Microcellular elastomers based on Kuraray MPD adipate polyester polyols

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Abstract

Kuraray developed a line of liquid, amorphous, MPD (3-methyl-1,5-pantanediol) adipate polyol diols and triols in a range from 500 to 6000 MW.

In this presentation we are reporting on properties of microcellular elastomers based on Kuraray's MPD adipate polyester polyol diols and diol/triols mixtures in comparison to the microcellular elastomers based on PPG diols and triols.

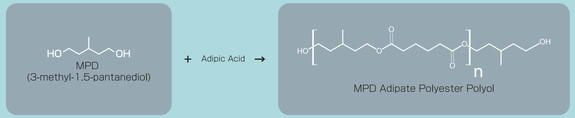
At the same density, microcellular elastomers based on Kuraray polyester polyol exhibited improved tensile strength and elongation, improved toughness, higher compression modulus, and significantly better tear and abrasion resistance. The hysteresis of the microcellular elastomers based on Kuraray polyester polyol was lower than that of the PPG system, which indicates better dynamic-mechanical properties.

Microcellular elastomers based on Kuraray's MPD polyester polyols also exhibited improved dry and humid aged compression sets. Also, microcellular elastomers based on Kuraray's MPD polyester polyols showed improved retention of compressive properties after hydrolytic age compared to reference microcellular elastomers based on PPG polyols.

The results show that Kuraray's MPD based polyester polyols could provide improved mechanical and dynamic performance in cellular materials associated with polyester polyols while maintaining good hydrolytic resistance.

Experimental : Kuraray Polyol

Properties of Kuraray Polyol				
Name of grade	Structure	Appearance at Room Temperature	Tg	Viscosity at 60℃
Kuraray Polyol P-4010	MPD Adipate, F=2, MW~4,000	Liquid	-64.4	3,800
Kuraray Polyol F-3010	MPD / TMP Adipate, F=3, MW=3,000	Liquid	-62.7	2,100



Experimental : Preparation of free-rise and molded microcellular foams

Two types of reference MC polyurethane foam systems were formulated based on polyether polyols and low functionality aromatic isocyanate. One reference was based on EO capped PPG diol, MW 4000. The other reference was a blend on EO capped PPG diol (MW 4000) and PPG triol (MW 6000). The other components of the system are: chain extender (1,4-butane diol), water (as a blowing agent), catalysts and surfactant.

Two types of MC elastomers based on Kuraray Polyol P-4010 diol (MW4000) and the other was based on a blend of Kuraray P-4010 diol and F-3010 triol (MW3000). Other components of the formualtions were the same as in the referent formulations .

Free - rise MC foams were prepared using a one-shot method. At first, Resin B was blended in a cup using a drill mixer. Afterwards, Resin A was added to Component B and all ingredients mixed at room temperature using a drill mixer. The foaming profile was measured via visual determination of cream time, gel time, rise time and tack free time.

Molded MC foams were prepared by pouring mixed polyurethane system (Resin A and B) prior to the cream time into a mold preheated at 50℃ in convection oven that was treated with mold releasing agent. The sample was removed from the mold 15 minutes after pouring.

Experimental : Testing of molded microcellular elastomers

All samples were allowed to cure for at least 1 week at room conditions prior to testing.

The following properties of molded MC elastomers were tested per ASTM D-3489:

- Density
- Hardness
- Resilience
- Tensile properties
- Compression set (50℃)
- Abrasion resistance
- Tear strength (Die C)
- Compression deflection force

Hydrolytic resistance of MC elastomers was tested as follows:

- Retention of tensile properties of molded MC samples in humidity chamber for 5 days at 50℃ and 95% humidity.
- Compression deflection force after exposure of test specimens for 22 hours at 50℃ and 95% humidity
- Compression set after exposure of test specimens compressed to 75% of the original thickness for 22 hours at 50℃ and 95% humidity.

