The Impact of Using a Coblowing Agent with HFO-1233zd(E) on the Performance and Properties of a Polyurethane Foam System

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ABSTRACT

Fluorochemical blowing agents have been an integral component in polyurethane foams since the 1950s. The unique combination of boiling point, solubility, and thermal conductivity, inherent in these materials, improves the insulation properties of rigid polyurethane foams and consequently reduces the energy consumption of the finished product it was used in, whether it be an appliance or residential dwelling. As the need for better performance with further reductions in energy consumption continues, blowing agents as well as other components in a polyurethane system are also being challenged to meet environmental, economic, and sustainability demands.

To meet some of those challenges, Arkema introduced the low Global Warming Potential (GWP) blowing agent, HFO-1233zd(E). The addition of various coblowing agents, such as methyl formate and methylal to the HFO-1233zd(E) blowing agent package, can help overcome some of the other challenges. These co-blowing agents, which are typically lower molecular weight and have good eco-toxicology properties, such as non-VOCs, allow for a reduction in the overall blowing agent package while still maintaining the necessary system requirements.

In this paper, we will show that the foams overall performance, especially insulation value, can still be maintained with the combination of HFO 1233zd(E) and a coblowing agent in a typical pour-in-place (PiP) polyurethane foam system. We will also show the superior performance of these blowing agent packages to a non-fluorochemical alternative, cyclopentane.

INTRODUCTION

Arkema introduced the Hydrofluoroolefin (HFO) 1233zd(E) (trans-1-chloro-3,3,3-trifluoropropene) blowing agent, Forane® FBA 1233zd in 2008 (as AFA-L1) and has worked since then to develop it as the low GWP fluorochemical blowing agent replacement for higher GWP Hydrofluorocarbon (HFC) blowing agents, offering the industry a non-flammable, low GWP, blowing agent with superior insulation value (1-10).

Several events prompted Arkema to do the work described in the paper. First, the American Innovation and Manufacturing Act (AIM), December 27, 2020, directed the Environmental Protection Agency (EPA), to address the HFC phasedown process, which would bring the US in line with the Kigali Amendment of the Montreal Protocol. A process already undertaken by several states such as California. Secondly, after almost a year under the Covid 19 global pandemic, raw material shortages were increasingly seen in many industries, including the polyurethane rigid foam area.

Using coblowing agents was not something new to the industry. From the early days of CFC 11, water and even CFC 12 were used as coblowing agents. Since a majority of the insulation value of a rigid polyurethane foam comes from the composition of the gas in the cells (11), we felt the above events warranted a project to look at the impact of a coblowing agent on the performance of foams made with HFO 1233zd(E) as a way to overcome raw material shortages but still maintain the superior insulation value of rigid polyurethane foams.

EXPERIMENTAL

This study looked at several loadings of four co-blowing agents with HFO 1233zd(E), to determine at what loading of the co-blowing agent the foam properties (either density, k-factor, dimensional stability, compressive strength, or percent closed cell) changed significantly from control foams made with all HFO 1233zd(E), HFO 245fa and cyclopentane (95% purity - cC5). The three control systems used 10% water blowing and 90% physical blowing. The four co-blowing agents examined in this series of experiments was one chemical - water (tap), and three physical - trans 1,2-dichloroethylene (Transcend® Additive or TDCE), dimethyoxymethane (methylal), and methyl formate. An HFO 1233zd(E) control foam was run with each co-blowing experiment. This allowed comparisons to be made with the experimental control as well as an accumulated average of the HFO 1233zd(E) controls.

As the experiments progressed, many of the coblown foams at the 80% loading (10% water and 70% co-blowing agent) showed shrinkage of k-factor samples kept at room temperature and excessive shrinkage under humid age dimensional stability test conditions. There was one, methyl formate, which showed no shrinkage in the kfac samples at RT, but did show similar borderline dimensional stability under humid age conditions as the other foams.

