

# RECOVERY OF PHENOLIC MONOMERS FROM INDUSTRIAL NOVOLAC PLASTICS

Stephen S. Kelley, Carolyn C. Elam, Robert J. Evans, and Michael J. Looker  
Center for Renewable Chemical Technologies and Materials  
National Renewable Energy Laboratory  
1617 Cole Blvd., Golden, CO 80401

**Keywords:** Plastic recycling; pyrolysis; phenol formaldehyde resins.

## Introduction

High performance thermoset composites used by the automotive, electronics and other industries are produced in large volumes using high value monomers. Resins used in thermoset composites include novolacs, crosslinked polyesters, epoxies, and polyarylates, and blends and alloys containing these components. These resins frequently contain aromatic monomers that provide the superior mechanical and thermal properties that are required for composite applications. Aromatic monomers are generally more expensive and have a higher embodied energy than most other classes of monomers (1).

Resins used in thermoset composites are generally viewed as non-recyclable. This perception exists for a variety of reasons including the presence of chemical crosslinks, inclusion of mineral fillers, and blend formulations that include a variety of different resins. These features prevent the use of traditional recycling techniques such as physical separation and melt extrusion, or simple chemical hydrolysis. Burning these composites for energy recovery or grinding into a flour for use as a filler does not provide any significant economic value. Landfilling is the most common route for disposal, illustrating the need for novel processes for the recovery and reuse of the monomers used in thermoset composites.

Selective pyrolysis has been demonstrated to be an effective method for the recovery of monomers or high-value chemicals from complex mixtures of waste plastics. Selective pyrolysis takes advantage of differences in the strengths of chemical bonds, and the potential for using catalysts and reactive atmospheres to selectively break specific bonds in the backbone of high molecular weight plastics.

Selective pyrolysis has been applied to novolac composites for the recovery of phenol and substituted phenolics. Novolac composites typically contain 30-50 percent organic resin. Inorganic fillers are added to improve mechanical properties and reduce the overall cost of the composite. Previous work on pure novolac resins has shown that the major pyrolysis products are phenol, ortho- and para-cresol, 2,4- and 2,6-xylenols, and some 2,4,6-trimethylphenol (2-5). To the best of our knowledge there is no work in the open literature on how inorganic fillers may effect the pyrolysis of novolac resins or the behavior of complex commercial thermosets. The goal of this work is to address these questions.

## Experimental

Samples were supplied by member companies of the Phenolics Division of the Society of Plastics Industries. These samples represent the expected variability of fillers and formulations found for commercial novolac resins. The composition of the samples is shown in Table 1.

Novolacs were characterized using Molecular Beam Mass Spectrometry (MBMS) and Thermal Gravimetric Analysis (TGA). The MBMS is a versatile tool that can be used for real-time sampling of complex gas streams produced by high-temperature processes, and has been used to characterize a wide variety of plastics and biomass samples (6-8). Free-jet expansion of the high-temperature gases and vapors allows for the effective quenching of species in their sampled state (9) making MBMS a valuable tool for identifying complex mixture of products produced in pyrolysis.

The MBMS analysis were performed in triplicate using a quartz tube reactor. Helium was used as the carrier gas. Samples were in the range of 20-50 milligrams and the pyrolysis temperature for most of these experiments was 600°C, although selected samples were also pyrolyzed at 450°C. The complexity of the product suite makes interpretation of the results difficult, so multivariate statistical techniques are used to identify and characterize trends and variable interactions, resulting in greatly enhanced data interpretation.

A TA Instruments TGA 2950 was used to characterize weight losses using nitrogen as a purge gas. Samples sizes were between 10-12 mg and the heating rate was 20°C/min. Activation energies were determined with variable heating rates (10,11).

## Results and Discussion

**TGA Analysis** - The results from the TGA studies were very complex due to the wide variety of fillers and commercial resin formulations. However several general trends in the weight loss data could be identified. The first derivative of the TGA weight curves of several of the samples are shown in Figure 1. Sample 1 contains resin and high amount of alumina filler, and shows a relatively sharp weight loss peak at about 284°C, which is assigned to bound water in the alumina, and a broad weight loss peak centered around 533°C, which is assigned to decomposition of the novolac resin. Sample 4 contains resin and wood filler, and shows a large weight loss peak at 380°C, which is assigned to decomposition of the carbohydrate component of the wood filler, and a broad weight loss peak between 482°C and 560°C which is assigned to both the lignin component of the wood and the novolac resin.

