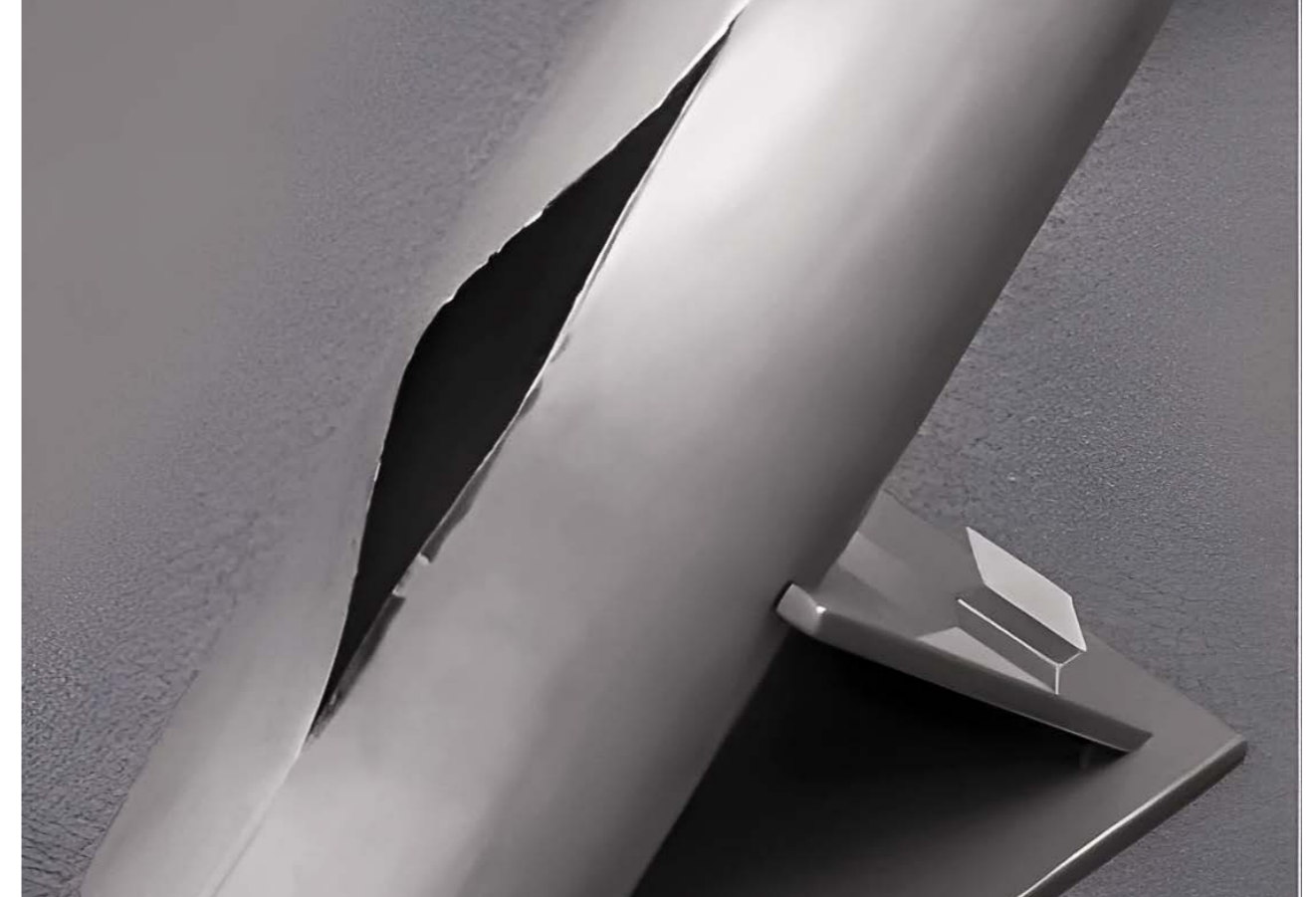


Fig 4: SSM – Concept of data extrapolation

Today, few international standards exist, which describe accelerated creep testing, e.g. ASTM D6992. Standard Test Method for Accelerated Tensile Creep and Creep-Rupture. The standard is based on SIM. The concepts of ACT, especially stress-based methods, are relatively young and still require further investigation and standardization. However, it has been shown that SIM and SSM extrapolation concepts are able to describe long term material behavior with good quality. The relevance of creep data is growing due to increasing use of engineering plastics in structural relevant parts and increasing capacity for computer aided product simulation. As availability of creep data is limited the potential of accelerated measurements is high.

Creep Testing Systems

Modern creep testing rigs of Coesfeld GmbH & Co. KG from Germany are specifically designed to fulfil the requirements of classic and advanced testing methods. The motorized creep testes are designed as multi-station machines with up to 10 stations effectively assuring good data quality via statistical validation. In contrast to classic creep rigs, which basically load a dead weight body to the loading rig, modern machines have an individual electro-mechanical drive for each test station.