Experimental : Microcellular Elastomer Formulations

Formulations of MC elastomers				
Designation:	Benchmark Diol	Benchmark Diol/Triol	Kuraray P-4010 Diol	Kuraray P-4010 Diol/F-3010 Triol
Formulation (pbw)				
Component B	RT	RT	Preheated at 50℃	Preheated at 50℃*
Poly G 55-28	91.3	81.7	0.00	0.00
Poly G 85-29	0	9.55	0.00	0.00
Kuraray P-4010 Diol	0.00	0.00	91.3	81.7
Kuraray F-3010 Triol	0.00	0.00	0.00	9.55
1,4-butanediol (chain extender)	7.99	7.99	7.99	7.99
Tegostab B4113 (surfactant)	0.475	0.475	0.475	0.475
Dabco 33LV (catalyst)	0.090	0.090	0.090 (0.08 molded)	0.090 (0.07 molded)
Dabco T-12 (catalyst)	0.009	0.009	0.009	0.009
Total water	0.295	0.295	0.295	0.295
Total Component B	100.06	100.02	100.11	100.06
Component A (Mondur CD)	35.65	36.11	35.65	36.33
Isocyanate index	0.98			

Free-rise Microcellular Elastomers

Reactivity and properties of free-rise MC elastomers				
Designation:	Benchmark Diol	Benchmark Diol/Triol	Kuraray P-4010 Diol	Kuraray P-4010 Diol/F-3010 Triol
Foaming Reactivity				
Mix time, s	20	20	20	20
Cream time, s	53	51	36	28
Gel time, s	118	115	155	51
Rise time, s	181	152	184	81
Tack free time, s	178	162	236	91
Free Rise Properties				
Density, pcf	23.5	24.0	21.8	22.1
Appearance	Uniform	Uniform	Uniform	Uniform
Hardness (Top Skin), Shore A	39±2	40±4	41±2	37±3
Hardness (Core), Shore A	20±1	23±1	21±1	23±1

Drop in replacement of PPG polyol with Kuraray P-4010 and F-3010 did not significantly impact the foaming reactivity or application of polyols in MC elastomers.

Molded Microcellular Elastomers - Density and Hardness

Properties of molded MC elastomers (Density and Hardness)				
Designation:	Benchmark Diol	Benchmark Diol/Triol	Kuraray P-4010 Diol	Kuraray P-4010 Diol/F-3010 Triol
Density of 6 mm molded samples pcf	30.9±0.3	32.1±1.5	31.6±1.3	33.4±0.3
Density of 12mm molded samples, pcf	33.8±0.2	33.0±0.3	33.7±0.3	33.9±0.6
Hardness (Top Skin), Shore A	40±2	39±1	43±6	44±0
Hardness (Bottom Skin), Shore A	41±2	42±2	44±7	45±1

At comparable density, hardness of molded MC elastomers slightly increased with drop in replacement of PPG polyols with Kuraray P-4010 and F-3010 polyester polyols.

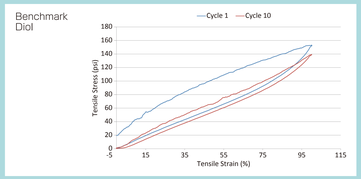
Molded Microcellular Elastomers - Physico-mechanical and Thermal Properties

