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Characterisation of Foulants in a PVDF Tubular Cross Flow Ultrafiltration Membrane by ATR/FTIR Spectrometry

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Attenuated Total Internal Reflection Fourier Transform Infrared Spectrometry (ATR-FTIR) was used to study the chemical nature of the deposits on the fouled polyvinylidene fluoride (PVDF) tubular membrane after the concentration of natural rubber skim latex by cross-flow ultrafiltration process. The subtraction spectroscopy analysis (subtraction of spectrum of the fouled membrane by the spectrum of the unused clean membrane) indicated that the major composition of the foulants found on the interior surface of the membrane could be of natural rubber latex protein derivatives (amino acids; bonded NH; NH_2 and amine) and the smaller rubber particles that plugged the membrane pores. The chemical nature of inorganic foulants originating from metallic ions from the preservation system of the natural rubber latex could not be determined. The current membrane cleaning procedure is not effective enough to remove all the organic foulants. This study only provides a preliminary identification of the functional groups and needs further confirmation by other analytical tools for a full characterisation of the foulants for formulating a more effective membrane cleaning procedure.

Keywords: ATR-FTIR spectroscopy; skim natural rubber latex; cross-flow ultrafiltration process; foulants

Natural rubber latex (NRL) exudes from the *Hevea brasiliensis* tree when it is tapped. The dry rubber content (DRC) of the latex usually ranges from 30% to 35%, the average being *ca*. 33%. The remainder of the latex is mainly water[1]. NRL is concentrated to a DRC of 60% before it is used as an industrial raw material for making latex-dipped goods, such as examination gloves, condoms, latex thread and other medical goods. Centrifugation is the preferred method for concentrating NRL and producing natural rubber skim latex (NRSL) as a by-product. NRSL processing involves the recovery of 4%–5% of dry rubber from skim latex by waste sulphuric acid coagulation, which is not eco-friendly[2-4].

Recently, the cross-flow ultrafiltration process (CFUF) was found to be a more viable option to recover skim latex which was obtained from the centrifugation process. The DRC of skim latex was increased from 5% to

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about 30% (equivalent to the DRC value of field latex), then added to the incoming field latex, and this mixture subsequently undergoes concentration by centrifugation producing a new raw material *i.e* skim latex concentrate. This process that by-passes the sulphuric acid coagulation of the skim latex for recovery of the dry rubber is more eco-friendly and could become an immediate measure to solve the environmental problems faced by the latex concentrate factories over the years. Latex free skim serum, which is not contaminated by sulphuric acid, is obtained from this CFUF process as a by-product. The serum has a potential to be turned into fertilizers as a low-end product. On the higher end, it can be used to extract value-added bio-chemicals. The concentrated skim latex is being currently evaluated as a new value-added raw material[5]. Therefore the CFUF process could prevent NRSL being turned into waste latex and eventually as scrap rubber. This process could also prevent the discharging of acid tainted effluent into the anaerobic pond and instead produce two new value-added raw materials: skim serum and skim latex concentrate[2,3,5].

Optimisation of CFUF process to concentrate skim latex includes reducing fouling during processing, and finding suitable methods to clean membranes to obtain good flux recoveries to increase the economic life of the membranes. To formulate an effective membrane cleaning method requires chemical characterisation of the foulants. ATR-FTIR spectroscopy is one of the vital analytical tools involved in determining the functional group which subsequently helps in the characterisation of the foulants[6]. FTIR spectrometry is also used to determine the functional chemistry of unknown materials. Samples exposed to infrared light absorb energy corresponding to the vibrational energy of atomic bonds. Functional groups absorb energy at specific wavelengths, which can be shifted in intensity or position by substituent effects from adjacent atoms. The resulting absorption spectrum is a unique fingerprint of a compound[6,7].

So far, no extensive study had been carried out to characterise the foulants after the membrane had been fully fouled during the NRSL concentration by CFUF process. Therefore, the objectives of this paper were to use ATR-FTIR spectroscopy to identify the functional groups and to characterise the organic foulants and also to determine the efficiency of the current membrane cleaning procedure.

