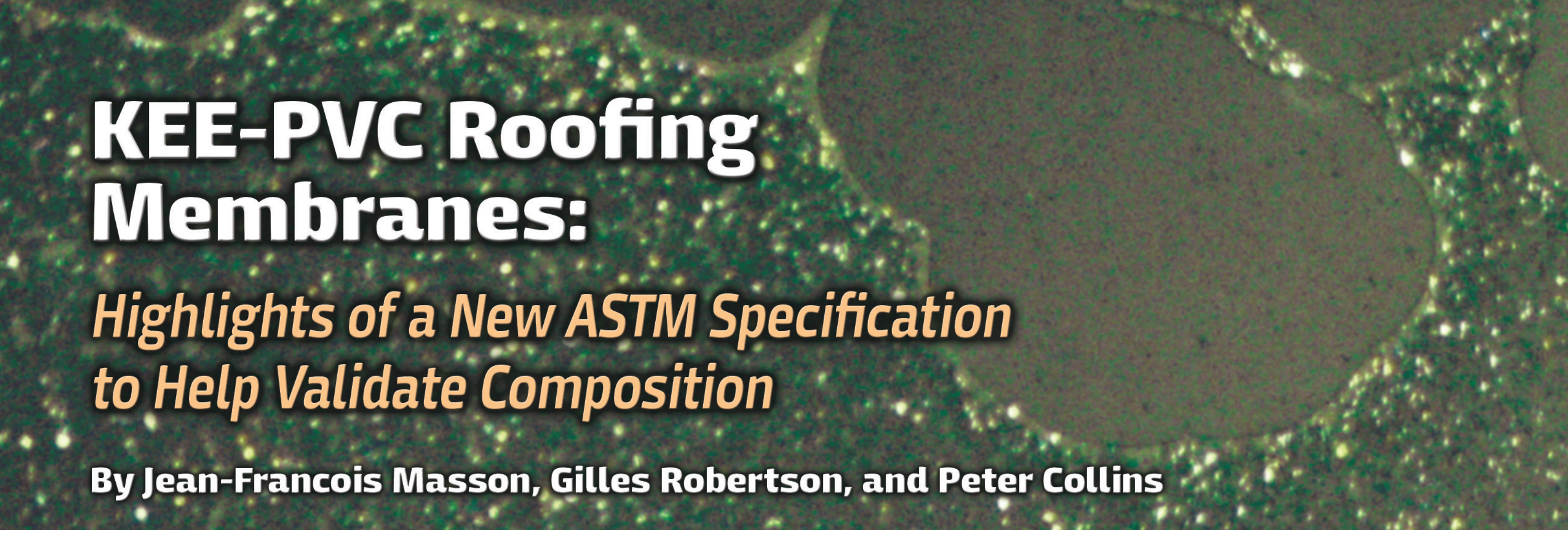

KEE-PVC Roofing Membranes:

Highlights of a New ASTM Specification to Help Validate Composition

By Jean-Francois Masson, Gilles Robertson, and Peter Collins

INTRODUCTION

Reflective roofing products are often used on buildings with flat roofs located in urban areas. This is an attempt to reduce the effects of local daily ambient temperatures in the summer months—the so-called heat island effect.[1] White- to cream-colored thermoplastic roofing membranes are often used for this purpose, including membranes based on blends of ketone ethylene ester (KEE) with polyvinyl chloride (PVC), known as KEE-PVC. The KEE plays the role of a PVC plasticizer. Its advantage over traditional phthalate plasticizers[2] is that it is non-volatile and it also reduces the concern over plasticizer migration.[3]

Engineers, architects, and building designers can specify KEE-PVC waterproofing membranes on the basis of ASTM D6754, *Standard Specification for Ketone Ethylene Ester Based Sheet Roofing*,[4] which requires that the membrane contain a minimum of 50% KEE by weight. However, it is only recently that a standard test method to quantify KEE has been available. The method, based on proton nuclear magnetic resonance (NMR), was developed by the Construction Research Center at the National Research Council of Canada. It is now accessible as ASTM D8154, *Standard Test Methods for 1H-NMR Determination of Ketone-Ethylene-Ester and Polyvinyl Chloride Contents in KEE-PVC Roofing Fabrics*.[5] This article provides a highlight of the NMR method.