In addition to classic creep tests, this enables to measure short term tensile tests, relaxation tests and programmed loading sequences required for SSM. Modern sensors and digital controller assure highest precision in motion and force over a wide testing range up to 20 kN. Large test ranges can be covered with the same machine and same set of load cells. Chambers embracing all test stations, precisely control temperature and humidity conditions. Via full integration to the machine controller, temperature sequences with quick temperature change and without overshoot can be realized, which is crucial for SIM. Strain data is measured optical via precision lenses and digital camera technology assuring highest precision. Optionally camera pictures can be used for digital image correlation to also obtain information about local strain fields. Company Coesfeld has been pioneer in setting up motorized multi-station creep test rigs starting in 2009.



Fig 5: Coesfeld 6 Station Creep Test System



Fig 5: Coesfeld Video Extensometer with Infrared-Light-LED



RECYCLING TECHNIQUES OF PET Comminution of Plastic Beverage Bottles



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Introduction

PET RECYCLING IS A crucial solution to reduce plastic waste and mitigate the crisis. The important recycling. Techniques of PET are mechanical recycling, chemical recycling and bio recycling. PET recycling is essential for sustainability and resource preservation. Mechanical recycling involves shredding PET waste into smaller pieces, followed by cleaning, melting, and molding. Chemical recycling processes like glycolysis and methanolysis produce high-quality PET monomers. Biological recycling uses enzymes or microorganisms to degrade PET waste into simpler compounds.

Mechanical recycling

Mechanical recycling is the most common method for recycling PET products, which involves collecting and shredding used PET products into small pieces, then washing and separating them from contaminants and melting them to create molten PET resin. The clean PET flakes are then melted and molded into new products, such as bottles, fibers, or films. Mechanical recycling is a cost-effective and energy-efficient method that can reduce greenhouse gas emissions and conserve natural resources. It can also reduce the amount of PET products that end up in landfills or oceans, and contribute to the development of a circular economy. However, it has several limitations, such as the quality and quantity of collected PET products, contamination, and material quality. The mechanical recycling process involves several stages, including collection, sorting, washing, separation, and extrusion.

- Collection and sorting

The first stage of the mechanical recycling process is the collection and sorting of PET plastic waste, which is collected from various sources and sorted based on its color, shape, and quality. The second stage is the washing process, which involves soaking the PET plastic waste in a solution of water and detergent and then agitated to remove any dirt, debris, or other impurities.

- Shredding and grinding

The second stage is the shredding and grinding of PET plastic, which involves shredding into small Pieces using a shredder machine and then ground into even smaller pieces. The shredding and grinding of PET plastic are a critical stage of the process, as it reduces the waste into small pieces and removes contaminants and impurities, ensuring high-quality material is used for recycling. The shredder machine, which has a series of rotating blades that chop the PET plastic into small pieces. The shredded PET plastic is then transferred to a grinding machine for

further processing. The size of the PET plastic flakes depends on the size of the grinding machine.

- Washing and separation

The third stage is washing to remove contaminants from post-consumer PET waste and separation to separate PET materials from other plastic polymers and non-plastic materials. processes, including fragmentation, immersion, mechanical agitation, and scrubbing to remove contaminants like labels, adhesives, dirt, and food residues.

- Drying and melting

The last stage of PET recycling is drying the materials to remove moisture, and melting them to create molten PET resin. This process ensures the integrity and quality of the recycled materials, ensuring their suitability for various industrial processes. The final stage of the mechanical recycling process is extrusion, where PET plastic flakes are melted and extruded into pellets, which can be used to produce new products.

A broad analytical evaluation is mandatory

The production of higher quality products from this recycled material requires a broad analytical evaluation. For this purpose, a comminution of the flecks as well as the granules is necessary.

The parameters to be evaluated are among others factors, the degree of polymerization and the color. A statement about the degree of polymerization and thus on mechanical or thermal damage is obtained via the determination of the melt-index. This determination is a wide spread method in the field of chemical polymers. The measured value depends on the particle size. The color is determined via white level measurement. But the measured data is greatly dependent on the reflected light and therewith also on the particle size. Therefore prior to the determination of the melt-index and before the measurement of the white level, the samples always must be prepared in a reproducible manner.

Comminution with the Variable Speed Rotor Mill

Utilized for the defined preparation of the samples is the Variable Speed Rotor Mill PULVERISETTE 14, including the impact rotor with 12 ribs and a sieve with 1 mm mesh width. The rotational speed control for the cutting rotor is for the achievement of the reproducible results immensely important.