MATERIAL AND METHODS

Constituents of Natural Rubber Latex and Skim Latex

Natural rubber latex has numerous constituents of which the polymer (natural rubber) is *cis-1, 4-polyisoprene* (30% – 35%) with a weight average (M_w) that ranges from 300,000 to about 10 million Dalton. The rubber particles are usually spherical; ranging from 0.02 to 3 µm in diameter. Only 5% of the particles have diameters larger than 0.4 µm. The non-rubbers are proteinous substance (1.4%), neutral lipids (1.0%), phospholipids (0.6%), ash (0.5%), inositol and carbohydrates (1.6%), nitrogenous compounds (0.3%) and water (60%)[1].

Large volumes of NRSL are produced as by-products in the concentration process of NRL by centrifugation. 10% – 15% of the rubber enters the centrifuge effluxes as skim latex. The DRC of skim varies from 2.5% to 10%. The ratio of non-rubber solids to rubber is very high being *ca*. 1/1. The non-rubber constituents are mainly proteinous and nitrogenous substances[1]. A typical composition of skim latex is rubber hydrocarbon 4.5% – 5.5%, protein 3.0% – 3.5%, carbohydrates

2.5% – 3.0%, other nitrogenous substances 1% – 1.5%, metallic ions, <1% and the rest is water. NRSL has a narrow particle size distribution ranging from 0.2 to 0.6 µm with a mean value of 0.5 µm[1,2].

Experimental

NRSL obtained from the centrifugation process carries along the remnants of the preservation chemicals from the previous process. Chemical analysis is needed to determine its chemical composition before a topping-up of preservation chemicals prior to commencement of the NRSL concentration, so as to stabilise and prevent coagulation of the latex during the concentration process. The UF system developed to concentrate NRSL is as shown in *Figure 1*. This was an in-house designed system incorporated with a tubular polyvinylidene (PVDF) type with a 200 kD molecular weight cut off (MWCO) membrane manufactured by PCI Membranes, United Kingdom. It consists of two tubes connected in series, with each tube measuring 0.3 meter in length and 10 mm of internal diameter with an effective membrane area of 0.024 m^2. The membranes were mounted onto a stainless steel module (PCI, Model MICRO 240). According to manufacturer's specifications, the membranes were utilised at temperatures below 80ºC with a trans-membrane pressure (TMP) not exceeding 10 bar and ideally at a pH of between 1.5 and 12.

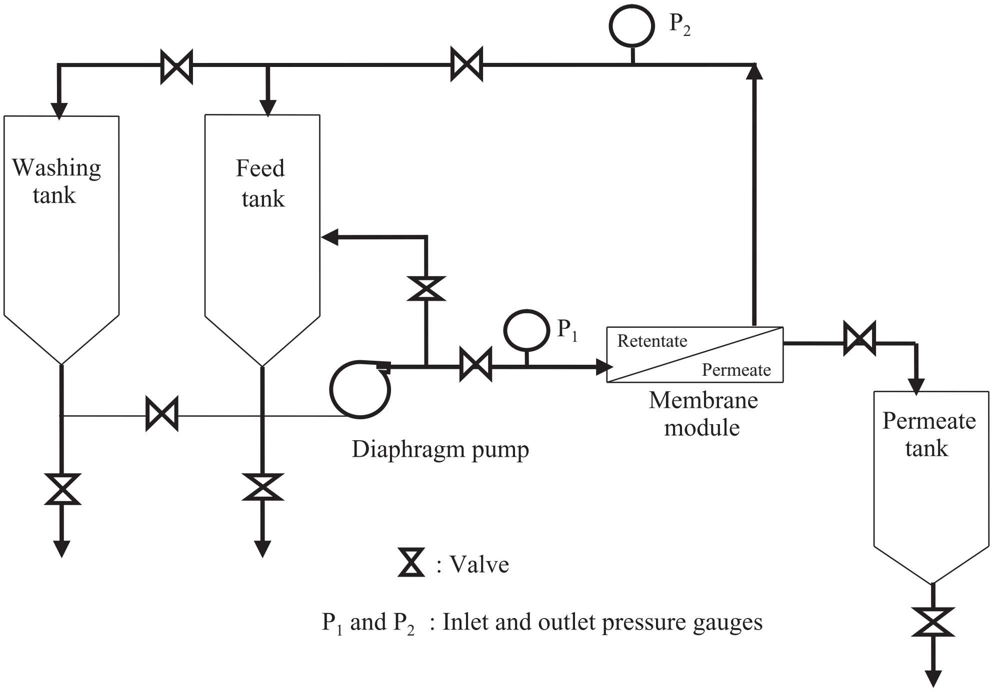

Figure 1. Schematic diagram of tubular cross-flow ultrafiltration system.