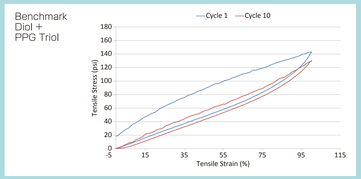
Properties of MC elastomers				
Designation:	Benchmark Diol	Benchmark Diol/Triol	Kuraray P-4010 Diol	Kuraray P-4010 Diol/F-3010 Triol
Physico-mechanical Properties				
Resilience (Bashore rebound), %	46.8±0.2	46.7±0.9	44.7±0.3	41.7±0.0
Tensile strength at break, psi	298.5±13.0	252.4±12.3	428.0±56.8	407.8±24.2
Tensile elongation at break, %	268.7±13.7	249.2±5.6	373.4±30.8	273.3±5.7
Tensile stress at 50%, psi	94.3±5.7	81.5±4.9	68.7±2.3	102.2±5.8
Tensile stress at 100%, psi	150.8±7.9	133.5±7.4	122.9±4.4	173.2±9.8
Tensile stress at 200%, psi	244.6±11.6	218.3±11.7	217.7±7.2	301.4±15.3
Area under curve (Tensile Toughness), (J)	2.2±0.2	2.3±0.10	5.0±0.9	3.3±0.2
Tensile set, %	4.0±2.2	3.6±1.8	5.6±2.2	3.6±2.2
Tensile set after 10th cycle at 100%, %	4.4	4.4	2.4	2.4
Hysteresis at 100% 1st curve	35.0	36.6	17.1	18.4
Hysteresis at 100% 10th curve	15.7	16.5	5.9	7.9
Tear strength (Die C), N/cm	136.7±15.3	147.1±5.3	184.8±22.6	199.2±20.0
Abrasion Resistance, mass loss mg/1,000 cycles	370	320	0	0
Thermal properties				
Tg (DMA, Loss Modulus Max.), ℃	-55	-39	-25	-32
Tg soft segment (DSC), ℃	-61.4	-60.2	-34.6	-34.5
Tg hard segment (DSC), ℃	176.3	174.8	176.1	168.4

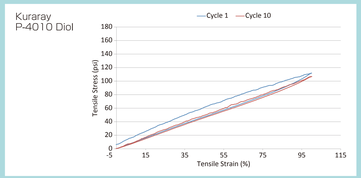
MC foams made from Kuraray polyols excelled in following properties:

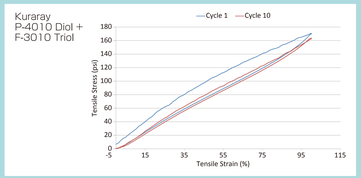
- Abrasion resistance
- Hysteresis loss
- Tensile Strength and Elongation at break
- Tear Strength

Molded Microcellular foams - Hysteresis in Tensile Mode









Impact of hydrolytic aging on tensile properties of microcellular elastomers

Impact of hydrolytic aging on tensile properties of molded MC elastomers				
Designation:	Benchmark Diol	Benchmark Diol/Triol	Kuraray P-4010 Diol	Kuraray P-4010 Diol/ F-3010 Triol
Tensile properties pre-aging				
Tensile strength at break, psi	298.5±13.0	252.4±12.3	428.0±56.8	407.8±24.2
Tensile elongation at break, %	268.7±13.7	249.2±5.6	373.4±30.8	273.3±5.7
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Tensile stress at 200%, psi	244.6±11.6	218.3±11.7	217.7±7.2	301.4±15.3
Area under curve, (J)	2.2±0.2	2.3±0.10	5.0±0.9	3.3±0.2
Tensile properties after hydrolytic aging (5 days, 50℃, 95%RH) (% change aged/non-aged samples)				
Tensile strength at break, psi	231.3±10.0 (77.7)	273.6±13.2 (91.6)	443.7±61.0 (96.3)	338.8±41.2 (83.1)
Tensile elongation at break, %	249.9±9.1 (93)	243.2±13.5 (97.6)	334.2±48.4 (89.5)	225.9±37.8 (82.7)
Tensile stress at 50%, psi	70.2±1.2 (74.4)	85.9±3.3 (105.4)	77.2±4.3 (112.4)	99.8±6.7 (97.6)
Tensile stress at 100%, psi	117.3±2.5 (77.8)	142.3±4.4 (106.6)	137.5±6.6 (111.9)	169.0±10.4 (97.6)
Tensile stress at 200%, psi	197.3±3.7 (80.7)	237.8±5.1 (108.9)	253.6±13.3 (116.5)	296.5±4.8 (98.4)
Area under curve, (J)	1.82±0.1 (83.1)	2.03±0.2 (89.8)	4.3±1.2 (86.9)	2.3±0.6 (69.9)

After hydrolytic age, tensile strength, and elongation at break, and toughness of MC elastomers based on Kuraray polyols remained higher compared to referent MC elastomers based on PPG.

