A Fundamental Study on the Effect of Chain Length, Functionality and Aromaticity of the Aromatic Polyetherols in Rigid Polyurethane Foams

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ABSTRACT

Rigid foams typically use low-molecular weight multi-functional polyols with multi-functional isocyanates leading to close-meshed, highly cross-linked structures and therefore, have high strength. Polymeric MDI (PMDI) with functionalities ranging from 2.6-2.8 are referred to as Part A. The main components of Part B are the polyols with short-chain and high functionalities ranging from 3 to 5.

Aromatic polyols are extensively used in rigid polyurethane foams for their influence on thermal insulation and reaction to fire. In general, the aromaticity of the polyol (Part B) stems from the use of aromatic polyesters (APP). A vast majority of APP have a functionality of 2 which necessitates the use of polyether polyols (PEP) with significantly higher functionality to achieve required mechanical properties. However, the mechanical property improvement comes at the expense of reducing foam thermal insulation and reaction to fire.

Resonance™ aromatic polyether polyols or polyetherols (APEP) are designed with aromaticity levels at or higher than typical APP along with functionalities at or higher than APP. Owing to their aromaticity and tailored functionalities and hydroxy equivalent weights, the Resonance™ APEPs can replace, partially or fully, high functional PEPs as well as some or all of the difunctional aromatic polyesters.

The experimental study demonstrates the effect of altering the level of aromaticity, chain length and functionality in the formulations using Resonance™ polyether polyols and blends. System properties such as viscosity of the mix and foam reaction profile along with rigid foam properties will be discussed. Study would also include the solubility of various blowing agents in Resonance™ aromatic polyetherols and a review of the key benefits of incorporating these in the rigid foams suitable for a variety of applications such as building industry, appliances, heated pipelines etc.

INTRODUCTION

Polyols furnish the hydroxyl group (OH group) required for the reaction with isocyanates and therefore, crucially influence the properties of the final urethane polymer. The most common and commercially relevant sources of hydroxyl groups are polyether polyols or polyetherols (PEP) and polyesters. The most common polyetherols are triols and polyols of higher functionality and are based on starter molecules such as glycerin, trimethylolpropane, sorbitol, sucrose, etc. Polyetherols with hydroxyl numbers (OHV) in the range of 350-600 are quite common for rigid foams.[1]

Polyols being one of the major ingredients in a foam dictates whether the foam will be rigid or flexible, brittle or nonbrittle and the extent of permeability to gas and moisture. The many properties of the foam such as processability, dimensional stability, friability, heat resistance, compressive strength etc. can be influenced by the polyol due to its hydroxy equivalent weight (HEW) and functionality (f). Several published literatures report the effect of varying the HEW and f in formulations that contain aromatic polyester polyols (APP) and PEPs such as pentaerythritol, sorbitol, sucrose, glycerol etc.[1] However, relatively less is known about the impact of introducing aromatic polyether polyols into PUR and PIR formulations and the effect of their physiochemical attributes on the properties of rigid foams.

Owing to their aromatic content, APPs are usually included in the formulation to improve reaction to fire and are widely used in polyurethane insulation foams.[2] However, they are limited in terms of their functionality and hence, high functional polyether polyols are often required to balance properties such as dimensional stability. When PEPs are added to improve mechanical properties, increasing levels of phosphorous or halogen-based flame retardants are added to the formulation. Halogenated fire retardants (FR) are under regulatory scrutiny.

Bakelite's Resonance™ aromatic polyether polyols (APEP) are a class of polyols that combines the aromaticity of an APP with the higher functionality of the common polyetherols. In this study, we wish to report the effect of chain length (HEW), aromaticity and functionality of some of these APEPs upon introducing them into PUR formulations on rigid foam properties. The study illustrates the value of these APEPs when it comes to maximizing flame resistance while maintaining mechanical properties or even improving them in some cases. This paper also shows the solubility of variety of hydrocarbons and halogen-based blowing agents in Resonance™ aromatic polyetherols.

The aromaticity of Bakelite's aromatic polyols varies between 33 and 75% across the Resonance™ PL91, PM91, TM91, and PM92 series. The Resonance™ TM (or TL) series are very novel in that they contain aromatic nitrogen coupled with a very high functionality which contribute to fast reactivity, improved mechanicals, and outstanding reaction to fire.[4,5] Products in the PM92 & TM91 series are not part of this research paper.

Previously, PL91-203 and PL91-205 APEPs were shown to effect significant improvements in reaction to fire (RTF) by replacing 100% of the high-functional sugar-based PEPs and partial replacement of APP in PUR formulations.[6] The APEPs used in this current study are the PL91-203, PM91-009, PL91-252 and PL91-650. The aromaticity and functionality of these polyols range from 33-48% and 2.6 to 3.6. While the polyols in the PL-series are liquids, PM91-009 is a low melting solid at room temperature.

EXPERIMENTAL

Materials & Test Methods

Table 1: List of raw materials used for the solubility study

Blowing Agents	Chemistry	Supplier		Resonance™	Chemistry	Supplier
Solstice® LBA	Hydrofluoroolefin (HFO)	Honeywell		PL91-252	APEP, OHV=300	Bakelite Synthetics
Enovate® 245fa	Hydrofluorocarbon	Honeywell		PL91-203	APEP, OHV=240	Bakelite Synthetics
Opteon™ 1100	Hydrofluoroolefin (HFO)	Chemours		PL91-650	APEP, OHV=240	Bakelite Synthetics
Cyclopentane	Hydrocarbon	Aldrich		PL91-450	APEP, OHV=225	Bakelite Synthetics
Isopentane	Hydrocarbon	Aldrich		PL91-507	APEP, OHV=175	Bakelite Synthetics
n-Pentane	Hydrocarbon	Aldrich		PL91-550	APEP, OHV=124	Bakelite Synthetics

The solubility of blowing agent (BA) with various Resonance™ polyols was measured by weight gain method: Excess amount of BA was vigorously mixed with known amount of polyol at 60-70°C in a sealed pressure tube. After cooled to room temperature and equilibrated overnight, the pressure tube was opened, and excess amount of BA was removed. The sample was then re-weighed, and the solubility was calculated based on the dissolved amount of BA in polyol.