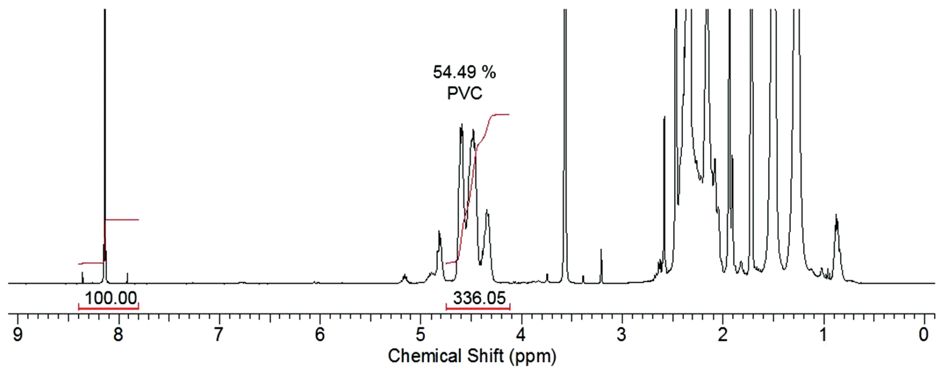

Figure 1 – A proton-NMR spectrum of a PVC-KEE blend in a solvent that contains a dissolved internal reference standard.

$$
\begin{aligned}
\text{PVC content} &= 100 * \frac{mass\ PVC}{mass\ sample} \\
&= 100 * \frac{molar\ quantity\ PVC * MW of\ PVC}{mass\ sample} \\
&= 100 * \frac{molar\ quantity\ TCNB * \left(\frac{integration\ PVC}{integration\ TCNB}\right) * MW\ of\ PVC}{mass\ sample} \\
&= 100 * \frac{\left(\frac{mass\ TCNB}{MW\ of\ TCNB}\right) * \left(\frac{integration\ PVC}{integration\ TCNB}\right) * MW\ of\ PVC}{mass\ sample} \\
&= 100 * \frac{\left(\frac{0.019938g}{260.89g/mol}\right) * \left(\frac{242.61}{100}\right) * 62.50g/mol}{(0.017846g + 0.011827g)} = 39.05\%
\end{aligned}
$$

Equation 1

NMR

Magnetic resonance imaging (MRI), a diagnostic tool found in many hospitals, is in the same family of analytical tools as NMR. Despite the name, no radiation is emitted when NMR or MRI is used. The word "nuclear" in NMR only indicates that the method probes the nucleus of atoms—in the case at hand, the hydrogen nucleus, also known as a proton; thus, the method name proton-NMR or 1H-NMR. The word "magnetic" implies that a magnet is used in NMR. Indeed, protons are like tiny magnets, and in the presence of a magnetic field, protons align themselves with this magnetic field. The process of magnetic alignment allows one to "see" protons, and so proton-NMR is used to "see" protons in roofing membranes. For example, a "photo" of these protons in KEE-PVC blends is shown in *Figure 1*. The "photo" is a series of lines and mounts—technically an NMR spectrum—which can be interpreted by a trained scientist who decodes the NMR spectrum in the same way that an electrocardiogram of the human heart would be interpreted by a heart speccialist.

NMR ANALYSIS OF KEE-PVC ROOFING MEMBRANES

The NMR spectrum in *Figure 1* shows many signals, including, from left to right, an internal reference, PVC, a solvent, and KEE. The internal reference, TCNB (1,2,4,5-tetrachloro-3-nitrobenzene), shows a strong signal near 8.2 parts-per-million (ppm); TCNB

Sample I.D.	Actual (wt %)		NMR (wt %)	
	KEE	PVC	KEE	PVC
1	60.14	39.86	60.95	39.05
2	50.97	49.03	51.72	48.28
3	50.08	49.92	50.57	49.43
4	50.20	49.80	51.44	48.56
5	41.16	58.84	42.19	57.81
6	30.75	69.25	31.69	68.31
7	19.95	80.05	22.18	77.82
8	20.47	79.53	22.78	77.22
9	19.78	80.22	22.01	77.99

Table 1 – Actual and measured PVC and KEE contents from Method A in ASTM D8154.

Step	
1.	Extract the plasticizer in hexane.
2.	Dissolve the membrane in THF.
3.	Separate the fillers by centrifugation.
4.	Precipitate the polymers with cold methanol.
5.	Filtrate the precipitated polymers.
6.	Iterate steps 2 to 5 twice more.
7.	Dry the isolated blend of KEE and PVC.