Natural Rubber Skim Latex Concentration Runs

Preserved NRSL was fed into the feed tank after obtaining its initial DRC and total solid content (TSC) values. The concentration process was carried out by starting the feed pump to circulate the feed in the UF system while maintaining a constant TMP. Experiments carried out using 200 kD PVDF membranes showed that the UF membranes were found to be fouled by NRSL when 75%–80% of the permeability was lost after 10 hours of continuous concentration runs. During these runs, DRC of NRSL was increased from *ca*.5% to *ca*.30%. The concentrated skim latex was drained from the system and replaced with deionised (DI) water to gently rinse the membrane surface. Rinsing was performed until rinsed DI water was clear. This set of membranes was deemed fully fouled and were dismantled from the module for membrane autopsy procedures to be carried out.

Membrane Autopsy Procedure

Membrane autopsy is a destructive procedure requiring a sacrificial membrane element to be removed from the plant for destructive analyses. Membranes are cut open and their surfaces are scientifically examined. Chemical, physical and microbiological analyses determine the types of foulants present and their effects on the membrane performance. Analytical techniques such as Fourier transform infrared spectrophotometer (FTIR), scanning electron microscope (SEM), nuclear magnetic resonance (NMR), atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS) could complement each other to completely characterise the chemical natures of membrane foulants present on the membrane surface when the more basic techniques (flux deterioration and increase in TMP) fail to reveal the cause of the problem. Nevertheless this study was limited to the use of ATR-FTIR for analysing and characterising the foulants. Results from the autopsy would be helpful in developing improved antiscalants and antifoulants as well as more effective cleaners and effective cleaning programmes. The standard autopsy investigation involves the dissection of a fouled membrane element taken from the problem plant. The key steps of membrane autopsy procedure are the selection of representative element (or elements), dissection, analysis and identification[7-10].

A replicate (second set of membranes) of this process was carried out using a different set of membranes. With the second set of fully fouled membranes kept intact in the membrane module of the UF system, membrane cleaning cycles using deionised (DI) water, NaOH and HNO_3 (the order is important) at a temperature of 50ºC was carried out. This is the current chemical cleaning procedure to bring about membrane permeate flux recovery of the fouled membranes[2]. ATR-FTIR spectrums of fouled and cleaned membranes would be compared with the spectrums of fouled but not cleaned membranes so as to determine the efficiency of the current membrane cleaning procedure.

ATR/FTIR Analysis Procedure

The infrared spectra were recorded using an attenuated total reflection-Fourier transform spectroscopy (ATR/FTIR) with OMNIC ESP software (Thermo Nicolet Instrument Corporation, Madison, WI). The cleaned and fouled membranes were dried at room temperature for three days before being analysed with FTIR. The resolution was 2.0 cm^{-1} and the results averaging 100 scans. All measurements were carried out at 20ºC ± 1ºC. The ATR accessory contained a Zinc Selenide (ZeSe) crystal at nominal incident angle of 45º. The FTIR was used to determine functional groups associated with the membrane surface materials and foulants. The spectra of the new, fouled and cleaned membranes were analysed using the OMNIC software[2,6,7].

RESULTS AND DISCUSSION

Spectroscopy Analysis

Spectroscopy technique, particularly ATR-FTIR, has been successfully employed to analyse functional groups of foulants in fouled PVDF and polypropylene (PP) membranes[2,6]. *Figure 2* is the ATR/FTIR spectrum of components of NRSL that fouled the PVDF membrane (the PVDF membrane spectrum has been digitally subtracted; the negative peaks from wave number 725 to 1450 were due to over subtraction). The peak at wave number 3291 is consistent with the N-H stretch of an unsubstituted amide, 2924 with the N-H stretch of a substituted amide (or C-H stretch of NR), 1647 with the C=O stretch of an amide, and 1540 with the N-H bend of an amide. The wave numbers of 1447 and 1357 are that of *cis*-polyisoperene peaks. These peaks still existed in the subtraction spectrum of fouled and cleaned membranes (top). This is indicative of the poor efficiency of the current membrane cleaning procedure which did not eradicate all of the foulants originating from the protein derivatives (amino acids and amine) of NR latex and NR latex particles (*cis*-polyisoperene) which might have plugged the pores of the PVDF membrane.