Fig 1: Granulate comminuted with 1 mm sieve



Fig 2: PET bottles comminuted with 1 mm sieve

Frequently for polyethylene terephthalate we recommend to work with 16.000 rpm. Tests by the users in this concrete case lead to the settings of lower rotational speeds. Dependent on products and testing parameters, the optimum rotational speed was set between 10.000 and 14.000 rpm.

These low rotational speeds of the rotors minimize the mechanical, respectively the thermal demands during the comminution. Consequently, a lower throughput is to be expected. Alternatively, could the material be embrittled and added at higher rotational speeds.



Fig 3: Pulverisette 14 Classic line (closed view)



Fig 4: Pulverisette 14 classic line (open view: Grinding Chamber)

In addition to the Variable Speed Rotor Mill PULVERISSETTE 14, models related to the cutting mill such as PULVERISSETTE 29 and PULVERISSETTE 19 are suitable for this purpose.



Fig 5: PULVERISSETTE 29 cutting mill

Reference:

1. Joseph, T. M., Azat, S., Ahmadi, Z., Jazani, O. M., Esmaeili, A., Kianfar, E., ... & Thomas, S. (2024). Polyethylene terephthalate (PET) recycling: a review. Case Studies in Chemical and Environmental Engineering, 100673.
2. <https://www.fritsch-international.com/sample-preparation/milling/rotor-beater-mills/details/product/pulverisette-14-classic-line/>



RAMAN SPECTROSCOPY for Reaction Advancement Monitoring



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Abstract:

Epoxy is a general term referring to epoxy resins, both the individual components and the cured results. Epoxy resins are a family of reactive polymer precursors and polymers that include epoxide groups. These resins are used in an extensive array of consumer and engineering applications because of their durability, strong adhesion, chemical resistance, and other specialized properties. Here, a readily available two-part epoxy was used as a model system for monitoring the kinetics and reaction completion of industrial processes, generally, and adhesive curing, specifically.

Introduction:

Epoxy resins are used in the manufacture of adhesives, plastics, paints, coatings, primers and sealers, flooring and other products and materials that are used in building and construction applications. Most materials known as “structural” or “engineering” adhesives are epoxies. These high-performance adhesives are used to make laminated woods for decks, walls, roofing and other building applications, as well as in other products that require strong bonds to a variety of substrates including concrete and wood. Epoxies can stick to metal, glass, stone, wood and some plastics, and are more heat- and chemical-resistant than most glues. However, all these properties are contingent on proper proportions and mixing. In this paper, a readily available two-part epoxy was applied as a model system for monitoring the kinetics and reaction completion of industrial processes, generally, and adhesive curing, specifically.

Experimental:

The two-part epoxy used in this demonstration was Devcon® 15 Minute Epoxy which is composed of bisphenol A diglycidyl ether resin and a polythiol/polyamine mixture (-2,4,6-tri-(dimethylaminomethyl)-phenol and mercaptan amine blend). Mercaptan is an organo-sulfur compound that donates a thiol group to the curing process. Thiols react readily with the epoxide group and are typically used where heat cures are not possible, or a fast cure is needed.

To monitor the curing process, an Ocean Optics QE Pro-Raman+ with a 300 mW, a 785 nm laser and a Raman probe suspended at a fixed distance over the curing epoxy were used (Fig. 1). Ambient light was excluded from the laser-sample interaction region with a black cloth. Raman signals were acquired with 3 s acquisition time and 10x averaging. Signals were acquired on the epoxy samples immediately upon mixing and then in 2-3 min intervals after that. In some cases, signals were acquired the following day, but in no instance did these signals vary appreciably from those collected at 40-45 min after mixing.

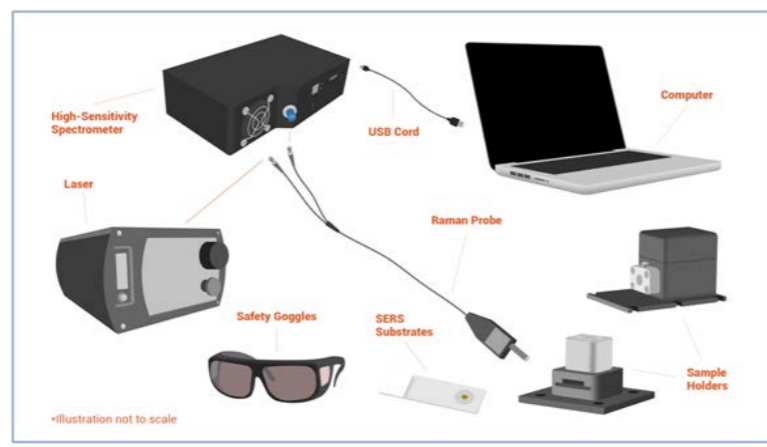


Fig 1. Schematic of a Raman set up.