The system used in this study was a generic Pour-in-Place (PiP) formula but with a reduced loading of water as the control in order to maximize the impact of the physical blowing agent. Typically, our generic PiP formula uses 40% water blowing but since we were looking at water as a coblowing agent the level was reduced for the purposes of this study. It should be noted that in most, if not all, rigid foam applications, some amount of water is used to help generate some initial blowing; a loading of 10% water blowing is typical for continuously laminated boardstock (CLBS) (12). The percent water blowing levels in the study were: 10 (control), 20, 40, and 80% (doubling each increase) with subsequent physical blowing from 1233zd at 90, 80, 60, and 20%. Using these levels as guidelines, the physical co-blowing agent levels were at 10, 30, and 70%, with water at 10% for all. The HFO 1233zd(E) levels matched the ones for the water blown study and allowed for direct comparison. For example, the blowing agent package break down for the formulation for TDCE at 40% co-blowing is 10% water blowing and 30% blowing from TDCE with the remainder of physical blowing from the HFO-1233zd. Tables 1-5 contain the formulation details for all five of the experiments in this study; note that formulas are in percent of total foam.

Table 1. Coblowing Study – Water (Tap)						
B side	1-1. Control (10%)	1-2. Water 20	1-3. Water 40	1-4. Water 80		
Mannich Polyol (425 OH)	11.96	11.73	11.27	10.34		
Sucrose Polyol (490 OH)	19.76	19.37	18.61	17.08		
Polyester Polyol (240 OH)	8.03	7.87	7.56	6.94		
PMDETA	0.13	0.13	0.13	0.13		
DMCHA	0.44	0.44	0.44	0.44		
Surfactant	0.71	0.71	0.71	0.71		
ТСРР	1.87	1.87	1.87	1.87		
Blowing Agent						
Added water	0.16	0.32	0.64	1.29		
HFO 1233zd(E)	10.49	9.32	6.99	2.33		
Total B Side:	53.55	51.78	48.23	41.13		
A Side						
ROH Index	110	110	110	110		
pMDI (150 - 200 cps)	46.45	48.22	51.77	58.87		
A/B	0.87	0.93	1.07	1.43		
B/A	1.15	1.07	0.93	0.70		
Total Blowing, ml/gm	20.00	20.00	20.00	20.00		
Water Blowing, %	10%	20%	40%	80%		

Table 2. Coblowing Study – Transcend Additive (TDCE)							
B side	2-1. Control (10%)	2-2. TDCE 10	2-3. TDCE 30	2-4. TDCE 70			
Mannich Polyol (425 OH)	11.96	12.01	12.10	12.26			
Sucrose Polyol (490 OH)	19.76	19.83	19.99	20.24			
Polyester Polyol (240 OH)	8.03	8.06	8.12	8.23			
PMDETA	0.13	0.13	0.13	0.13			
DMCHA	0.44	0.44	0.44	0.44			
Surfactant	0.71	0.71	0.71	0.71			
ТСРР	1.87	1.87	1.87	1.87			
Blowing Agent							
Added water	0.16	0.16	0.16	0.16			
TDCE		1.01	2.85	5.91			
HFO 1233zd(E)	10.49	9.13	6.65	2.53			
Total B Side:	53.55	53.37	53.04	52.48			
A Side							
ROH Index	110	110	110	110			
pMDI (150 - 200 cps)	46.45	46.63	46.96	47.52			
A/B	0.87	0.87	0.89	0.91			
B/A	1.15	1.14	1.13	1.10			
Total Blowing, ml/gm	20.00	20.00	20.00	20.00			
Water Blowing, %	10%	10%	10%	10%			