Superimposed ATR/FTIR Spectrums of Foulants and NR Latex Film

Figure 3 is ATR/FTIR of NRL film which shows the finger print wave numbers of NR at 842, C-H stretching at 2927 and other distinctive peaks of NR include wave numbers of 1447 and 1357. *Figure 4* is the ATR-FTIR spectrum of natural rubber latex film superimposed on the spectrum of the fouled PVDF membrane. The large broad peaks on the fouled membrane spectra at wave numbers 3000–3400 were due to the presence of moisture (OH) on the foulant. This figure clearly shows the matching of the spectra of NR latex particle foulants with the finger print regions of NR latex film (842 cm^{-1} and 2927 cm^{-1}). The unmatched region with wave numbers of 1740, 1643, 1619 and 1509 indicate the presence of amino acids and amine which are foulants of NR latex protein derivatives. This analysis suggests that the major foulants of PVDF membranes were NR latex particles and NR latex protein derivatives.

Spectra of Cleaned, Unused and Fouled Membranes

Figure 5 shows the superimposition of the ATR/FTIR spectrums of PVDF membranes: the fouled (top), fouled and cleaned (middle) and new (bottom). When a membrane is fouled, the FTIR peaks of the membrane changed in absorbance intensity, indicating the covering of the original clean surface by functional groups of foulants. The fouled membrane had distinct peaks at wave numbers 3288, 1649 and 1545. These wave numbers indicate the presence of the following functional groups: free – OH aromatics, bonded – OH, free NH, amino acids, bonded NH and NH_2. The wave numbers 1619 and 1515 indicate the presence of amino acids and amine. The majority of these foulants were derivatives of rubber proteins and amino acids which were constituents of NR latex. The presence of NR as foulants can be seen from the high peaks of the fouled membrane spectrum at wave numbers 800 to 950 (finger print region of NR).

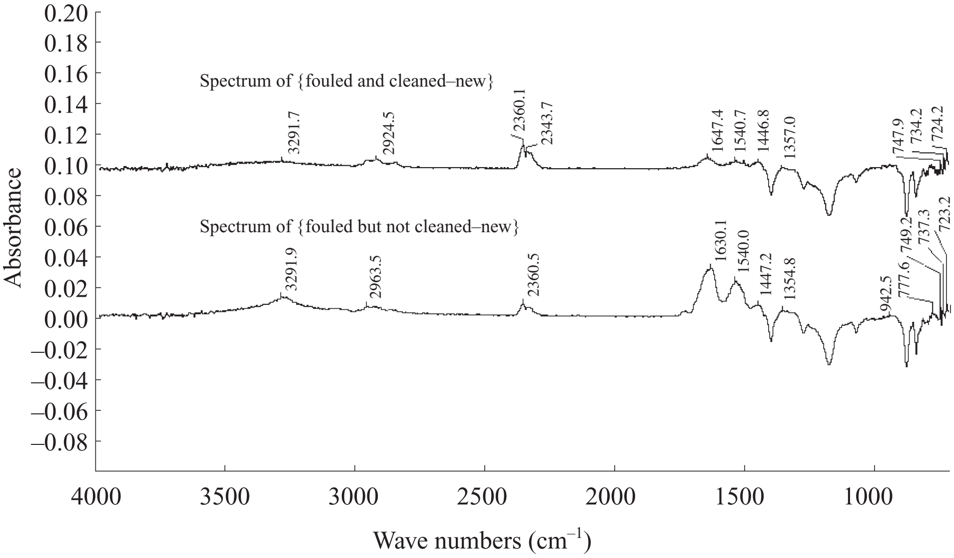

Figure 2. ATR/FTIR subtraction spectrums of fouled and cleaned (top), fouled but not cleaned (bottom) membranes.

