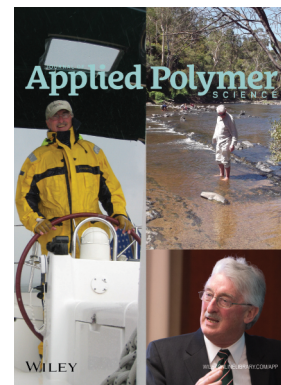


Special Issue: Sustainable Polymers and Polymer Science
Dedicated to the Life and Work of Richard P. Wool

Guest Editors: Dr Joseph F. Stanzione III (Rowan University, U.S.A.)
and Dr John J. La Scala (U.S. Army Research Laboratory, U.S.A.)



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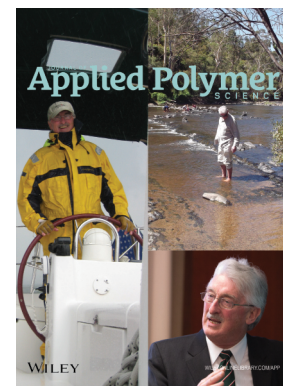
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Flexible polyurethane foams formulated with polyols derived from waste carbon dioxide

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ABSTRACT: In this study, flexible polyurethane foam samples were prepared using concentrations of up to 50% of two novel polycarbonate polyols, Polyol D 251-20 and Polyol D 351-30, derived from the copolymerization of carbon dioxide (CO₂) and epoxides, to determine whether the final foam products meet automotive standards for use in seating applications. In other words, CO₂-based polyols were substituted for a portion of petroleum-based polyols in the foam formulations. Characterization of the foam samples was carried out by mechanical, physical, and thermal analysis. Overall, inclusion of both types of CO₂-based polyol led to an increase in wet compression set, compression modulus, compression stress at various strain levels, maximum tensile strength, Young's modulus, and tear resistance properties in the flexible polyurethane foams. Density, SAG factors, and elongation properties remained relatively constant compared to petroleum-based control samples. Dynamic mechanical thermal analysis showed increasing storage modulus with increasing concentrations of CO₂-based polyol at temperatures below 0 °C. Thermogravimetric analysis showed that the thermal stability of the foam decreases with an increase in the concentration of CO₂-based polyol. Images of foam samples were taken using a Keyence VHX digital microscope. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44086.

KEYWORDS: foams; mechanical properties; polyurethanes; thermal properties

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INTRODUCTION

Humans have become highly dependent on the use of petroleum as a feedstock for transportation fuels, oils, plastics, and other synthetic materials which are incorporated into many aspects of daily life. Globally, use of plastic each year is approximately 260 million tons for items such as packaging, building materials, household commodities, clothing, automotive components, furniture, and toys.^{1,2} However, petroleum is a non-renewable resource, and if we continue using it without looking for alternative sources, it will eventually be depleted. Additionally, exploration, drilling, and extraction of petroleum can have adverse environmental and human health impacts which include: deforestation, ecosystem destruction, contamination of land and water, harm to animal populations, and health and safety risks to humans in neighboring communities and those who work in the oil industry.³ There has been an increasing trend towards finding environmentally friendly and renewable material alternatives to replace the petroleum-based commodities currently used.

Polyurethane foams (PUFs), such as conventional flexible foams based on an ether polyol or an ester polyol, high-resilience (HR) foam, and rigid foams, as well as foams with properties between these classifications are used in automotive applications such as seat foam, sound absorption and vibration damping, dashboards, bumpers, headliners, energy absorbers, etc.⁴ Currently, the polyurethane industry is looking for renewable materials to replace two major feed stocks, polyols and isocyanates, because of the uncertainty about the cost of petroleum in the future and the need to move toward more environmentally friendly feedstocks.^{5,6} Polyurethanes can be synthesized by using renewable sources as polyols, such as starch, soybean, alginic acid, palm, sugar-cane bagasse, lignin, cork, coffee ground, corn, sunflower, rapeseed, coconut, and castor oils, by replacing petrochemical polyols partially or totally.⁵⁻¹⁴ In addition to the economical pricing advantages compared to petroleum-based sources, renewable-based PUF provide higher thermal and dimensional stability than traditional polypropylene oxide-based foams because of its abundant triglycerides.¹⁵ The synthesis of

polyols based on renewable sources is also expected to reduce carbon footprints and promote the management of natural sources.¹⁶

A family of chemicals derived from waste carbon dioxide (CO₂) and waste carbon monoxide (CO), which are combined with traditional chemical feed stocks to create chemicals, can be used for a wide variety of applications including adhesives, coatings, elastomers, sealants, rigid foams, and flexible foams.¹⁷ Incorporation of CO₂-based polyols into foam products has previously been investigated.^{18,19} Additional information regarding the use of CO₂-based polyols for polyurethane applications are available from the literature and conference proceedings.^{20–22} However, this is a relatively new technology and the information available is somewhat limited. These findings provide a solid foundation to research this material for use in flexible PUF applications within the automotive industry. The environmental benefits of using CO₂-based polyols in automotive seating foam compared to conventional polyether polyols are reductions in greenhouse gas emissions, the use of fossil fuel resources as well as lowering eutrophication, ionizing radiation, ozone depletion, particulate matter formation, photochemical oxidant formation, and terrestrial acidification.²³ As CO₂ is present throughout the world and there is a need for CO₂ being released into the atmosphere to be reduced, the CO₂-based polyols have potential to be an environmentally friendly option for use in seating applications globally.