Results and discussion:

Two samples of different proportions of resin and hardener were mixed, at the recommended ratio of 1:1 and at a 2:1 hardener-to-resin mixture. Following the mixing of the two components, the curing process was monitored with Raman spectroscopy. The analytical focus was principally on the epoxide and thiol features, which diminish upon curing.

Raman bands corresponding to epoxide vibrational frequencies have been reported previously [1], with 1254 cm^{-1} assigned to be the breathing mode of the epoxide ring (Fig. 2). The intensity of this peak is linearly dependent on the concentration of epoxide groups in the resin mixture [1 and references therein]. The peak at 921 cm^{-1} is likely the epoxide ring deformation and is much weaker. The Raman peaks at 1114 cm^{-1} , 1186 cm^{-1} and 1610 cm^{-1} have been assigned to resin backbone vibrations and do not

change in intensity during the curing reaction.

The change of the 1254 cm^{-1} feature with time can be interpreted as the consumption of the free epoxide groups during the vitrification of the epoxy. The reduction of the intensity of the Raman feature at 2575 cm^{-1} shows the consumption of the thiol in the hardener as the material reacts. The rate of the initial loss of the S-H feature appears to be a function of the initial concentration of the hardener. The S-H stretch, related to the presence of thiol, is readily observed at 2575 cm^{-1} . In the case of the measurement of 1:1 hardener-to-resin, the S-H feature is still present when the curing process stops. Note that this sample was still slightly sticky to the touch the next day, far after the 15 min cure time assured on the package. This result could be due to either the incorrect proportions of the two substances or perhaps inadequate mixing of the two.

In the 2:1 hardener-to-resin sample, the initial peak of the thiol feature is slightly higher than in the 1:1 case (Fig. 3). This was not evaluated for quantitative behavior, but the ratios of peak heights seem reasonable given that in the 2:1 case, the hardener accounts for %67 of the total material present (two-thirds) and in the 1:1 case, only %50 (one-half). In this second case, there is not enough resin to react stoichiometrically with the available resin, and there is an appreciable amount of thiol remaining in the product epoxy. It is not surprising that the epoxy did not cure well in this case, either. The S-H feature (analyzed using peak area from 2487-2639 cm^{-1}) in the case of the 2:1 mix comprises about 1.36x more integrated area than that associated with the 1:1 mix. This agrees with the fact that in the 1:1 mix, there is %50 hardener. In the 2:1, there is %67 hardener (a 1.34x increase). The 2:1 mixture has an appreciable amount of S-H remaining; 1:1 has less S-H remaining at the end of the cure.

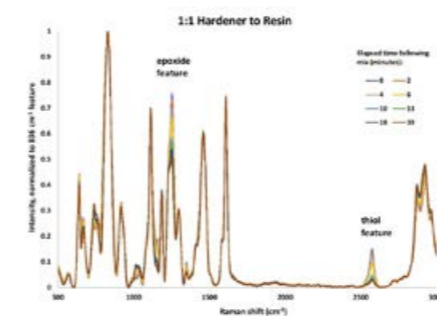


Fig 2. Devcon® 15 Minute Epoxy (1:1 resin to hardener), as a function of cure times (minutes).

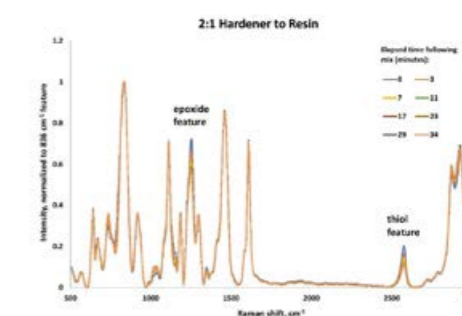


Fig 3. Devcon® 15 Minute Epoxy (1:2 resin to hardener), as a function of cure times (minutes).

Kinetics Analysis: A kinetic analysis of the S-H loss is readily performed on the data produced with this Raman system. Behavior as a function of time of the S-H feature is shown in Fig. 4. A visual comparison of the two data traces (markers) shows that first, there is more S-H at the beginning of the process in the case of the 2:1 hardener-to-resin mix than in the 1:1 case.