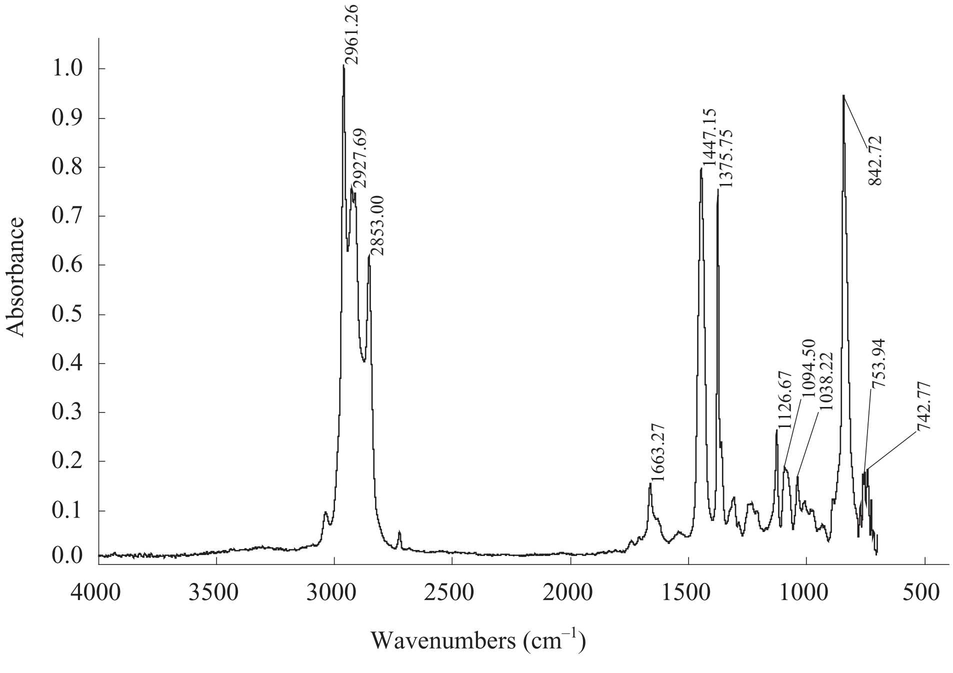

Figure 3. ATR/FTIR spectrum of NRL film.

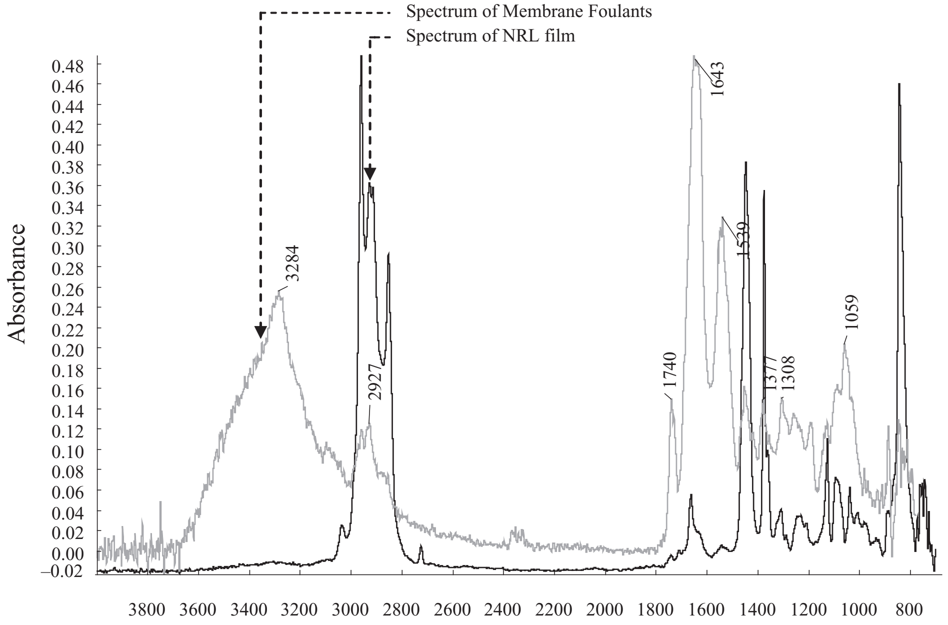

Figure 4. ATR-FTIR spectrums of NRL film super imposed on membrane foulants.