Table 3. Coblowing Study – Methylal					
B side	3-1. Control (10%)	3-2. Methylal 10	3-3. Methylal 30	3-4. Methylal 70	
Mannich Polyol (425 OH)	11.96	12.06	12.23	12.47	
Sucrose Polyol (490 OH)	19.76	19.92	20.19	20.58	
Polyester Polyol (240 OH)	8.03	8.10	8.21	8.37	
PMDETA	0.13	0.13	0.13	0.13	
DMCHA	0.44	0.44	0.44	0.44	
Surfactant	0.71	0.71	0.71	0.71	
ТСРР	1.87	1.87	1.87	1.87	
Blowing Agent					
Added water	0.16	0.16	0.16	0.16	
Methylal		0.98	2.59	4.89	
HFO 1233zd(E)	10.49	8.80	6.05	2.09	
Total B Side:	53.55	53.18	52.58	51.72	
A Side					
ROH Index	110	110	110	110	
pMDI (150 - 200 cps)	46.45	46.82	47.42	48.28	
A/B	0.87	0.88	0.90	0.93	
B/A	1.15	1.14	1.11	1.07	
Total Blowing, ml/gm	20.00	20.00	20.00	20.00	
Water Blowing, %	10%	10%	10%	10%	

Table 4. Coblowing Study – Methyl formate					
Daida	5-1. Control (10%)	5-2. Methyl formate	5-3. Methyl formate	5-4. Methyl formate	
D slue		10	30	70	
Mannich Polyol (425 OH)	11.96	12.12	12.35	12.64	
Sucrose Polyol (490 OH)	19.76	20.01	20.40	20.87	
Polyester Polyol (240 OH)	8.03	8.13	8.29	8.48	
PMDETA	0.13	0.13	0.13	0.13	
DMCHA	0.44	0.44	0.44	0.44	
Surfactant	0.71	0.71	0.71	0.71	
ТСРР	1.87	1.87	1.87	1.87	
Blowing Agent					
Added water	0.16	0.16	0.16	0.16	
Methyl formate		0.93	2.33	4.03	
HFO 1233zd(E)	10.49	8.46	5.42	1.73	
Total B Side:	53.55	52.98	52.12	51.08	
A Side					
ROH Index	110	110	110	110	
pMDI (150 - 200 cps)	46.45	47.02	47.88	48.92	
A/B	0.87	0.89	0.92	0.96	
B/A	1.15	1.13	1.09	1.04	
Total Blowing, ml/gm	20.00	20.00	20.00	20.00	
Water Blowing, %	10%	10%	10%	10%	

Table 5. Coblowing Study – HFC 245fa and Cyclopentane (cC5) Controls					
B side	5-1. Control (10%)	5-2. 245fa control	5-3. cC5 control		
Mannich Polyol (425 OH)	11.96	11.92	12.66		
Sucrose Polyol (490 OH)	19.76	19.69	20.91		
Polyester Polyol (240 OH)	8.03	8.00	8.50		
PMDETA	0.13	0.13	0.13		
DMCHA	0.44	0.44	0.44		
Surfactant	0.71	0.71	0.71		
ТСРР	1.87	1.87	1.87		
Blowing Agent					
Added water	0.16	0.16	0.16		
HFO 1233zd(E)	10.49				
HFC 245fa		10.78			
cyclopentane			5.62		
Total B Side:	53.55	53.70	51.00		
A Side					
ROH Index	110	110.00	110.00		
pMDI (150 - 200 cps)	46.45	46.30	49.00		
A/B	0.87	0.86	0.96		
B/A	1.15	1.16	1.04		
Total Blowing, ml/gm	20.00	20.00	20.00		
Water Blowing, %	10%	10%	10%		

PREPARATION OF HANDMIX FOAM

Standard blending and handmix procedures were used for these experiments, with chemicals conditioned to 60° F (15°C). Handmixing was performed using a typical air powered mixer at 4000 rpm with a 5 cm (2") mix blade and a 1-liter (32 oz) paper cup for blending A and B-sides to measure reactivity and free rise density. Test samples for k-factor testing and other physical properties were made using the same mixer with a 7.6 cm (3") blade and 6"x 6"x 6" (15 cm x 15 cm x 15 cm) open box pours. Due to the nature of the free rise foams, the k-factor samples were cut such that the foam rise was parallel to the test face, in order to minimize the effect of any defects running completely through the sample thickness. In addition, since the k-factor samples were undersized, 5"x 5" x 1" (12.7 cm x 12.7 cm x 2.54 cm), each test piece was surrounded by like material to fill the 12" x 12" (30.5 cm x 30.5 cm) cavity in the LaserComp.