The purpose of this study was to synthesize flexible PUFs resulting from the product of a reaction between isocyanate and waste CO₂-based polyols as a partial replacement for petroleum-based polyols to determine the potential to be used in automotive seating formulations. It is imperative that the physical and thermal properties as well as the cell structure of the foam meet or exceed automotive specifications in place for these applications. Mechanical and physical properties of the produced foams were tested and thermal properties of the foams were characterized by dynamic mechanical analysis (DMTA) and thermogravimetric analysis (TGA). Images of foam samples were taken with a Keyence VHX digital microscope.

EXPERIMENTAL

Materials

PUFs are made from a two part mixture in which side A is an isocyanate and side B is a polyol and additives mixture. Isocyanate (Rubinate 7304), petroleum-based polyol (Voranol 4701), and CO₂-based polyols (Converge polyol D 251-20 and Converge polyol D 351-30) were kindly provided by Huntsman International LLC (Auburn Hills, MI), Dow Chemical (Midland, MI), and Novomer (Waltham, MA), respectively. Comparisons of the physical properties of the CO₂-based polyols and conventional, petroleum-based polyol are provided in Table I. These data were measured and provided by the suppliers. Polyol D 251-20 is an amorphous, linear aliphatic polycarbonate diol while Polyol D 351-30 is an amorphous, branched aliphatic polycarbonate triol. Carbon dioxide accounts for approximately 20% of the polyol mass in both Novomer polyol types used in this study. Polyol D 251-20 and polyol D 351-30 are

Table I. A Comparison of the Typical Physical Properties of Petroleum (Voranol 4701) and CO₂-Based Polyols (Polyol D 251-20 and Polyol D 351-30)

	Polyol D 251-20	Polyol D 351-30	Voranol 4701
Functionality	2.0	3.0	3
Molecular weight (g/mol, GPC)	2000	3000	4900
Polydispersity index (Mw/Mn)	1.1	1.1	
OH number (mg KOH/g)	56	56	34
Density (g/mL)	1.13	1.14	1.02
Viscosity (cPs at 75°C, 66°C*)	600	1000	147*
Acid number (mg KOH/g)	<0.5	<0.5	
Water content (ppm)	<500	<500	

Information provided by suppliers. Viscosities were measured at high temperatures. If viscosities were to be measured at room temperature, the viscosities would be higher.

predominately secondary hydroxyl with some primary hydroxyl (<15%). CO₂-based polyols are viscous liquids/soft solids at room temperature, easily able to be processed at 50–80°C and compatible with traditional ether or ester polyols. The foaming additives included: a reactive cell opener, Lumulse POE (26) GLYC (Lambent Corporation, Gurnee, IL), a silicone-based surfactant, Tegostab B4690 (Evonik, Hopewell, VA), a cross-linking and co-catalyst agent, Diethanolamine (Sigma-Aldrich, St. Louis, MO), catalysts, Niox A300 and Niox A1 (Momentive, Waterford, NY), and a blowing agent, deionized water. The chemicals were mixed according to the proportions shown in Table II. The concentrations of additives included have been chosen based on our preliminary experiments and have been proven to be optimal for flexible foam formulations.

Synthesis of the PUFs

Flexible PUFs were prepared with 10%, 20%, 30%, and 50% polyol D 251-20 and polyol D 351-30, respectively, on laboratory scale in one step synthesis by mixing A and B components. Firstly, CO₂-based polyols were mixed with petroleum-based polyols, catalysts, cross-linking agent, surfactant and water (component B) using a standard laboratory hand-mixer at 1500 rpm for 3 min. Rubinate-7304, which is a liquid blend of MDI series polyisocyanates, as component A was added to the mixture of components B and the combined mixture was stirred for 12 s with a hand-mixer at 1500 rpm. The mixture was immediately poured into a closed mold system (17.8 × 38.1 × 10.2 cm³) that had been coated with Chem-Trend PU-11331 release agent and preheated in an oven for 15 min at 65°C. The foam was able to rise in the vertical direction and demolding time was 6 min. Each PUF was placed in an oven preheated to 65°C for 30 min and then at room temperature for a minimum of 12 h in order to allow the foam to cure properly. Reference foams were prepared using only petrochemical polyols. The nomenclature and compositions used for preparation of the foam samples are shown in Table II. The amount of each additive was calculated on 100 parts by weight of total polyol and isocyanate components.