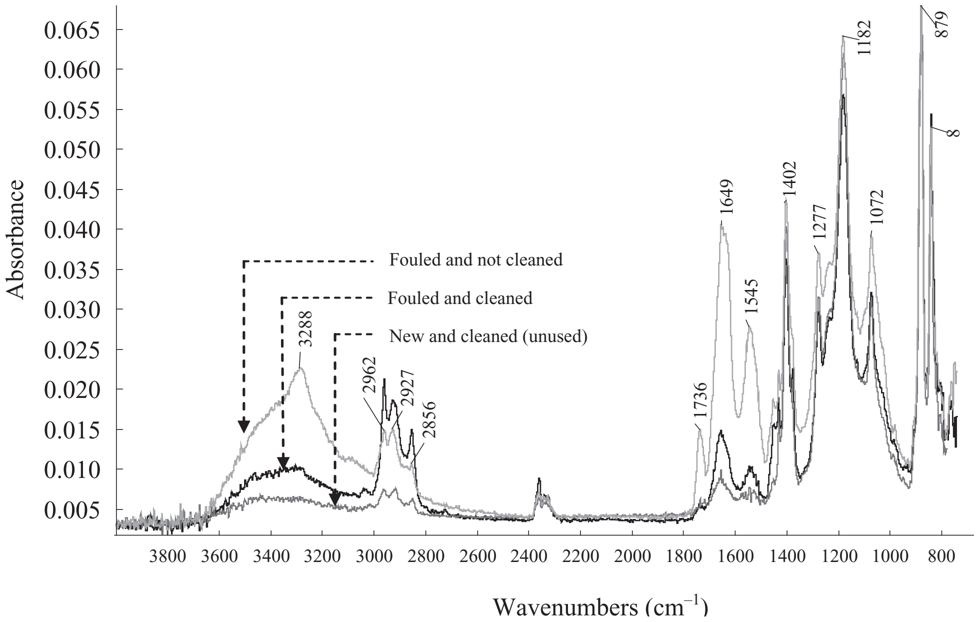

Figure 5. ATR-FTIR spectrums of new cleaned (bottom), fouled but not cleaned (top), fouled and cleaned (middle) membranes

CONCLUSIONS

Natural rubber skim latex was concentrated by the CFUF process using 200 kD MWCO PVDF membranes. The interior surfaces of the fouled membrane were examined by ATR/FTIR spectroscopy. The vibrational bands associated with foulants could be clearly distinguished from those of the membrane material. The foulants on these membranes produced relatively sharp absorption bands. The analysis by subtraction spectroscopy which indicated that wave numbers 3291 is the N-H stretch of an unsubstituted amide, 2924 with the N-H stretch of a substituted amide (or C-H stretch of NR), 1647 with the C=O stretch of an amide and 1540 with the N-H bend of an amide. The wave numbers 1447 and 1357 were that of *cis*-polyisoperene peaks. These indications suggest that the major composition of the foulants could be amino acids, bonded NH, NH_2 and amine suggesting that they are mainly protein derivatives of natural rubber latex. The other major foulant are latex particles. Foulant peaks still existed in the subtraction spectrum of fouled and cleaned membranes (slightly reduced in intensity). The amide functionality should have been removed by the membrane cleaning process and in addition OH/NH/CH stretching peaks still existed in the cleaned membrane. This is an indication of the poor efficiency of the current membrane cleaning procedure which did not eradicate all of the foulants.

The complete characterisation of all the foulants was not within the scope of the present study. The inorganic foulants which might have been derived from the preservation system of the original feed for the centrifugation process could not be determined. This study suggests that the ATR/FTIR could be a useful tool for a preliminary identification of functional groups of the organic foulants only. It could also be used to effectively gauge the efficiency of the membrane cleaning procedure. For confirmatory identification of the chemical nature (functional groups) of the foulants, ATR/FTIR analyses need to be complemented with other analytical techniques such as XPS, NMR, AFM and SEM. The combined usage of these analytical techniques could confirm the chemical nature of the foulants and would contribute immensely in formulating a more effective membrane cleaning procedure for the fouled PVDF membrane.

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