Additionally, the data markers show that onset of the reaction is slightly accelerated when excess hardener is present. Fitting the data in the region where S-H reactivity is the fastest (excluding the first three points in the 1:1 case) to a simple exponential with an offset (Eq. 1), it is apparent that the kinetics of the bulk of the reaction are the same in both mixtures with τ (1/e half-life) of 4.5 min. Finally, it is also clear from the tail of both sets of data (markers) that more unreacted S-H

remains in the case where more hardener has been added, which is reasonable because the hardener is the source of the thiol.

$$\text{Eq. 1: } y = y_0 + A * \exp[-(x-x_0)/\tau]$$

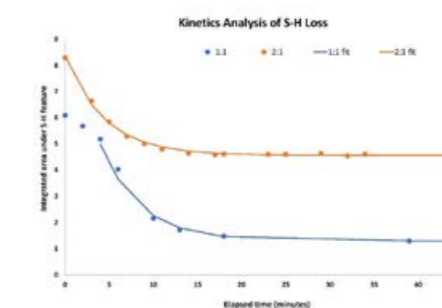


Fig 4. Integrated areas under the S-H feature in both the described cases; also, the exponential fits to the data.

Conclusion:

This brief application note details the use of Raman spectroscopy to elucidate details of the epoxy curing process in real time. This utility can be extended easily to other types of reactive processes, even those that are faster than this relatively slow epoxy vitrification. Ocean Insight supports a line of Raman spectrometers and lasers that are ideal to perform this type of analysis, and the applications expertise to help you solve similar problems.

Reference:

- [1] V. Křesálek, H. Vašková, "Raman spectroscopy of epoxy resin crosslinking," Recent Researches in Automatic Control, Conference Paper, May 2011.
- [2] <https://www.oceanoptics.com/blog/raman-spectroscopy-for-reaction-advancement-monitoring>.



CHARACTERIZATION OF BIODEGRADABLE Polymers Using HPLC and GPC



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Abstract

Biodegradable Plastics are emerging as pivotal alternatives to conventional polymers, offering potential solutions to plastic pollution. Biodegradable polymers define as materials that can degrade into smaller fragments by enzymatic or microbial action, eventually forming non-toxic byproducts such as water and carbon dioxide. This study employs High-Performance Liquid Chromatography (HPLC) and Gel Permeation Chromatography (GPC) to systematically analyze these materials. By examining molecular weight distribution, polydispersity, and compositional purity. The findings underscore the significance of these analytical techniques in the advancement of environmentally sustainable materials for industrial and societal applications.

Introduction

Conventional plastics, derived from petrochemical sources, have led to pervasive environmental

challenges. Approximately 300 million tons of plastic waste are generated annually, a significant portion of which persists in ecosystems for centuries. The persistence of these materials contributes to the accumulation of microplastics in marine environments, soil contamination, and adverse effects on wildlife.

Biodegradable plastics offer a promising alternative, designed to decompose under controlled conditions such as composting, industrial treatment, or exposure to natural microbial activity. Their applications span various sectors:

- **Agriculture:** Biodegradable films, such as mulch sheets, eliminate the need for retrieval and disposal, enriching soil as they degrade.
- **Healthcare:** Polymers used in sutures, drug delivery systems, and temporary implants dissolve within the body, minimizing the need for secondary procedures.
- **Packaging and Consumer Goods:** Compostable packaging and single-use items reduce landfill dependency.



The International Union of Pure and Applied Chemistry (IUPAC) defines biodegradable polymers as "polymers capable of undergoing degradation into smaller molecules by the action of microorganisms or enzymes, resulting in non-toxic byproducts under specific environmental conditions." This distinction is critical in differentiating true biodegradability from other forms of material disintegration, such as photodegradation or thermal breakdown, which do not necessarily yield environmentally benign residues.

The diversity of biodegradable plastics, including aliphatic polyesters (e.g., PLA, PHA), polysaccharides (e.g., starch derivatives), and synthetic blends, necessitates rigorous analytical characterization. Variations in molecular structure, weight distribution, and additive composition directly impact their degradation behavior and application suitability.

High-Performance Liquid Chromatography (HPLC) and Gel Permeation Chromatography (GPC) are indispensable tools for characterizing biodegradable plastics. HPLC enables the identification of monomers, additives, and impurities, providing insights into material composition and purity. GPC determines molecular weight (M_w), weight distribution (PDI), and chain architecture, which influence mechanical properties and degradation kinetics. Together, these techniques establish a comprehensive profile of biodegradable materials.

Materials and Methods

Samples of biodegradable plastics were sourced from various commercial products, including packaging films,

agricultural sheets, and disposable utensils. Reference polymers such as polylactic acid (PLA), poly hydroxyalcanoates (PHA), starch-based derivatives, and aliphatic-aromatic copolymers were included for benchmarking.



- **HPLC:** The 3000 ISS HPLC system was equipped with a high-pressure gradient pump, automatic sample injection system, column oven, UV-Vis detector and a C18 reverse-phase and an organic acid ion exclusion column.

- **GPC:** The 3200 ISS GPC system was conducted using a system equipped with a high-pressure gradient pump, automatic sample injection system, column oven, refractive index (RI) detector and SEC (GPC) column. Polymer or degradation residues samples were dissolved in suitable solvents (e.g., chloroform for PLA, acetone for PHA) at a concentration of 1 mg/mL. Solutions were filtered using 0.45 μ m syringe filters before injection.