Sample 3 is a more typical resin formulation and shows more complex behavior. The weight loss curve for sample 3 shows at least four separate peaks, and several shoulders. The low temperature peak at about 269°C is assigned to loss of bound water from the inorganic filler, while the peak at 379°C is assigned to decomposition of the carbohydrate in the wood filler. The large broad peak centered around 517°C is assigned to decomposition of the novolac and lignin in the wood filler, while the high temperature peak at 678°C is assigned to decomposition of the calcium carbonate filler. All of the TGA curves showed a broad weight loss in the 500-600°C range, consistent with decomposition of the novolac resin (4,5). Thus, MBMS analysis of all the resins was conducted at 600°C.

**MBMS Analysis** - Multivariate analysis techniques allow for extensive data manipulation and interpretation. The average MBMS spectra, taken over all of the samples, is shown in Figure 2. The spectra shows that the major products seen at mass numbers of 94, 108, 122, and 136 are phenol, cresols (positional isomers were not distinguishable with the technique used), xylenols, and trimethyl phenol, respectively. A series of dimeric species are also seen in the mass region 180 to 230.

More detailed analysis of the MBMS spectra showed distinct differences due to the chemical nature of the novolac and the presence of specific fillers. The factor spectra relate to the chemical nature of the novolac resin is shown in Figure 3. This factor indicates the variability in the concentration of substituted phenols. Samples positively correlated with this factor have higher concentrations of phenol and cresol relative to xylenol and trimethyl phenol than do the rest of the samples. These variations are consistent with more methylene bridges connecting the phenolic rings or differences in the degree of crosslinking. Resins with more connecting methylene bridges have a higher degree of crosslinking.

An additional factor was related to the chemical structure of the novolac resins. This factor (not shown) is related to high concentrations of phenol relative to the other reaction products. This factor appears to be associated with the evolution of free phenol, phenol which is not fully incorporated into the polymer, but is physically trapped within the cured resin. Time-resolved results that show phenol is released from some samples at temperatures well below pyrolysis temperature.

The relationship between the degree of crosslinking and the amount of free phenol is shown in Figure 4. (This figure shows each of the individual data points, demonstrating the reproducibility of the MBMS experiment.) There are significant differences in the degree of crosslinking, as determined from the ratio of non-substituted and mono-substituted phenolics compared to di- and tri-substituted phenolics, across the samples. Samples with the highest degree of crosslinking and least amount of unreacted phenol are found in the upper, left-hand quadrant, such as samples #1 and #3. Surprisingly, the degree of crosslinking in the fully cured resin is not correlated with the amount of hexamethylene tetraamine (hexa) 'crosslinker' added to the resin. Hexa is a source of formaldehyde that can react with free sites on the phenolic rings and complete the conversion of the low molecular weight, melt processible resin into a fully cured product. Higher novolac/hexa ratios should result in a lower degree of crosslinking and produce fewer of the di- and tri- methylated phenols. In this case the extent of crosslinking appears to be related to the chemical structure of the original resins produced by different manufacturers rather than the novolac/hexa ratio. Samples 1-5, all produced by one manufacturer, show a higher degree of crosslinking than do samples 16-20, which were all produced by a second manufacturer. It is also worth noting that the sample with the highest amount of free phenol was formulated with a large amount of hexa. Thus, it appears that hexa is not capable of capturing all of the free phenol that is contained in the resin.

The ability to detect the presence of organic fillers is shown in Figure 5. In this figure the degree of crosslinking and the presence of wood filler are compared. Examination of the average spectra shows that the 'wood filler' response is due to

guaiacols that are generated by the decomposition of the lignin present in the wood. All of the samples with negative loadings for this factor did not contain any wood filler, while all of the samples with positive loadings contain varying amounts of wood filler.

The effect of a second filler, alumina, on the chemical composition of the pyrolysis products was also examined. Under some conditions alumina can act as a catalyst and could influence the chemical composition of the reaction products. However, for this set of novolacs, the chemical composition of the reaction products did not appear to be affected by the presence of alumina. Activation energies for the high temperature peak seen in samples 1 and 4 were also calculated. The activation energies were 215 kJ/mol and 230 kJ/mol for samples 1 and 4, respectively. These activation energies are essentially the same, indicating that the alumina filler present in sample 1 does not influence the decomposition of the novolac resin. These activation energies are similar to those measured for phenol-formaldehyde resins. (3).