Table 2: List of polyols and isocyanate used for the PUR study replacing 3f PEP

Raw Material	Aromaticity (%)	f	HEW	Chemistry	Supplier
APP	ca. 28	2.0	234	PET recycled	COIM
Sugar-based PEP	-	4.8	112	Propoxylated glycerin/sugar	Various
PEP	-	3.0	224	Propoxylated glycerol	Various
Glycerol	-	3.0	31	Glycerin as is	Various
Isotem P600	ca. 61	2.85	--	Polymeric Diphenylmethane Diisocyanate	BCI
Resonance™ PM91-009	48	2.6	137	APEP	Bakelite Synthetics
Resonance™ PL91-203	33	2.6	234	APEP	Bakelite Synthetics
Resonance™ PL91-252	41	2.6	187	APEP	Bakelite Synthetics
Resonance™ PL91-650	33	3.6	234	APEP	Bakelite Synthetics

Other ingredients include the standard materials used in PUR such as surfactants, blowing agents and flame retardants. Water/ n-pentane were the blowing agents; TEP/TCPP were used as FRs. Iso index was kept at 120.

Table 3: List of polyols and isocyanate used for the PUR study replacing ~5f Sugar

Raw Material	f	Chemistry	Supplier
APP	2.0	PET recycled	COIM
Sugar-based PEP	4.5	Propoxylated glycerin/sugar	Various

Mannich polyol	4.0	Mannich base	Various
Isotem P600	2.85	Polymeric Diphenylmethane Diisocyanate	BCI
Resonance™ PM91-009	2.6	APEP	Bakelite Synthetics
Resonance™ PL91-203	2.6	APEP	Bakelite Synthetics
Resonance™ PL91-252	2.6	APEP	Bakelite Synthetics

All foams were prepared via hand-mixing using a high-torque mixer at 3,000 rpm speed. In this stage foams were prepared at 250-gram scale. Polyol components and isocyanate components of the foam systems were put in a plastic cup and mixed for 10 seconds. Afterwards, the mixture was transferred into a plastic bag before the cream time and let free rise. Cream time, gel time and tack-free time were measured on all foams. Isocyanate excess was kept constant in all the trials. Pentane content and number of moles of gas generated were the same in all the tests. Fire retardant content was also kept constant in % in total foam. Formulations were optimized to meet gel time and density of the reference formulation.

The optimized formulations were also used to prepare free-rise blocks. The polyols and isocyanate components were put in a wood mold having a volume of 13L. Foam blocks were cut for testing after aging at room conditions for one day after preparation.

The following tests were made on the foam:

- Dimensional stability (according to ISO 2796) at 100°C (48h), 70°C 90% RH (48h) and RT (30 days). Sample size: 100mmX100mmX25mm. The test at 70°C/90% RH was also run for 7 days.
- Compressive strength (according to EN 844). Sample size: 50mmX50mmX50mm.
- Reaction to fire (RTF) test B2 (according to DIN 4102). Sample size: 90mmX200mmX20mm.

Dimensional stability was tested measuring the specimen with a micrometer before and after the conditioning.
Compressive strength was measured on all the dimensions of the specimen using a LLYOD LR 30K dynamometer with a 5KN load cell.
Reaction to fire was tested using a closed fume cupboard equipped with a small Bunsen burner.

RESULTS and DISCUSSION
Solubility of various blowing agents in Resonance™ polyether polyols

Table 4: Solubility of BAs in Resonance™ polyetherols

Color represents solubilty range of BA in Resonance PL-series polyols			1-5%	5-10%	10-15%	> 15%
Resonance™ Polyol	Solstice® LBA	Enovate® 245fa	Opteon™ 1100	7/3 Cyclo/Iso pentane	Cyclopentane	n-Pentane
PL91-252, OHV=300						
PL91-203, OHV=240						
PL91-650, OHV=240						
PL92-450, OHV=225						
PL91-507, OHV=175						
PL91-550, OHV=124						

Blowing agents are compounds that can be gas or liquid that provide cellular structure to the foam and a good blowing agent is considered to have considerable solubility in the polyol.[7] In addition to environmental concerns, the solubility of the BA in the polyol is an important criterion in selecting the right one for the desired application. The degree of foaming and cellular structure is dictated to a large extent by the solubility of the BA.[8]

It is evident from Table 4 that blowing agents of different chemistries were quite soluble in Resonance™ PL-polyol series. The solubility of these blowing agents were found to be anywhere in the range of 3% to > 15%. Overall, the

Resonance™ polyols exhibit greater affinity towards halogen containing blowing agents, particularly towards the Solstice LBA, an HFO. Furthermore, polyols with lower OHV tends to have stronger affinity to halogenated blowing agents. For example, HFOs dissolve particularly well in both PL-507 and PL-550. This is due to the higher polarity of these polyols that makes them have particularly stronger affinity towards HFOs more so than others.