Results and Discussion

HPLC Analysis

HPLC effectively resolved monomeric components, residual solvents, and processing additives in the samples.

• **Monomer Identification:** Distinct peaks corresponding to common monomers (e.g., lactic acid, succinic acid, and ...), confirming the presence of specific biodegradable polymers as shown in Fig 1.

• **Additive Detection:** Peaks associated with plasticizers and stabilizers, such as glycerol and phthalates, detecting in certain samples. These compounds influence the mechanical properties and degradation rates of the materials.

GPC Analysis

GPC analysis provided detailed molecular weight distributions:

• **Weight-Average Molecular Weight (Mw):** Ranged from 100 Da to 20,000,000 Da

• **Polydispersity Index (PDI):** Varied from 1.3 (indicating uniform chains) to 3.0 (suggesting significant heterogeneity).

Figs 2 and 3 show GPC analysis of two type of biodegradable polymer samples.

Sample :

1. Citric acid
2. Tartaric acid
3. Pyruvic acid
4. Malic acid
5. Succinic acid
6. Glycolic acid
7. Lactic acid
8. Fumaric acid
9. Acetic acid
10. Levulinic acid
11. Pyroglutamic acid
12. Propionic acid
13. Isobutyric acid
14. n-Butyric acid

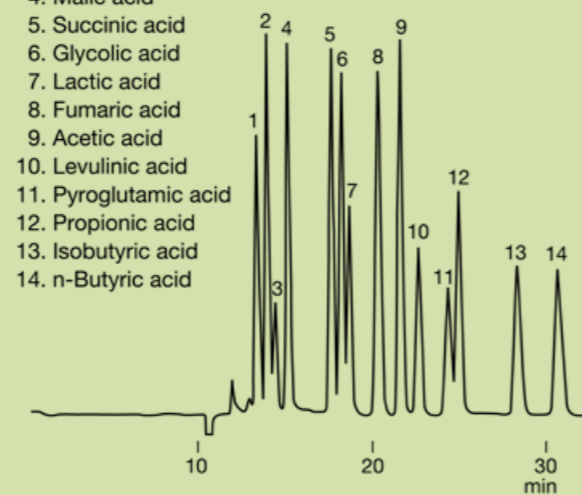


Fig 1. Polymer bio degradation products. Column: RSpak KC811- x 2. Eluent : 6 mM HClO₄ aq., Flow rate : 1.0 mL/min, Detector : VIS (430 nm) post column method, Column temp.: 50 °C

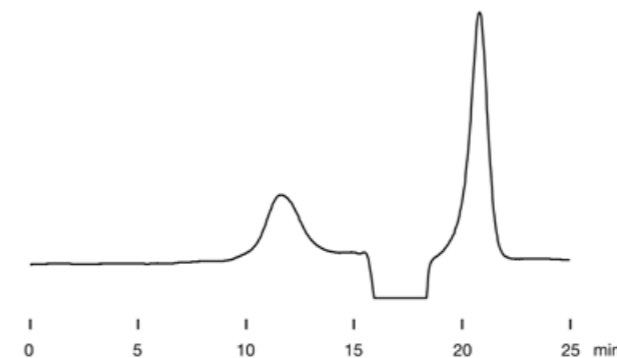


Fig 2. GPC Analysis of Poly(lactic-co-glycolic acid) 0.02 %, 200 µL, Column Asahipak GF-7M HQ, Eluent : CH₃CN, Flow rate: 0.6 mL/min, Detector : RI, Column temp.: 40 °C

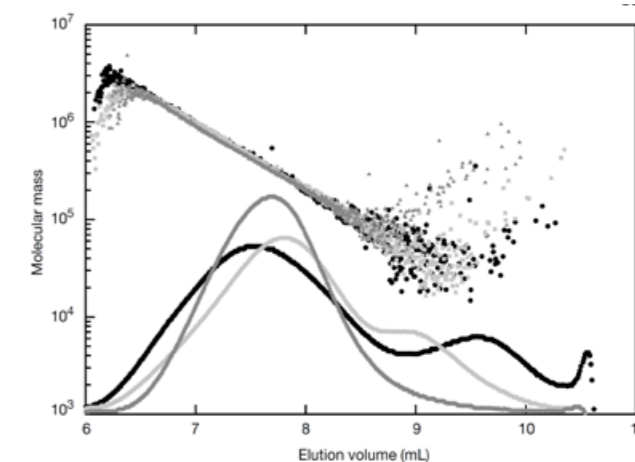


Fig 3. Sample is Cellulose 0.05 % each, 100 µL, Column GPC KD806-M, Eluent : 1 % LiCl in DMI, Flow rate : 0.5 mL/min, Detector : RI,

These results underline the importance of molecular uniformity in determining polymer performance. For instance, narrow PDI values correlate with predictable mechanical and degradation properties, critical for applications such as packaging and biomedical devices.