Table 2 – Step-wise procedure to isolate and purify KEE and PVC for NMR analysis.

allows for a quantitative assessment of the composition. Its signal strength, known as the integration beneath the curve, is related to its mass in the mixture, and it is shown in red in *Figure 1*. Its signal is generally set to 100. Signals specific to PVC alone arise between 4.2 and 4.7 ppm. Signals between 0 and 3 ppm arise from both PVC and KEE, and they are not useful for quantitative analysis because they overlap. In fact, only non-overlapping signals are used for completing a quantitative analysis.

As such, and as described in ASTM D8154, the NMR integration values from the TCNB and lone PVC signals are used to calculate the PVC molar content. From the molar content of PVC, the percent mass of PVC is calculated as per *Equation 1* and the percent KEE content is taken as 100% – PVC.

Table 1 shows results of nine mixtures of PVC and KEE as measured by ASTM D8154, Method A. For blends with 20% KEE, the measured KEE content is within 2.2% of the actual content. For blends with 50% KEE or more, where the KEE signal is stronger, the measured KEE content is within 1.2% of the actual value.

ASTM D8154 provides for two quantitative methods to assess the content of KEE in blends with PVC. In Method A, the polymer ratio is obtained from the analysis of a single sample, and the approach may be most useful in quality control. Method B requires a calibration curve, the slope

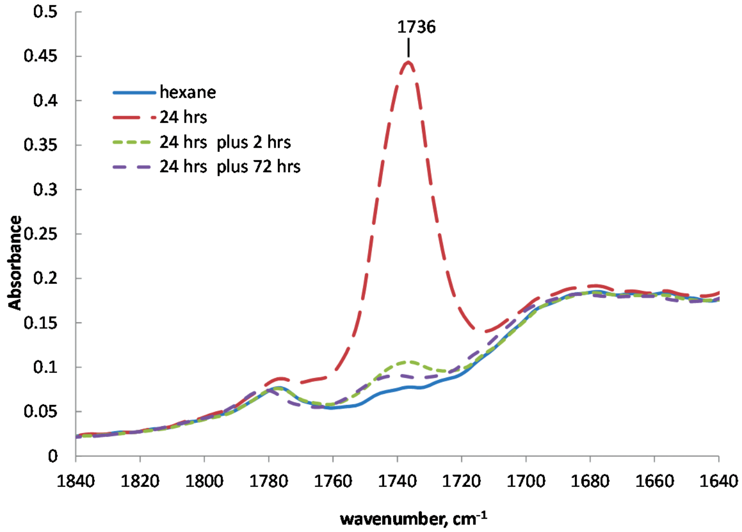

Figure 2 – Portion of FTIR spectrum of hexane and hexane extracts after different extraction times. The plasticizer extracted with hexane shows a signal at 1736 cm^{-1}.

of which provides for a correction factor applied to the PVC signal. The accuracy of Method B is better than 0.75%, and it may be best used for research and development or investigative work.

SAMPLE PREPARATION

ASTM D8154 is based on solution NMR; that is to say, PVC and KEE must be dissolved to provide for sharp NMR signals (*Figure 1*). Solution work also allows for the use of an internal reference that enhances accuracy of results. PVC and KEE are readily dissolved in deuterated tetrahydrofuran (THF-d8) for NMR analysis, but roofing membranes also contain non-soluble stabilizers, flame retardants, antioxidants, and process additives that can all affect the resolution of the NMR signals and reduce the accuracy of the quantitative analysis. All these foreign materials need to be removed to ensure useful test results.

To obtain KEE+PVC blends free of formulation materials (which could affect the quantitative assessment of KEE), the two polymers are isolated from the original roofing product. *Table 2* shows the step-wise approach used in ASTM D8154 to isolate and purify the polymer blend.

In Step 1, the extent of extraction in ASTM D8154 was validated by means of Fourier-transform infrared spectroscopy (FTIR), which allows for monitoring the plasticizer signal (*Figure 2*). In Step 2, dissolution time is not constant; it depends on blend composition. Optical microscopy is thus used to determine appropriate dissolution times for KEE-PVC blends (*Figure 3*). In the ASTM method, microscopy is used to ascertain that total polymer dissolution has been achieved.