For each experiment in the study, two cup foams were prepared for measuring reactivity and free rise density. Foam physical property samples as described above were prepared in a total of five 6" x 6" boxes (250 gms total foam each) - 1 for k-factor/closed cell/perpendicular compressive strength, 1 for dimensional stability and parallel compressive strength, 2 for dimensional stability, 1 extra. Dimensional stability conditions: -20°C, 70°C/97% RH, and 70°C/ambient RH for 7 and 14 days. All the above required about 600 g of B-side for each formulation; batch size was set at 1000 g to allow for additional material if needed. Samples for k-factor testing were run initially and every month up to six months.

DETERMINATION OF FOAM PROPERTIES

Measurement of all foam properties was conducted using standard ASTM procedures for rigid polyurethane foams. Foam density was measured according to ASTM D1622. Measurement of k-factors was done on 1" thick core foam samples using a LaserComp FOX 314 heat flow meter according to ASTM C518. Percent closed cell content was measured using a Gas Pycnometer according to ASTM D6226. Dimensional Stability was measured after 14 days at the above-mentioned conditions according to ASTM D2126. Compressive strength was measured according to ASTM D1621.

RESULTS and DISCUSSION

REACTION TIMES AND FREE RISE DENSITY

Table 6 shows the reaction times and free rise density (FRD) for all the foam systems. The reaction times and FRD of the HFO 1233zd(E) controls across the experiments showed little variability and would be well within specifications for a typical commercial system. When examining the data set as a whole, there was a fair amount of variability in both reaction times and FRD, which would likely not be in spec. This variation was due in large part to the contribution of the coblow studies with increased amounts of water blowing. This change typically makes for faster reaction times and more expansion (higher exotherm and blowing) or lower density (see Table 6). Note that in the following tables and charts of various test results, the coblown foams were listed as 20, 40, and 80%, which includes 10% from water. For example, for the TDCE 20 foam, 10% of the blowing was from water and 10% from TDCE, with the remaining 80% of the blowing agent package coming from HFO 1233zd(E). The high density of foams with a high level of physical blowing agent was due to unoptimized systems for reaction times.

Table 6. Summary of reactivity* and free rise density (FRD)**						
Exp	Formula type	СТ	GT	TFT	RT	FRD
	1233zd control (10%)	17	62	93	123	2.13
1 (tan watan)	Tap Water 20	17	60	90	117	2.09
1 (tap water)	Tap Water 40	13	48	83	90	2.02
	Tap Water 80	13	37	54	68	1.89
	1233zd control (10%)	18	65	117	133	2.13
2 (TDCE)	TDCE 20	16	65	112	120	2.13
2 (IDCE)	TDCE 40	21	63	115	125	2.28
	TDCE 80	21	58	91	110	2.44
	1233zd control (10%)	18	65	109	139	2.16
2 (mathylal)	Methylal 20	18	63	99	130	2.08
5 (methylal)	Methylal 40	22	64	105	138	2.29
	Methylal 80	20	60	79	123	2.45
	1233zd control (10%)	16	65	129	135	2.13
1 (mathul formata)	Methyl formate 20	18	65	121	136	2.19
4 (methyl lormate)	Methyl formate 40	16	60	110	130	2.35
	Methyl formate 80	15	50	85	105	2.50
5 (245fa & aC5	1233zd control (10%)	20	68	113	120	2.22
$3(2431a \approx 0.05)$	245fa control	12	69	145	NR	2.20
controis)	cC5 control	24	67	130	NR	2.38
1233zd control (Avg)		18	65	112	130	2.15
1233zd control (Std Dev)		1	2	13	8	0.04
	Avg for all		60	103	121	2.21
Std Dev for all		3	9	21	19	0.15

*in seconds, CT=cream or initiation time, GT=gel or string time, TFT=tack free time, and RT=rise time **in lbs/ft3 (pcf)

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FOAM PROPERTIES DIMENSIONAL STABILITY (PERCENT VOLUME CHANGE)

The foam samples were tested for dimensional stability under three conditions, humid aged at 70°C/97% RH, dry aged at 70°C/ambient humidity, and cold aged at -20°C/ambient humidity for 7 and 14 days. The below charts contain the test results, as percent volume change, for each condition after 14 days.