## Conclusion

The results of this study show that valuable, monomeric phenols can be recovered from the pyrolysis of cured commercial novolac resins. The major phenolic products are phenol, cresols, xylenols and trimethyl phenol, along with a small amount of dimeric species. The novolac/hexa ratio does not appear to have a significant an effect on the relative ratio of the various substituted phenols while the source of the original resin does influence the product composition. The presence of organic fillers can be easily detected and the pyrolysis degradation products from these fillers may complicate isolation of the desired phenols. The presence of inorganic fillers such as alumina did not influence the chemical composition of the pyrolysis product.

## Acknowledgements

The support of the U.S. Department of Energy Office of Industrial Technology and Mr. Charlie Russomanno is gratefully acknowledged.

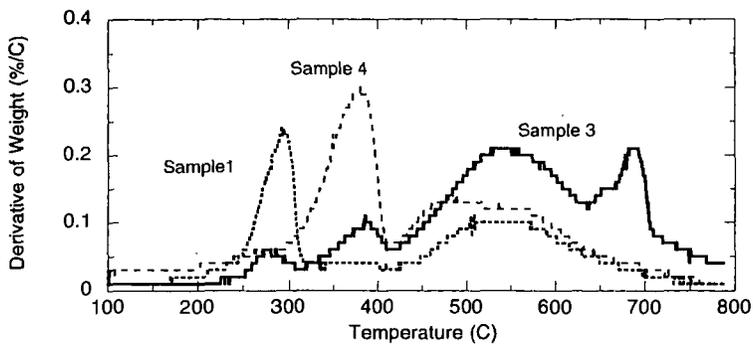
The assistance of member companies of the Phenolics Division of the Society of the Plastics Industry is also gratefully acknowledged.

## References

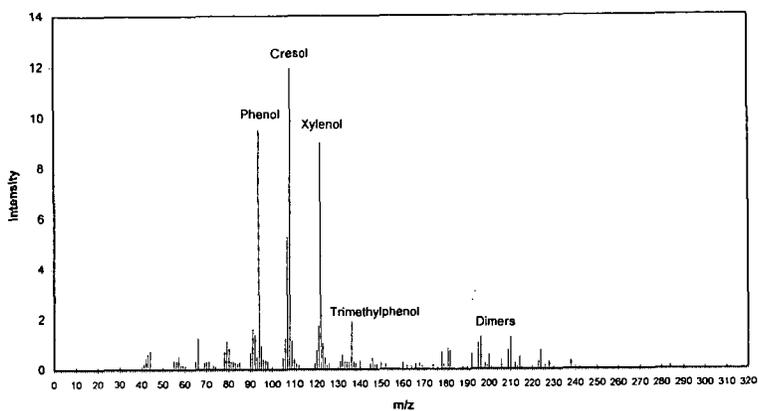
1. Lipinsky, E. S., Ingham, J. D., Brief Characterization of the Top 50 Commodity Chemicals, DOE report ILA 207376-A-H1, Batelle Memorial Institute, (1994)
2. Blazso, M., Toth, T., J. Anal. and Appl. Pyrolysis, 10, 41, (1986)
3. Cohen, Y., Aizenshtat, J. Anal. and Appl. Pyrolysis, 22, 153, (1992)
4. Shulman, G. P., Lochte, H. W., J. Appl. Polym. Sci., 10, 619, (1966)
5. Chang, C., Tackett, J. R., Thermochemica Acta, 192, 181, (1991)
6. Chum, H. L., Evans, R. J., WO 92/2169, (1992)
7. Evans, R. J.; Tatsumoto, K.; Czernik, S.; and Chum, H. L., Proceedings of the RecyclingPlas VII Conference: Plastics Recycling as a Business Opportunity, 175 (1992)
8. Evans, R. J. and Milne, T. A., Energy & Fuels, 1(2), 123 (1987); 1(4), 311 (1987)
9. Atomic and Molecular Beams, Vol. 1, G. Scoles, ed., Oxford University Press, New York, 14-53, (1988)
10. Flynn, J.H., Wall, L. A., Polym. Lett., 4, 323, (1966)
11. Krizanovsky, L. J. Therm. Anal., 13, 571, (1978).