IDENTIFICATION AND EFFECT OF ROGUE POLYMERS

A rogue polymer is an undue substitute of KEE. In the NMR method developed to quantify KEE in blends with PVC, the PVC content is measured against the internal standard, whose content is precisely known; and the KEE concentration is obtained as 100% – PVC%. It follows that questions may arise on the effect of the presence of a third polymer in the blend—a "rogue" polymer—on the quantification of KEE. Can the presence of a rogue polymer be identified? Can such a polymer be inadvertently identified as KEE?

To answer these questions, blends of PVC-KEE with a third polymer were prepared and compared to a control blend with PVC and KEE alone. The third polymer was either chlorinated polyethylene (CPE) or nitrile rubber, both of which are polymers that might be identified as KEE. Even though both nitrile rubber and CPE are sparingly soluble in THF, sufficient material dissolves to provide a fingerprint trace in 1H-NMR.

Figure 4 shows the liquid-state proton NMR spectra for blends with and without the presence of a rogue polymer. The presence of a rogue polymer can readily be determined by NMR because of the appearance of signals atypical of KEE-PVC blends. Nitrile rubber, for instance, shows NMR signals around 5.5 ppm, whereas CPE shows a signal near 3.9 ppm.

CONCLUSION

ASTM D8154 is of interest to material suppliers, building owners, and building officials. It is an effective method to assess the KEE content in roofing fabrics made

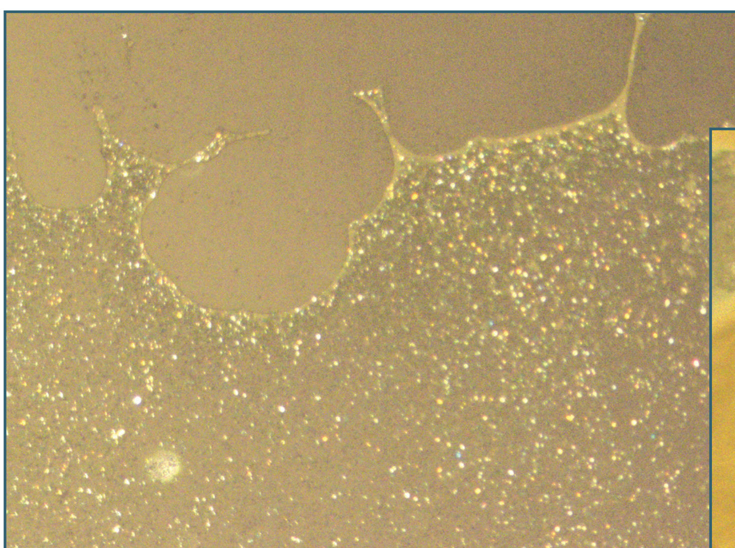
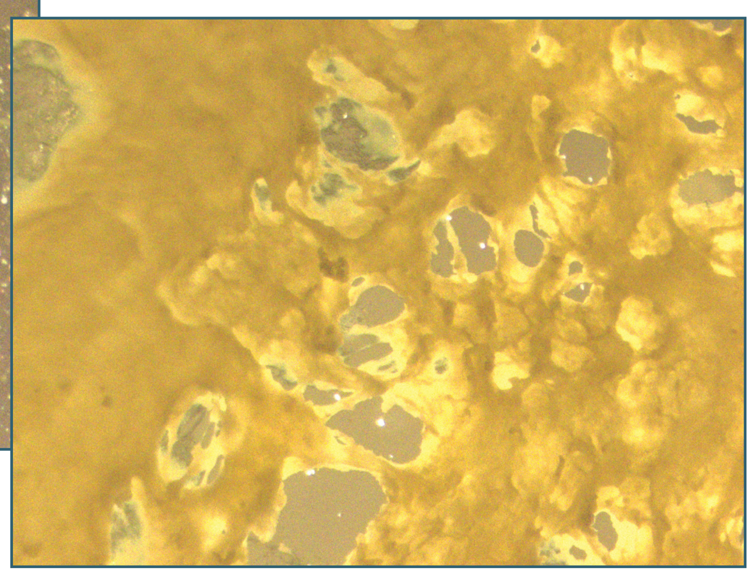

Figure 3 – Microphotographs of two KEE-PVC blends after 1 hour in THF: dissolved (above) and partly dissolved (right).