Resonance™ polyether polyols replacing 3f PEP in PU Rigid Foam

Table 5: Polyol amounts wherein 3f PEP replaced by Resonance™ polyetherols

Designation	Ref	Mod. A	Mod. B	Mod. C	Mod. D	Mod. E
Aromatic Polyester f=2.0, OHV 240	15	15	15	15	15	15
Aliphatic Polyether f=4.8, OHV 500	26.5	26.5	26.5	26.5	26.5	26.5
Glycerol f=3, OHV 1827	6.5	6.5	6.5	6.5	6.5	6.5
Aliphatic Polyether f=3.0, OHV 250	25	-	-	-	-	-
Resonance PL91-203 f=2.6, OHV 240	-	25	12.5	-	-	-
Resonance PM91-009 f=2.6, OHV 410	-	-	12.5	25	-	-
Resonance PL91-252 f=2.6, OHV 300	-	-	-	-	25	-
Resonance PL91-650 f=3.6, OHV 240	-	-	-	-	-	25

The PUR reference formulation in the above table contains four different polyols. An APP and two PEPs and glycerol. The main theme of this study is to replace the 3f PEP with Resonance™ APEPs and in doing so, to study the effect of varying the OHV, f and aromaticity of the APEPs on the rigid foam properties such as reaction to fire (RTF), compressive strength and dimensional stability.

Table 6 provides the formulation details that includes, in addition to the polyol amounts, the quantity of catalysts, FRs, BAs, isocyanate, iso index, reaction profile, density, etc. The isocyanate quantity had to be adjusted slightly to keep the index constant. Blowing agents and FRs were maintained at same percentage in the foams across all samples. Polycat 5, Polycat 8 and Kosmos 45MEG were used as catalysts. TCPP and TEP blends were used as flame retardants; n-pentane and water were used as blowing agents.

The introduction of Resonance™ polyols increased the reactivity of the system. Reduction of catalysts, mainly Polycat 8 brought the reactivity of Resonance™ polyols close to the reference. Formulations were thus optimized for target reaction profile (cream time, gel time) and free-rise density to match the reference. Viscosity of the Part B blends remained nearly the same or increased slightly compared to the reference formulation.

All foams prepared with Resonance™ PL polyols exhibited significantly better RTF in comparison to the reference foam as shown in Figure 1. The flame height for the reference was 16.3 cm, whereas it was between 13.3 to 14.3 cm for the Resonance™ foams. Thus, Resonance™ foams burnt 15-20% lower than the Reference foams and all of them passed the B2 test while the Reference foam failed. There was no significant difference in RTF between the Resonance™ foams.

Figure 1 also demonstrates that the compression strength (parallel to rise) for all the Resonance™ foams were higher than the reference albeit not by a big margin. Modification C, which contains PM91-009 with the highest OHV of 410 exhibited the highest compressive strength of all. Though the Resonance™ polyols used in Mod. A and E have the same OHV of 240, Mod. E exhibited higher compression strength which can be attributed to its higher functionality (3.6 vs. 2.6).

Dimensional stability data are listed in Table 7. For both the 48-hour and after 7-days, all foams exhibited volume reduction. However, overall, Resonance™ foams exhibited less volume change compared to reference. Just as in the case of the compressive strength, Modification C, which contains PM91-009 with the highest OHV of 410 exhibited the greatest dimensional stability of all. Mod. B which is the blend of PL91-203 and PM91-009 and Mod. D, which is PL91-252 with the OHV of 300 had nearly the same dimensional stability which was better than the Reference.

Table 6: Formulation wherein 3f PEP replaced by Resonance™ polyetherols

Materials	Ref.	Mod. A (PL-203)	Mod. B (50/50)	Mod. C (PM-009)	Mod. D PL-252	Mod. E PL-650
Aromatic polyester polyol (f=2)	15	15	15	15	15	15
Propoxylated glycerin/sorbitol polyol (f=4,8)	26.5	26.5	26.5	26.5	26.5	26.5
Glycerol (f=3)	6.5	6.5	6.5	6.5	6.5	6.5
Propoxylated polyol from glycerol (f=3)	25	-	-	-	-	-
Resonance PL91-203 (f=2.6)	-	25	-	-	-	-
Resonance PL/PM 50/50 blend (f=2.59)	-	-	25	-	-	-
Resonance PM91-009 (f=2.58)	-	-	-	25	-	-
Resonance PL91-252 (f=2.6)	-	-	-	-	25	-
Resonance PL91-650 (f=3.6)	-	-	-	-	-	25
Catalyst	1.28	1.05	1.05	1.13	1.05	1.06
Silicone surfactant	2	2	2	2	2	2
Flame retardants (TCPP: TEP blend)	55	55	58.6	59	56.4	55
Blowing agents (n-pentane: water)	8.27	8.25	8.52	8.82	8.48	7.27
Isocyanate Component						
Isocyanate	164	163	170	172	167	164
Iso excess	13.0	13.0	12.8	13.1	13.2	12.9
Iso Index (%)	132	132	131	128	132	131
Reaction Profile and Density						
Cream time (sec)	26	27	27	26	25	24
Gel time (sec)	78	76	79	75	71	72
Tack free time (sec)	130	98	105	94	100	108
Density (Kg/m^3)	35.8	36.0	35.2	35.9	34.8	35.3

Thus, introduction of Resonance™ aromatic polyetherols through replacement of the 3f PEP, regardless of their physio-chemical characteristics, improve the RTF and mechanical properties. Both dimensional stability and compressive strengths data gives a clue that the HEW and functionality of the polyols play a role in dictating the final mechanical properties.