Implications of Analytical Results

The integration of HPLC and GPC findings reveals critical insights into the structure-property relationships of biodegradable plastics:

- Higher molecular weights and narrower PDI values are advantageous for structural applications requiring mechanical strength and controlled degradation.
- The presence of additives, while improving processability, may complicate biodegradation, necessitating careful formulation.

Conclusion

This study highlights the pivotal role of HPLC and GPC in the comprehensive characterization of biodegradable plastics. By elucidating their compositional and molecular properties, these techniques facilitate the optimization of these materials for diverse applications. The findings underscore the need for robust analytical frameworks to support the development of environmentally sustainable solutions.

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DETERMINATION OF HEAVY METALS in polyethylene and polypropylene after xylene treatment by EDXRF



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Abstract:

A CONVENIENT ORGANIC solvent treatment method was developed for determining Cd, Cr, Hg, and Pb in polyethylene and polypropylene matrices using energy dispersive X-ray fluorescence spectrometry. Calibration curves were created with organometallic compounds in xylene, spanning a concentration range of 1–80 mg/kg. The apparent recoveries of elements with certified values ranged from 0.81 for Hg to 1.14 for Pb. Precision was typically better than 8% RSD, except for Hg, which had a 10% RSD. The detection limits were 12 mg/kg for Cd, 24 mg/kg for Cr, 12 mg/kg for Hg, and 12 mg/kg for Pb. Polyethylene and polypropylene samples were analyzed using both the XRF method and a reference technique for comparison. This proposed method can also be applied to various xylene-soluble plastics.

Introduction:

Plastics that introduce many beneficial properties to materials are widely used in our daily life. The elemental contents of the plastic materials must not exceed the concentration limits specified by regulations, such as Packaging & Packaging Waste Directive 1994/65/EC, Waste Electrical & Electronics Equipment (WEEE) Directive 2002/96/EC, and the Restriction of the Use of Certain Hazardous Substances in Electrical & Electronics Equipment (RoHS) Directive 2002/95/EC, which regulate the maximum amount of heavy metals (Cd, Cr(VI), Hg, and Pb) in different kinds of plastic materials. These compounds might originate from flame retardants, antimicrobial reagents, plasticizers, heat stabilizers, including Pb and Cd (as heat stabilizers); or rather as pigments; or are simply

present as catalyst residues. The increasing needs of the plastic industry and the new regulations can be met only by improvements in the accuracy and precision of the analytical methods applied to plastic research.

A candidate for spectrochemical analysis is X-ray fluorescence (XRF) spectrometry. The aim of this study was to provide an organic solvent treatment step with xylene to polyethylene (PE) and polypropylene (PP) samples for the determination of some hazardous elements (Cd, Cr, Hg, and Pb) by EDXRF. Calibration curves were prepared using diluted solutions of organometallic compounds in xylene in order to eliminate matrix effects and homogeneity problems. Different shapes and types of samples, which were PE bags of different colors and PP materials, were also analyzed by the above-mentioned method. The results were also compared with atomic

absorption spectrometry after microwave digestion.

Results and discussion:

The sample preparation time for microwave digestion was about 2 h for up to six samples. On the other hand, for 12 samples using organic solvent treatment, the time was reduced to 20 min. The solvent treatment procedure provided rapid and reliable sample preparation for soluble plastics. However, the stability of the dissolved samples had to be studied because of xylene evaporation during the measurements. A single prepared CRM sample analyzed four consecutive times (total time: approx. 60 min) showed good repeatability (Fig. 1). Despite evaporation, relative standard deviations for these measurements were better than 10%. In this period, any film relaxation that affects the measurement was not observed.

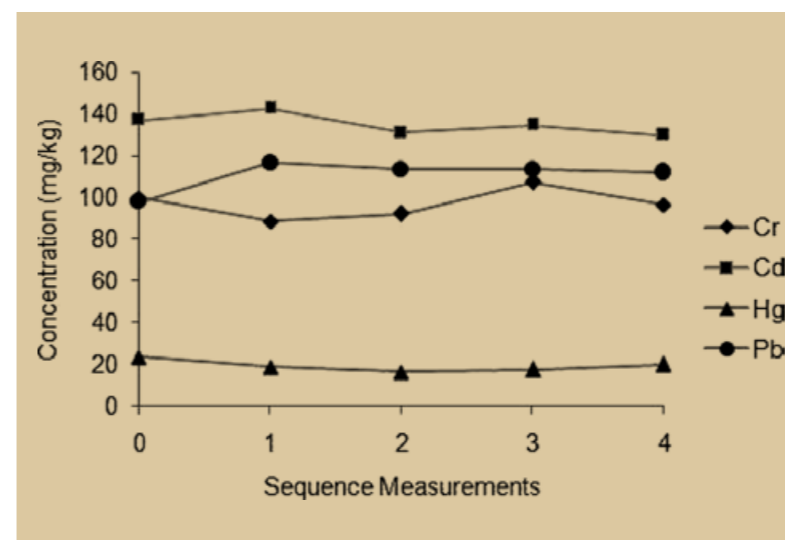


Fig 1. Repeatability measurement results.