Table 1. Composition of Formulated Novolac Resins

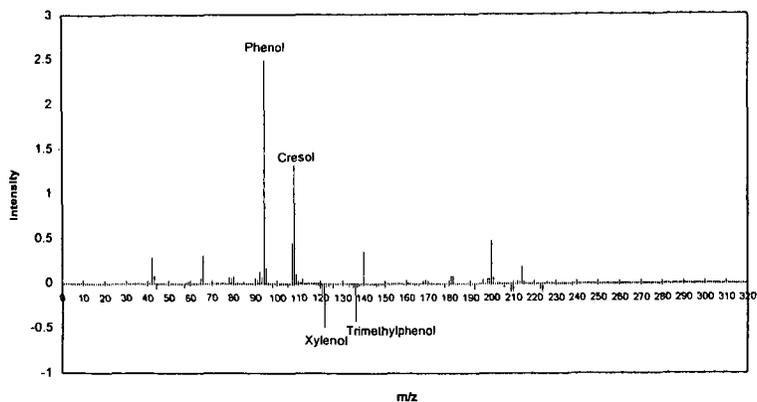
Resin Component	Sample Number									
	1	2	3	4	5	16	17	18	19	20
Novolac	35	36	45	54	35	34	49	35	40	35
Hexa	9	4	8	10	9	4	4	4	8	10
Wood	0	5	4	35	33	14	39	0	13	4
CaCO <sub>2</sub>	0	0	5	0	0	0	0	14	10	0
Clay	15	15	25	0	10	39	0	0	10	0
Alumina	40	15	5	0	10	0	0	38	0	4
Talc	0	15	5	0	0	0	0	0	10	39
Glass	0	5	0	0	0	0	0	0	5	0
Ca(OH) <sub>2</sub>	0	1	1	0	0	6	6	6	1	6
Brown Umber	0	2	0	0	2	2	0	2	2	0
Nigrosine	0	0	1	0	0	0	1	0	0	1
Steric Acid	1	1	1	1	1	1	1	1	1	1



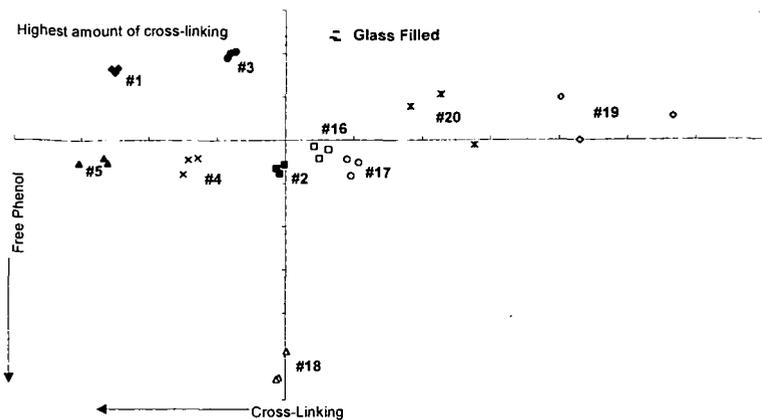
**Figure 1** - DTGA Curves for Commercial Novolac Samples: a) Sample 1, b) Sample 4, and c) Sample 3.



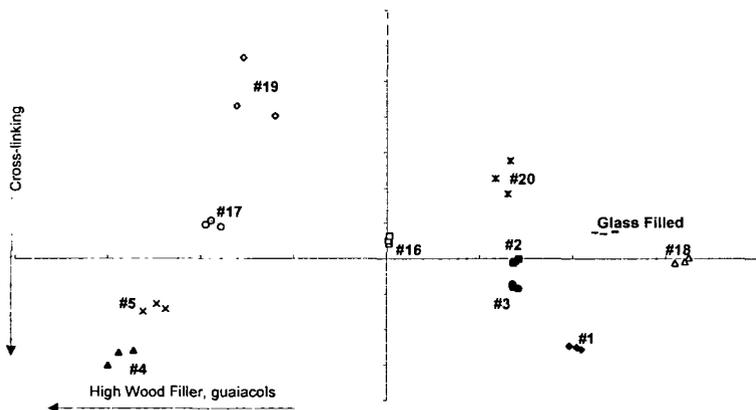
**Figure 2** - Averaged MBMS spectra, taken over all of the samples, shows major phenolic products (phenol, cresol, xylenols, and trimethylphenol) and the characteristic dimer region.



**Figure 3** - Factor related to the degree of crosslinking. Those samples positively correlated with this factor have higher concentrations of less substituted phenolics and are considered to be "less" crosslinked than the other samples in the dataset.



**Figure 4** - Plot showing the relationship between free phenol and the degree of crosslinking. Those samples in the upper, left-hand quadrant are those with the highest degree of crosslinking and the least amount of unreacted phenol. Samples 1-5 were prepared by one manufacturer, while samples 15-20 were prepared by another. This shows that manufacturer has a greater influence on degree of crosslinking than does the amount of crosslinker or filler.



**Figure 5** - Comparison of samples with and without wood filler. The presence of guaiacols in the pyrolysis spectra is indicative of the decomposition of the lignin from the wood filler.