Figure 1: Reaction to Fire and compressive strength (normalized to the reference as 100)
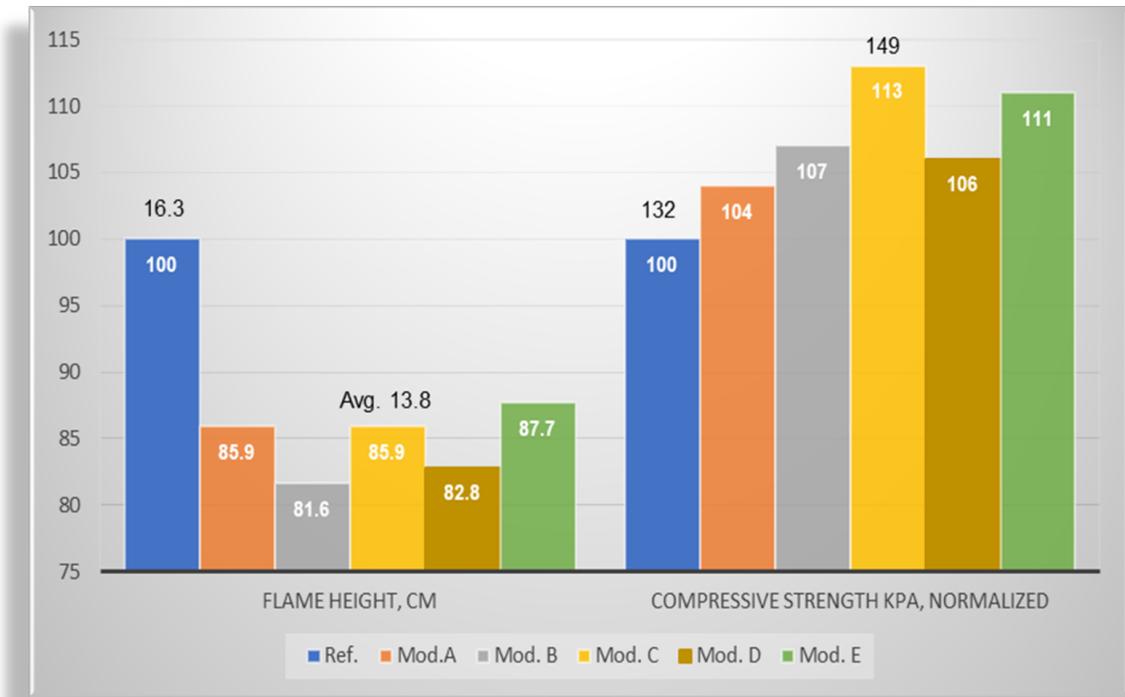
Table 7: Dimension stability ΔVolume (%)

	Ref	Mod A	Mod B	Mod C	Mod D	Mod E
7 days at 70°C/90% RH *	-8.92	-9.50	-6.87	-4.88	-6.20	-9.09
48 hours @ 100°C *	-7.92	-6.60	-4.74	-2.69	-4.75	-6.56

*average of 2 samples

Figure 2 and 3 show the relationship between the ratio of HEW to functionality (HEW/f) of the polyol system and the mechanical properties. Overall, lower HEW/f ratio led to better mechanical properties. From Fig. 2, it is evident that the PL91-203 containing Mod. A with the highest HEW/f had the lowest dimensional stability (not much different from the Ref.) and the PM91-009 containing Mod. C with the lowest HEW/f had the greatest dimensional stability. The Mod. B and Mod. D with similar HEW/f fell in between. However, PL91-650 containing Mod. E seem to be an outlier.

Figure 2: Correlation between HEW/f of the polyol system and dimensional stability
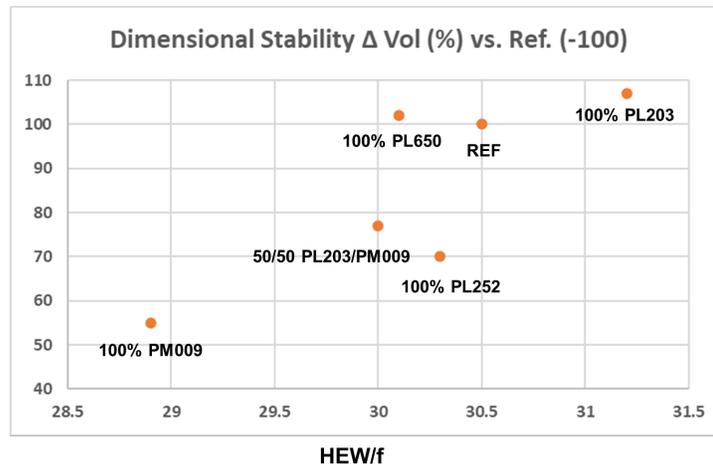
Fig. 3 illustrates similar correlation between HEW/f ratio and compression strength. The compression strength of the foams containing Resonance™ polyols were higher than the reference and, for Resonance™ containing samples, the values in general increase with decreasing HEW/F ratio.