HUMID AGE (CHART 1)

The lines in the chart represent the dimensional stability results for each of the control foams (HFO 1233zd(E), HFC 245fa, and cC5). For example, the HFO 1233zd(E) controls averaged (Exp1-5) after 14 days, 12.5% change. The remaining controls for HFC 245fa and cC5 showed significantly higher change; all above 20%. Each group of bars represent the results for the various foams made with HFO 1233zd(E) and a coblowing agent. The first set shows the results for 20% coblowing (10% water, 10% physical coblowing agent); second and third set of bars represent 40 and 80% coblowing respectively. Note that the layout of the chart described here is the same for the remaining dimensional stability charts for dry and cold aging.

The first set of coblown foams (20%) showed a more acceptable volume change of around 5%; much less than all the controls, with the exception of methylal at just over 10%. The second or middle set of bars (40%), showed minimal change for most of the coblowing agents, except methylal, which gave a percent volume change of just under 10%. Lastly, the 80% coblowing agent foams showed severe shrinkage with water and methyl formate, borderline shrinkage for TDCE, and severe expansion for methylal. The results are not surprising given the plasticizing nature of many of these coblowing agents.



DRY HEAT AGE (CHART 2)

The HFO 1233zd(E) control average, after 14 days, showed under 2% percent volume change. The other controls showed slightly more increase in percent volume but all under 5%. Note that the oven malfunctioned during testing of Exp5 foams so there were only results for the 7-day reading. However, those foams showed only 2-4% change. All the coblown foams at all levels showed acceptable percent volume change of under 2%.



COLD AGE (CHART 3)

All the control foams after 14 days showed under 2% volume change. As with the dry aging, all foams showed acceptable percent volume changes except Methylal 80% coblow, which exhibited -10.3% volume change after 14 days.



COMPRESSIVE STRENGTH (CHART 4)

Since there was a fair amount of variability in the densities, normalized mean compressive strength (NMCS) was calculated to make a better comparison over the five experiments at a density of 2.0 pcf. The average NMCS for all the HFO 1233zd(E) controls was 19.2 +/- 1 psi. All of the 20% coblow foams, with the exception of methyl formate, gave similar results to the HFO 1233zd(E) control. However, at the 40% loading, only the water coblowing foam gave similar NMCS as the HFO 1233zd(E) control. Since the formulations were not optimized for each coblowing agent, changes to the polyol blend might help to improve the compressive strength of some of the 40% coblowing agents. Finally, at the 80% level of coblowing agents, none of the foams gave acceptable NMCS. This is not surprising, as most of the samples made for k-factor testing showed shrinkage at room temperature after a month, which will be discussed in the next section. It should be noted that the cC5 control exhibited the lowest NMCS of any of the control foams, 15.7 psi, and HFC 245fa exhibited the highest, 21.1 psi.



k-FACTOR DENSITY AND PERCENT CLOSED CELL (TABLE 7)

The difference in density within each coblow series was noted and explained in the section on reaction times and free rise density The percent closed cell for the HFO 1233zd(E) controls over the entire study was very consistent at \sim 95% +/- 1.5. This was also the case when comparing the whole data set, which gave an average of 94.7% +/- 1.3% closed cell. A high percent closed cell would be one of the main contributors to good thermal conductivity. Since all foams showed a similarly high percent closed cell, the majority of any differences in k-factor would come from the composition of the cell gas (11). To a lesser extent, differences in k-factor could also be attributed to differences in cell size and density.