Molded Microcellular Elastomers – Compressive Properties

Compressive properties of molded MC elastomers				
Designation:	Benchmark Diol	Benchmark Diol/Triol	Kuraray P-4010 Diol	Kuraray P-4010 Diol/ F-3010 Triol
Compressive properties at RT				
Tensile properties pre-aging				
Compressive stress at 5% strain, psi	10.13±3.38	11.19±1.39	14.06±2.32	10.92±1.92
Compressive stress at 10% strain, psi	19.65±3.69	21.10±2.00	24.87±2.94	23.00±0.83
Compressive stress at 15% strain, psi	28.22±3.77	29.97±2.12	35.04±3.32	32.28±0.77
Compressive stress at 20% strain, psi	37.86±3.62	39.93±2.13	46.73±3.66	41.68±1.38
Compressive stress at 25% strain, psi	49.96±3.30	52.34±2.65	60.69±3.98	52.91±2.11
Modulus (Young's), KPa	1922±51	1927±48	2052±180	2007±54
Compressive properties after hydrolytic aging (22 hours, 50℃, 95%RH)				
Modulus (Young's) KPa	1749±108	1708±71	2049±39	1970±46
CFD at 25% strain retention, % (wet aged/dry)	87.7	81.4	91.9	100.7
Compression set properties				
Dry compression set, % (percent change of original thickness, 50℃, 22hrs, 25% deflection)	8.5±0.4	7.8±0.3	6.6±1.1	5.9±0.4
Wet aged compression set, % (percent change of original thickness, 50℃, 22hrs, 25% deflection)	14.0±1.5	13.6±0.9	11.1±0.9	12.1±0.6

The compression set (dry and humid aged) of MC elastomers made from Kuraray polyols was slightly lower (better) than those based on PPG.

MC elastomers based on Kuraray polyester polyols offered better retention of compressive properties after hydrolytic age than MC based on PPG polyols.

Microcellular Elastomers – Blend of Kuraray's MPD Polyester Polyol/ PPG

MC polyurethane foam systems were formulated based on a 50/50 blend of PPG diol (Poly-G 55-28) and Kuraray's MPD based polyester polyol diol (P-4010).

The viscosity of P-4010 and Poly G 55-28 blend was relatively low at 2710 cps at room temperature, which was convenient for processing at room conditions.

Most of the properties of MC elastomer based on a blend of P- 4010 and PPG diol were in-between the properties of referent MC elastomers.

However, MC elastomers based on a blend of P-4010 and Poly G 55-28 exhibited better compression set and tensile set than the referent MC elastomer based on PPG diol only and MC elastomers based on P-4010 only.

Compressive properties of molded MC elastomers			
Designation:	Benchmark Diol	Kuraray P-4010 Diol	50/50 pbw Benchmark Diol & Kuraray P-4010 Diol
Tensile set following hysteresis at 100%, %	4.41	2.44	1.4
Compression Set Properties			
Dry compression set, % (percent change of original thickness, 50℃, 22hrs, 25% deflection)	8.5±0.4	6.6±1.1	4.76±0.54
Wet aged compression set, % (percent change of original thickness, 50℃, 22hrs, 25% deflection)	14.0±1.5	11.1±0.9	7.0±0.98

Summary

- ✓ Kuraray's MPD based 4000 MW polyester diol and 3000 MW triol have low degree of crystallinity and are liquid at room conditions making them viable for use in broad range of flexible foam applications.
- ✓ Microcellular elastomers based on Kuraray polyol have higher elasticity and toughness than those based on polyether polyols, resulting in improved tear resistance and significantly improved abrasion resistance.
- ✓ Microcellular elastomers based on Kuraray polyol have improved dry and wet compression set than the referent materials based on PPG polyols.
- ✓ Even after hydrolytic age, microcellular elastomers based on Kuraray polyol retained higher tensile strength and toughness and compressive modulus than the referent materials based on PPG polyols.