Figure 3: Correlation between HEW/f of the polyol system and compressive strength
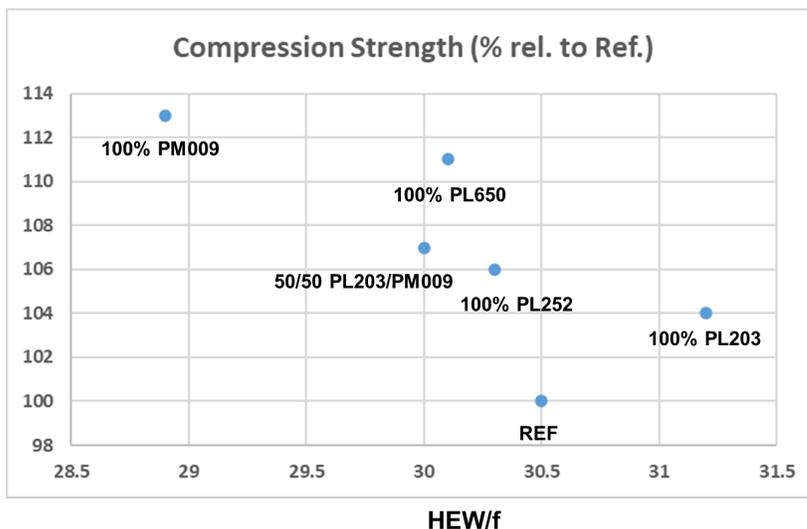
The rationale behind the influence of HEW/f can be understood from the basis of its impact on the cross-link density of the foams. For the same functionality, a lower HEW results in a more compact cross-linking which increases the compression strength of the foam. Mod. E with PL91-650, exhibits slightly higher compression strength than Mod. B and D despite having similar HEW/f ratio. This can be explained by including the % aromaticity of these polyols into the equation. This is illustrated by Figure 4.

Figure 4: The impact of aromaticity, f and HEW on compressive strength
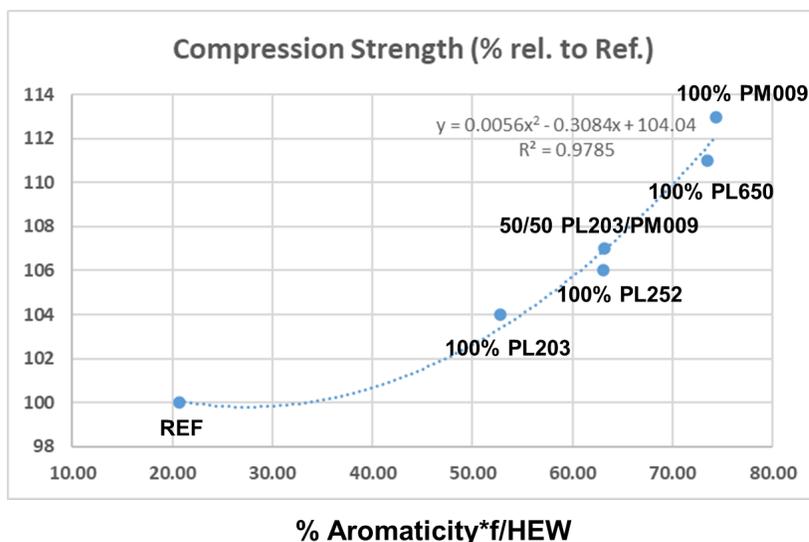
The % Aromaticity (%A) here is that of the polyol system (not including the aromaticity from the isocyanate). And the functionality (f) referred to in Fig. 4 is that of the 3f PEP for the reference (that is being replaced) and the Resonance™ APEPs for Mod. A-E. HEW is for the overall system as before.

The most striking thing to notice in Figure 4 is how significantly the Resonance™ polyols are differentiated from the Reference owing to their high aromaticity. As the value of (%A) x (f)/HEW increase, the mechanical performance increase consistently.

The reference foam whose aromaticity is originating only from the APP has the lowest %A*f/HEW and hence, the lowest compression. Whereas, PL91-650 (Mod. E) and PM91-009 (Mod. C) with the highest %A*f/HEW exhibited the highest compressive strengths of all. The regression for this correlation resulted in > 97%. The power of this correlation is further validated by how close the values were for the Mod. B (the 50:50 blend) and Mod. D (PL91-252). The aromaticity, HEW and functionality of Mod. B which is a 50:50 blend of PL91-203 and PM91-009 is nearly the same as Mod. D which is based on polyol PL91-252 and hence, their mechanical properties were also similar. This study illustrates that Resonance™ APEPs can be mixed or used as is when introducing them into the formulation to achieve the desired results.

The Cone Calorimeter data in Figure 5 shows the significantly lower peak heat release rate (pHHR) for the foams made from Resonance™ polyols Mod. A and Mod. C compared to the Reference foam. This further demonstrates the significant improvement in fire performance upon introduction of the Resonance™ polyols.

Figure 5: Cone Calorimeter data: Peak Heat Release Rate (pHRR)
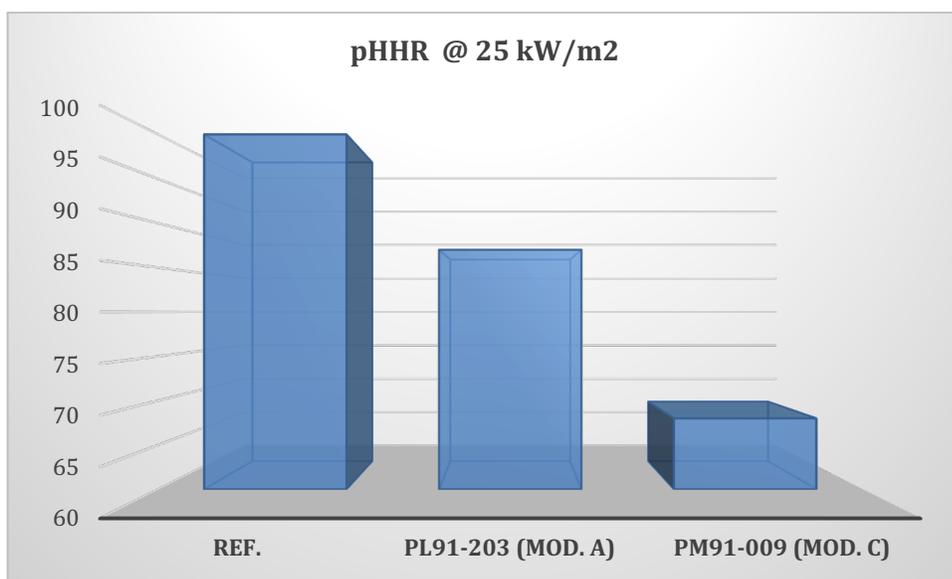
Resonance™ polyether polyols replacing 4.5f sugar-based PEP in PU Rigid Foam