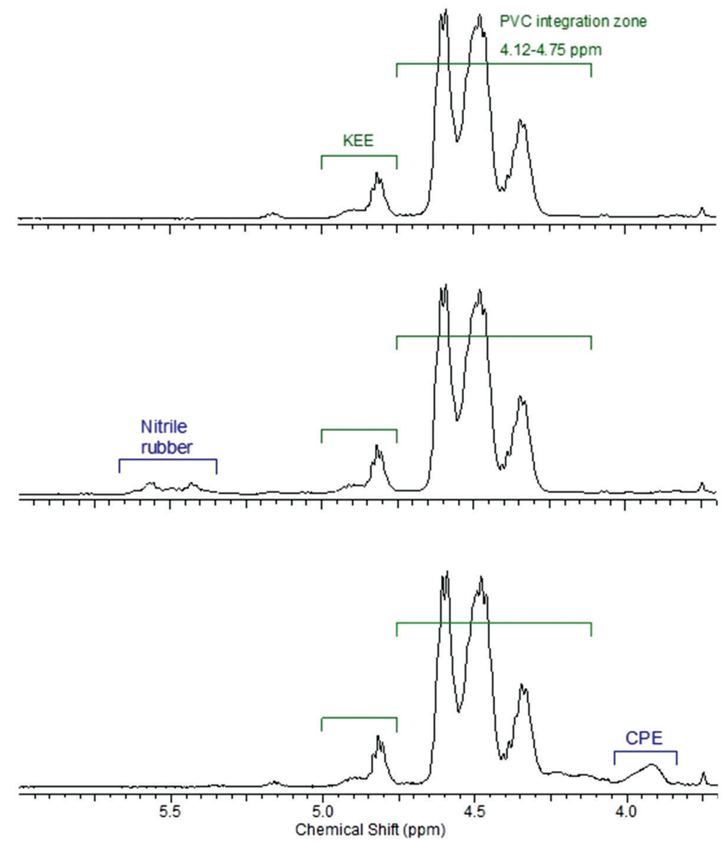

Figure 4 – 1H-NMR spectra for the control blend (top), the nitrile blend (middle), and the CPE blend (bottom).

with KEE and PVC, and it serves to support specification ASTM D6754, which requires a minimum of 50% mass of KEE in KEE+PVC roofing fabrics.

ASTM D8154 allows for the use of two solution-state proton-NMR methods: Method A, the simplest, has an accuracy better than 2.2%; Method B is more protracted, but its accuracy is better than 0.75%.

The experimental work for ASTM D8154 was performed at the Construction Research Centre at the National Research Council of Canada in collaboration with Seaman Corporation. Analysis as per the new ASTM standard method requires extensive investments in equipment—namely, a 400-MHz nuclear magnetic resonance spectrometer, a Fourier-transform infrared spectrometer, and an optical microscope. Analysis is thus best provided by laboratories that typically serve the construction, materials, and chemical industries to provide chemical analyses of products.

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Jean-François Masson

Dr. Masson is a senior research officer in the Centre for Construction Research at the National Research Council of Canada (NRCC). For more than 28 years, he has been involved in the development and testing of polymer-based construction products, combining field and laboratory evaluations. He is the author or coauthor of more than 100 publications, including a book chapter on the aging of polymer-modified asphalt. His current research focus pertains to building envelope materials, including insulation, structural-insulated panels, water-sheathing and waterproofing membranes, and air barrier material and systems.

Gilles Robertson

Gilles Robertson is a senior technical officer with the materials analysis group at the National Research Council of Canada, where he has worked since 1992. His expertise is in polymer synthesis and materials characterization by nuclear magnetic resonance, infrared spectroscopy, and thermal analysis. Robertson earned his degree in chemistry at the Université de Sherbrooke in Quebec, Canada, and has over 27 years of experience in research and development.

Peter Collins

Peter Collins is a technical officer in the Façade Systems and Products Group at the NRCC. He has a bachelor's degree in chemistry from the University of Waterloo and 30 years of experience in evaluating the chemical and physical durability of products and systems in the building envelope. He specializes in spectroscopy, rheology, thermal analysis, and the accelerating aging of construction products. He has authored over 120 research publications in peer-reviewed journals and conferences, client reports and trade magazines. Before joining the NRC, he worked for two years as a formulation chemist at a major construction chemicals manufacturer.