Table 7. k-factor density and closed cells					
Ехр	Foam System	kfac density, pcf	CC		
	1233zd control (10%)-1	2.20	95.3		
1 (tap water)	Tap Water 20	2.13	95.3		
i (tap water)	Tap Water 40	2.05	93.2		
	Tap Water 80	1.93	92.0		
	1233zd control (10%)-2	2.15	96.2		
2(TDCE)	TDCE 10	2.21	94.4		
2 (IDCE)	TDCE 30	2.33	95.8		
	TDCE 70	2.53	96.3		
	1233zd control (10%)-3	2.21	93.8		
3 (methylal)	Methylal 10	2.27	94.4		
5 (methylar)	Methylal 30	2.43	94.4		
	Methylal 70	2.59	94.6		
	1233zd control (10%)-4	2.21	92.8		
1 (methyl formate)	Methyl formate 10	2.24	95.2		
+ (methyr formate)	Methyl formate 30	2.40	96.0		
	Methyl formate 70	2.55	95.1		
	1233zd control (10%)-5	2.26	94.5		
5 (245fa & cC5 controls)	245fa control	2.22	95.7		
	cC5 control	2.48	97.0		
zd Control (Avg)		2.21	94.5		
zd Control (Std D	zd Control (Std Dev)		1.3		
Average for all		2.28	94.8		
Std dev for all		0.18	1.3		

INITIAL AND AGED INSULATION PERFORMANCE

Although samples were tested for k-factor every month, this paper will focus on the initial and final 6 month aging results, which will show the shifts in performance due to aging of the coblown foams in relation to the aging of the controls. A comparison was made of all the experimental foams against the average of the HFO 1233zd(E) controls for the five experiments in this study. The following charts show the thermal conductivity (k-factor in Btu.in/hr.ft².°F) results at three mean test temperatures, 32°, 50°, and 75°F. The reason for measuring the samples at various mean test temperatures was to assess the insulation performance at different possible application temperatures, which can be impacted depending on the boiling point of the blowing agent and possible condensation at lower test temperatures (11).

INITIAL INSULATION PERFORMANCE (CHARTS 5 AND 6)

As with the previous charts for dimensional stability and NMCS, the lines represent the control k-factor results and each group of bars represent the various HFO 1233zd(E)/coblown foams at the three mean test temperatures. Initially, all the foams with 20% coblowing agent (Chart 5) showed similar performance to the HFO 1233zd(E) control at all test temperatures with the exception of the methylal foam. This foam was significantly higher than the HFO 1233zd(E) control but similar to the HFC 245fa control. All coblown foams gave significantly better insulation performance (lower k-factor) than the cyclopentane control.



The same could be said for the foams made using 40% coblowing (Chart 6) for the TDCE and methyl formate foams. However, the tap water foam exhibited similar but slightly worse k-factor at 32°F and increasingly worse at the higher test temperatures, but now similar to the HFC 245fa control and the methylal coblown foam. As at 20%, all the 40% coblown foams exhibited significantly better insulation performance than the cC5 control.



The blends at 80% coblowing level were really more of an academic exercise since the main blowing agent of this study, HFO 1233zd(E), would now be considered the coblowing agent. This plus the fact that most of the coblowing

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agent k-factor samples at this level showed shrinkage at room temperature on the test surface within a month, so there will be only a brief discussion of the results. At the lower test temperature of 32°F, all the coblown foams showed significantly worse k-factors than the HFO 1233zd(E) controls. In fact, this was also true at the higher test temperatures.

Also at the lower temperature, the tap water, methylal, and methyl formate foams were worse than the HFC 245fa control and the TDCE foam showed slightly better results. Compared to the cC5 control at that temperature, TDCE and methyl formate foams were better, water similar and methylal significantly worse.

At 50°F, only the TDCE was similar to the HFC 245fa; all others gave significantly worse k-factors. This was also true at 75°F. Similarly, at the 50°F, only the TDCE was lower than the cC5 control and the methyl formate showed similar values, which were repeated at 75°F.