Table 8: Polyol amounts wherein 4.5f Sugar-based PEP replaced by Resonance™ polyols

Designation	Ref	Mod. A2	Mod. B2	Mod. C2	Mod. D2
Ar. Polyester f=2.0	46.56	46.56	46.56	46.56	46.56
Mannich f=4	15.18	15.18	15.18	15.18	15.18
Ali. Polyether (sugar-based) f=4.5	15.18	-	-	-	-
Resonance PL91-203 f=2.6	-	15.18	7.59	-	-
Resonance PM91-009 f=2.6	-	-	7.59	15.18	-
Resonance PL91-252 f=2.6	-	-	-	-	15.18

In this study, a model spray rigid PUR foam formulation was used to evaluate the effect of replacing 100% of the high-functional sugar-based PEP with Resonance™ APEPs- PL91-203 (Mod. A2), PM91-009 (Mod. C2), the PL/PM blend (Mod. B2) and PL91-252 (Mod. D2) on PU system reactivity, foam density, compressive strength and RTF through vertical B2 test and cone calorimetry.

The reference formulation is a mixture of sucrose-based polyol PEP-GS2, an APP and a Mannich polyol which is quite common for a spray foam. Table 8 gives the summary of formulation details related to the polyols used. Table 9 gives the complete summary of the formulation and the results that include reaction profile, density, etc. Due to the higher reactivity of Resonance™ APEPs, the catalyst level had to be adjusted as shown to match the reaction profile. Except for these replacements, other raw materials such as APP, Mannich polyol, blowing agents, FRs, surfactant etc. were kept constant.

Table 9: Formulation wherein 4.5f Sugar-based PEP replaced by Resonance™ polyols

Materials	Ref.	Mod. A2 (PL-203)	Mod. B2 (50/50)	Mod. C2 (PM-009)	Mod. D2 PL-252
Aromatic polyester polyol (f=2)	46.56	46.56	46.56	46.56	46.56
Mannich polyol (f=4)	15.18	15.18	15.18	15.18	15.18
Propoxylated sucrose/glycerol (f=4.5)	15.18	-	-	-	-
Resonance™ PL-203 (f=2.6)	-	15.18	-	-	-
50/50 blend (f=2.59)	-	-	15.18	-	-
Resonance™ PM-009 (f=2.6)	-	-	-	15.18	-
Resonance™ PL-252 (f=2.6)	-	-	-	-	15.18
Catalyst	0.9	0.48	0.48	0.46	0.48
Silicone	2	2	2	2	2
Flame retardant	3.9	3.9	3.9	3.9	3.9
Blowing agents	5.2	4.87	4.98	5.1	4.95
Isocyanate Component					
Isocyanate	106	94	98	103	97
Iso excess	9.1	9.2	9.1	9.2	9.2
Reaction Profile and Density					
Cream time (sec)	21	21	21	22	21
Gel time (sec)	50	52	54	54	54
Tack free time (sec)	71	70	76	70	70
Density Kg/m^3	37.7	37.9	37.5	38.3	37.7