The accuracy of the procedure used was evaluated by examination of CRM, ERM-EC681k (ca. 0.9 g samples examined, dilution ratio 1:12). The mentioned elements concentrations and standard deviations, which were obtained with proposed methods in the CRM, are shown in Table 1. The apparent recoveries of the elements with certified values were in the range of 0.81 (Hg) to 1.14 (Pb). When mercury concentration in CRM solution was far from the LOD level (dilution ratio 1:8), it was observed that apparent recovery of mercury reached 0.93. The apparent recovery value of Pb was higher than that of others. This situation can be explained by interference effects from Br, because the Br (K_{β}) spectral line (11.924 keV) is close to the Pb (L_{β}) spectral line (12.614 keV), and the CRM contained a large amount of Br (0.77 g/kg⁻¹). The precision was

normally better than %8 RSD, with the exception of Hg (%10). The element contents of CRM by EDXRF after using direct and proposed sample preparation methods are also outlined in Table 1. Although direct measurement was found to be adequate for Hg, Cd, Cr, and Pb were not reliable. However, the proposed method has a better agreement than direct measurement results.

Table 1. Results Obtained for Determination of Cd, Cr, Hg, and Pb in ERM-EC681k Certified Reference Material by EDXRF (n=3)

Elements	Certified Value (mg kg ⁻¹)	Proposed Method (mg kg ⁻¹)	Apparent Recovery	Direct Method (mg kg ⁻¹)
Cr	100 ± 5	94 ± 7	0.94	191 ± 13
Cd	137 ± 4	138 ± 4	1.01	62 ± 3
Pb	98 ± 6	112 ± 2	1.14	118 ± 2
Hg	23.7 ± 0.8	19.2 ± 2	0.81	22.7 ± 0.4

Five PE shopping bags of different colors and two PP samples were analyzed by EDXRF after xylene treatment. The results were also compared by AAS after microwave digestion. The results and standard deviations are given in Table 2. As can be seen, good agreement with the reference AAS technique was achieved in all the samples. The maximum relative deviation was 12%. The analytical data obtained were tested with analysis of variance (ANOVA), and the differences were not statistically significant at the 95% confidence level.

	Cr (mg kg ⁻¹)		Cd (mg kg ⁻¹)		Pb (mg kg ⁻¹)		Hg (mg kg ⁻¹)	
	EDXRF	AAS	EDXRF	AAS	EDXRF	AAS	EDXRF	AAS
Yellow	613 ± 11	691 ± 60	<12	<2	3003 ± 39	2981 ± 30	<12	<0.1
Black	22 ± 3	25 ± 4	<12	<2	143 ± 4	140 ± 10	<12	<0.1
Blue	44 ± 8	44 ± 12	<12	<2	231 ± 16	217 ± 17	<12	<0.1
Red	226 ± 23	227 ± 21	<12	<2	1567 ± 37	1490 ± 48	<12	<0.1
Green	<28	<3	<14	<2	<14	<6	<14	<0.1
PP1	228 ± 28	213 ± 38	<12	<2	1259 ± 31	1229 ± 51	<12	<0.1
PP2	<24	<3	109 ± 13	99 ± 2	108 ± 13	97 ± 8	<12	<0.1

Table 2. Results Obtained for Determination of Cd, Cr, Hg, and Pb in ERM-EC681k Certified Reference Material by EDXRF (n=3)

Conclusion:

A solvent treatment procedure provided rapid and reliable sample preparation for xylene soluble plastics such as PE and PP for EDXRF. Although AAS methods have better sensitivity, the time required for analysis is significantly longer. EDXRF permits the fast and reliable quantification of Cr, Cd, Hg, and Pb in the plastic matrices. The described method can also be applied to routine analyses for the determination of target analytes in plastic samples. Although the data were collected for PE and PP materials, the proposed method might be applicable to different kinds of plastic materials, and all light organic and soluble matrices such as pharmaceuticals, agrochemicals, organic dyestuffs, and pigments. The proposed method has been shown to be a useful approach in the determination of Cd, Cr, Hg, and Pb in plastics, which may then be tested to discern whether the concentration of elements exceeds the regulated limits.



Reference:

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