SIX MONTH AGED INSULATION PERFORMANCE (CHARTS 7 AND 8)

As might be expected, the story changes a bit over time. In general, rigid polyurethane foams show an increase in k-factor over time, which is due to changes in the cell gas composition. As the foams age, there is an ingress of air, replacing the CO_2 generated from the water blowing, and diffusion of the physical blowing agent (11). All the data shown in Charts 7 and 8 were from one-inch thick core foam samples aged at room temperature for six months.

After six months aging, the two fuorochemical blowing agent controls, HFC 245fa and HFO 1233zd(E), are very close in k-factor or insulation performance and still much lower or better than the cC5 control. The 20% coblown foams (Chart 7) have aged to a similar level as the fluorochemical controls; most giving comparable insulation performance. The methylal foam showed a slight difference at the lower test temperature but increased to a more significant difference at the two higher temperatures indicating poorer insulation value after aging.



At the 40% level of coblowing, only the foam made with tap water as the coblowing agent showed similar aging to the fluorochemical controls. The other coblowing agents were bordering on significantly higher k-factors to HFO 1233zd(E) and HFC 245fa but still much lower than the cC5 control at the lower test temperatures. However, this difference was not seen at the higher test temperature of 75°F where most showed similar k-factor to the cC5 control or even worse such as the methylal foam. All of this being related to the boiling point of the various blowing agents (11).



The above results have shown that fluorochemicals, coblown with other materials or not, generally provide better insulation performance than hydrocarbons like cyclopentane. So how does HFO 1233zd(E) compare to other HFOs? Earlier experiments were completed comparing the insulation performance of two other HFO options, HFO 1224yd(Z) (trans-1-Chloro-2,3,3,3,-Tetrafuoropropane) and HFO 1336mzz(Z) (cis-1,1,1,4,4,4-Hexafluoro-2-butene). Those experiments used the same generic PiP formulation as the coblown work presented here. Due to limited amounts of the alternate HFOs, only handmix samples were prepared for k-factor testing. The percent water blowing was 40%, so for a direct comparison, the tap water at 40% coblowing from this work was used in Chart 9.

The aged results show that all the HFOs exhibited similar insulation performance for the two higher test temperatures of 50° and 75° F. However, at the lower temperature of 32° F, the effects of condensation of a higher boiling point blowing agent, HFO 1336mzz(Z), were seen, which negatively impacted the k-factor of that foam(11). Beside boiling point, there are other factors to influence blowing agent selection. A major one is the molecular weight of the blowing agent(13), which directly effects the amount of material needed to achieve a certain density of the finished foam. The higher the molecular weight, the more moles of gas needed, hence the more blowing agent required in the formulation. HFO 1224yd(Z) with a molecular weight of 148.5 compared to HFO 1233zd(Z) with a molecular weight of 130.5, would require approximately 14% more HFO 1224yd(Z) to achieve the same foam density. Similarly, HFO 1336mzz(Z), with a molecular weight of 164, would require about 26% more to achieve the same density as an HFO 1233zd system.



CONCLUSION

The results show that it is very possible to obtain better insulation performance using a variety of coblowing agents with HFO 1233zd over HFC 245fa and cC5, while maintaining other physical properties such as dimensional stability and compressive strengths. The experiments showed that at 20% loading of coblowing agent, most of the materials examined produced foams with comparable properties to the HFO 1233zd control. Even at the 40% coblowing level, most coblowing agents produced foam with acceptable dimensional stability. However, only the tap water foam had similar k-factor and compressive strength to the control. Several others, such as TDCE and methyl formate were close to the control k-factor and could be improved with formula optimization of surfactants and catalysts. All suggesting that fluorochemicals blowing agents remain a strong contender for producing rigid polyurethane foams with superior insulation value. Additionally, we showed that Forane[®] FBA 1233zd remains the best fluorochemical option.

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