Figure 6: Reaction to Fire (B2 test) results
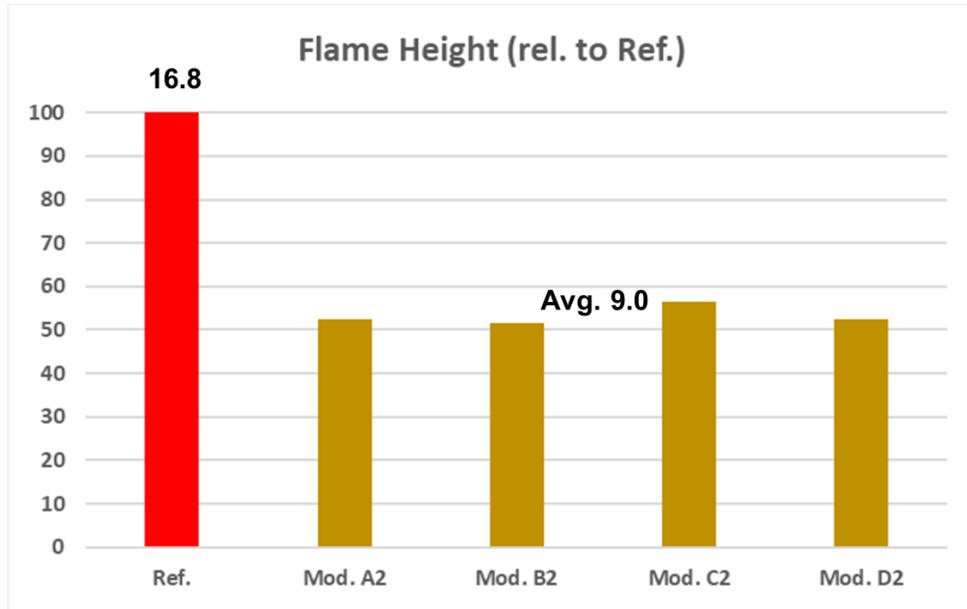
Figure 7: The impact of HEW/f on compressive strength
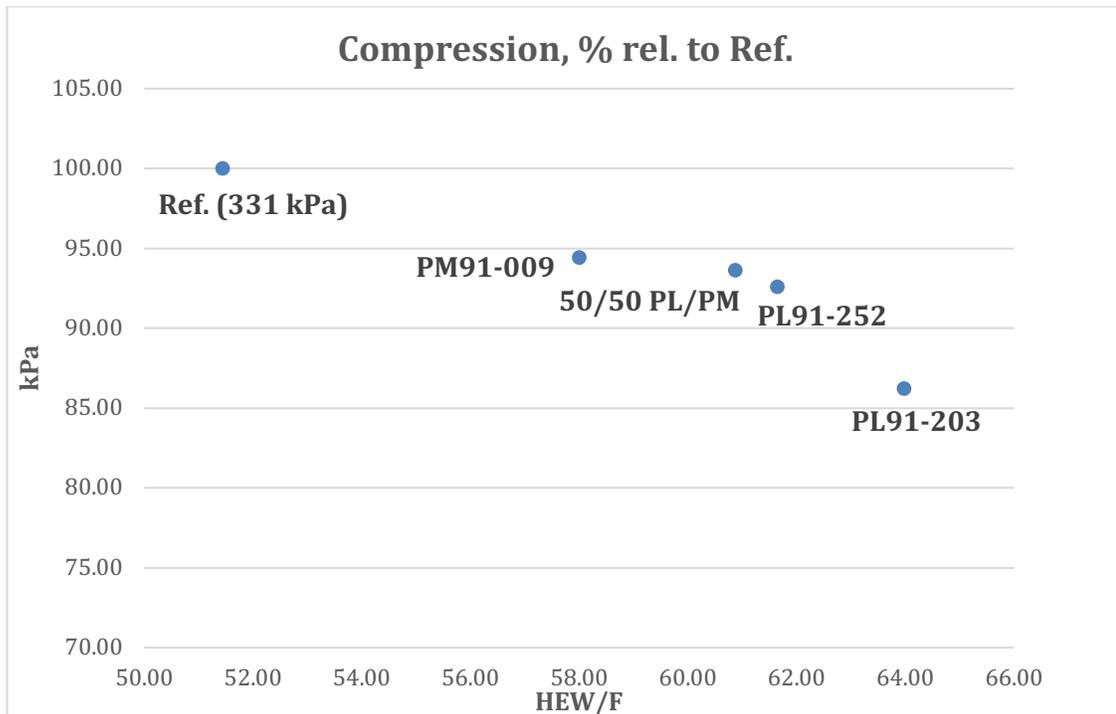
Total replacement of sugar-based PEP with Resonance™ APEPs- Mod. A2-D2, resulted in a dramatic reduction in flame height as shown in Figure 6. While the reference foam failed the test averaging at 16.8 cm, all the foams made from Resonance™ polyols passed the test averaging between 8.7-9.5 cm, a staggering 43-48% reduction in flame height! The

tremendous improvement in RTF occurred while maintaining the mechanicals at an acceptable level as shown by compression strength data in Figure 7. Again, the slightly lower compressive strengths for the Resonance™ foams (avg. 304 kPa vs Ref. 331 kPa) can be explained by the higher system HEW/f ratio of these compared to that of the Reference.

The Cone Calorimeter in Figure 8 shows the significant reduction in pHHR values for the Resonance™ foams compared to the reference foam. This further demonstrates the excellent potential of Resonance™ aromatic polyols to boost the flame-retardant properties of the foam.

Figure 8: Cone Calorimeter data: pHRR
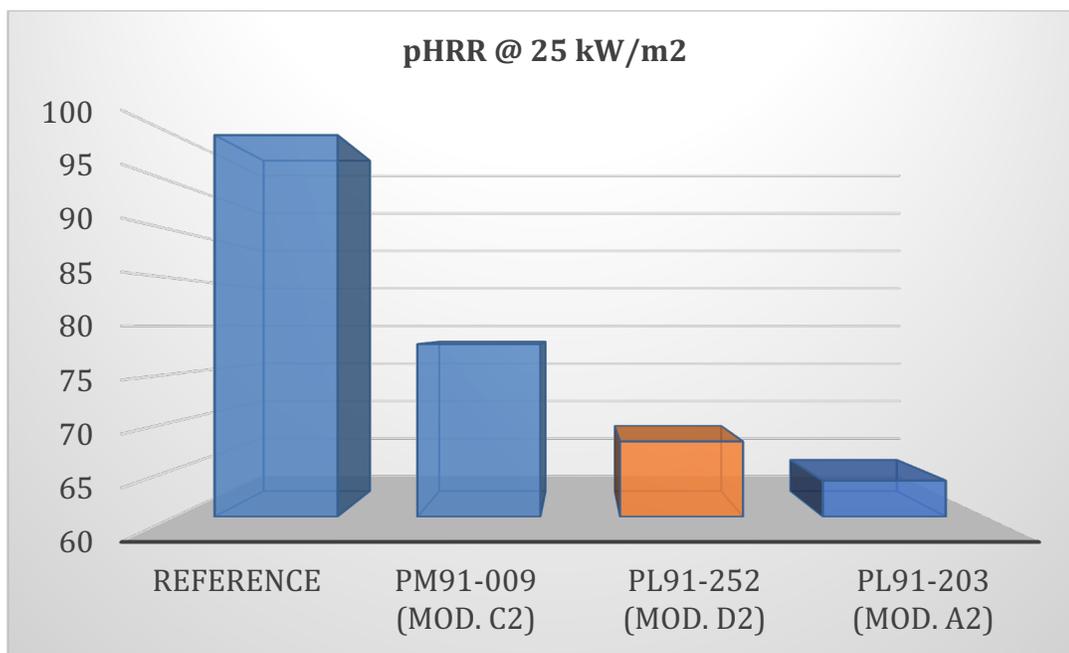
The outstanding burn characteristics of Resonance™ APEPs is quite evident and makes it extremely valuable wherever flame resistance is needed. This allows the formulators to reduce the amount of fire retardants needed, which can help with cost effectiveness and enhance other properties critical to the quality (CTQ) of the foams. Alternatively, for the same levels of FR additives, the Resonance™ APEPs can potentially help improve the fire ratings for the foam compared to the conventional PEPs.

CONCLUSIONS

Bakelite's highly aromatic, multi-functional Resonance™ aromatic polyetherols- PL91-203, PM91-009, their 50:50 blend, PL91-252 and PL91-650 were evaluated for their compatibility with various blowing agents and their performance in PU Rigid foam systems replacing 3f PEP in one case and 4.5f sugar-based polyether polyol in another case.

Overall, a variety of blowing agents were found to be quite compatible with Resonance™ polyetherols. Their solubilities range from 3-15% or greater in these polyols. The solubility of HFO and halogenated blowing agents were found to increase with the Resonance™ polyols with lower OHV.

Total replacement of the 3f-polyether polyols with the Resonance™ polyols resulted in significant improvement in reaction to fire as evidenced by lower flame height compared to the reference. While the reference foam failed, all the Resonance™ foams passed the B2 test. The dimensional stability and compressive strength for Resonance™ foams were also better than the reference.

Total replacement of the high-functional sugar-based polyether polyols with the Resonance™ APEP blends resulted in remarkable reduction in flame height while maintaining mechanicals at an acceptable level. The improved RTF by

vertical B2 test (DIN 4102) was further validated by Cone Calorimeter data for select modifications from these formulations, which showed significantly lower pHHR values for Resonance™ foams compared to the reference.

The dimensional stability of all the foams were well within the specifications of the PUR foams in the industry. In general, Resonance™ APEPs demonstrate higher reactivity as evidenced by shorter gel, rise and tack-free times. The reactivities were matched with the reference and optimized by adjusting the catalyst amounts.

The trends in mechanical property within the Resonance™ polyols and against the Reference could be explained by looking at the system HEW/f ratio for all the foam formulations. Overall, lower HEW/f led to better mechanical properties. Further, by bringing in aromaticity into the equation through the formula (%Aromaticity x f)/ HEW, a clear pattern emerged, which also gave new insights into looking at the data and understand the direct effect of introducing these highly aromatic polyetherols into PUR formulations.

This research paper elucidates the uniqueness of Resonance™ aromatic polyether polyols compared to polyols traditionally used in PUR formulations when it comes to fire performance thereby providing value. The Resonance™ polyols can be selected based on their physio-chemical properties such as HEW, f, etc. to introduce them as blends or as is into the polyurethane formulation to tailor the desired properties. Thus, the use of Resonance™ APEPs could unlock simplified and enhanced foam formulations for polyurethanes by reducing the amount of fire retardant, which can help cost effectiveness and have a positive influence in other CTQs of the foams in a variety of applications.

REFERENCES

1. Szycher, M. Szycher's *Handbook of Polyurethanes*; 2nd Ed.; CRC Press: Boca Raton, FL, 2013.
2. Dominguez-Rosado, E.; Liggat, J.J.; Snape, C.E.; Eling, B.; Pichtel, J. Thermal degradation of urethane modified polyisocyanurate foams based on aliphatic and aromatic polyester polyol, *Polymer Degradation and Stability*, **2002,** 78, 1-5.
3. Viswanathan, G.S.; Kukkala, P.; Malhotra, V.; Sendijarevic, I. Novel Nitrogen Containing Aromatic Polyols for Rigid Polyurethane Foams. *PU Magazine* **2019,** *16* (3)*,* 170-174.
4. Viswanathan, G.S.; Maiorana, A.; Kukkala, P.; Malhotra, V.; Sendijarevic, I. Novel Nitrogen Containing Aromatic Polyols for Rigid Polyurethane Foams, Presented at the 61st Polyurethanes Technical Conference, Atlanta, Georgia, October 1-3, 2018.
5. Viswanathan, G.S.; Kukkala, P.; Crain, S.; Rizmanova, M.; Basilissi, L.; Sendijarevic, I. A Fundamental Study on Aromatic Polyether Polyols for Rigid Polyurethane Foams, Presented at the 62nd Polyurethanes Technical Conference, Orlando, Florida, October 5-7, 2019.
6. Yelisetty, S.S.; Visco, D.P. Jr. Solubility of HFC32, HFC125, HFC152a, and HFC143a in Three Polyols. *J. Chem. Eng. Data* **2009,** 54, 781-785.
7. Decaire, B. R.; Pham, H. T.; Richard, R. G.; Shankland, I. R. Blowing Agents: The Next Generation. *J. Cell. Plast.* **1994**, 30, 11–33.

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