Table II. Flexible Polyurethane Foam Materials and Formulations with Parts by Weight

	Component type	0%	10%	20%	30%	50%
Component B						
Voranol 4701	Petroleum polyol	100.0	90.0	80.0	70.0	50.0
Polyol D 251-20/351-30	CO ₂ Polyol	0.0	10.0	20.0	30.0	50.0
Lumulse POE (26) GLYC	Cell Opener	1.0	1.0	1.0	1.0	1.0
Tegostab B4690	Surfactant	0.5	0.5	0.5	0.5	0.5
Diethanolamine	Cross-linker	1.5	1.5	1.5	1.5	1.5
NiAx A300	Catalyst	0.6	0.6	0.6	0.6	0.6
NiAx A1	Catalyst	0.3	0.3	0.3	0.3	0.3
Water	Blowing agent	3.0	3.0	3.0	3.0	3.0
Component A						
Rubinate 7304	Isocyanate (MDI)	53.8	54.3	54.8	55.4	56.4

Characterization and Material Properties

A standard band saw was used to cut the foam into small blocks 25 mm × 50 mm × 50 mm and sheets 10 and 12.5 mm thick. The sheets were die stamped with a USM Hytronic Model B press into pieces for tensile and tear testing. The cut and stamped pieces for all three blocks were combined, and six samples were randomly selected for each test to get a more accurate average for each concentration. Selected physical and mechanical properties of foams were measured according to the appropriate standards; the apparent density (ASTM 3574-08, Test A), wet heating aging (compression set), (ASTM 3574-08, Test L), compression force deflection (ASTM 3574-08, Test C), tensile strength at break (ASTM 3574-08, Test E), elongation at maximum load (ASTM 3574-08, Test E) and tear strength (ASTM D 624, Die C). SAG factor values of the foams were also calculated from compression stress values. DMTA samples (5 × 3 × 14 mm³) were prepared with a band saw and a die stamp. The samples were placed in the tension test holder in the Rheometric Scientific DMTA 3E. Strain controlled dynamic temperature ramp testing was done in rectangular tension geometry from -60 °C to 150 °C with temperature ramp of 5 °C/min. The frequency was 10 Hz and the strain was 0.5%. Three samples of each polyol type and concentration were measured and the results were averaged. TGA analysis was run on a Mettler Toledo TGA/DCS 1 with STAR^e software. Foam samples of around 5 mg were placed in the crucible. TGA analysis was run from ambient temperature to 600 °C with nitrogen gas applied at a rate of 30 mL/min. Three samples of each polyol type and concentration were measured and the results were averaged. A Keyence VHX digital microscope was used to image the foam samples.

RESULTS AND DISCUSSION

Density

Density is a key parameter of flexible PUFs because it is an indicator of foam performance with regards to comfort, support, and durability. Additionally, foams with lower density that meet all other specifications help reduce overall vehicle weight which improves fuel performance and lowers exhaust emissions. Density for seat cushions and backs should be in the range of

20–95 kg/m³. The densities of each concentration and type of CO₂-based polyol are shown in Table III. As the concentration of CO₂-based polyol increases, the density remains relatively constant when compared to the 100% petroleum-based sample. Overall, there is less than 5% difference between the 100% petroleum-based samples and each of the CO₂-based polyol samples. There is also little difference between the densities of foams made with polyol D 251-20 and those made with polyol D 351-30. The density difference can be explained by the difference in viscosity which, when compared to the petroleum-based polyol, is four times higher for polyol D 251-20 and seven times higher for polyol D 351-30. Similar results have also been observed with the incorporation of palm oil-based polyol into foam materials.²⁴ Foams containing 50% CO₂-based polyol have larger standard deviations. The flexible PUFs prepared with CO₂-based polyol have densities within the accepted range for seating applications for vehicles. In addition, Seo *et al.* and Thirumal *et al.* found that water played an important role in determining the density, mechanical properties, glass transition temperature, and morphology of foams.^{25,26} The density of PUFs decreased with an increase in the amount of water in the foam formulations.^{25,26} It should not be surprising that density of CO₂-based PUFs can be adjusted with water level to meet automotive density requirements.

Wet Compression Set

Compression properties are critical for seating and armrest applications in the automotive industry as it is imperative that the foams will rebound to its original shape after it has been deformed even under high temperature and high humidity conditions and it is important that the foams have the required softness. Compression properties are affected by the morphology of foam. This study measured compression properties in different ways to determine these characteristics. Wet compression set measures the permanent deformation of a foam after it has been compressed. Lower values indicate that the material is capable of rebounding closer to its original shape. Vehicle applications that involve a load being placed on them for an extended period of time such as seating or armrests require lower compression set values because the lower the value, the more the foam will rebound to its original shape. Wet compression

Table III. Physical and Mechanical Data of Polyurethane Foams Containing CO₂-Based Polyol

	Density (kg/m ³)	Wet compression set [% compression]	Compression modulus (MPa)	Compression stress at 25% strain (MPa)	Compression stress at 50% strain (MPa)	Compression stress at 65% strain (MPa)	SAG factor 65%/ 25%	SAG factor 50%/ 25%	Maximum tensile strength (kPa)	Elongation at maximum load (mm)	Young's modulus (kPa)	Tear resistance (N/m)
0% 251-20	44.6 (1.1)	13.6 (2.5)	0.032 (0.005)	0.0031 (0.0001)	0.0048 (0.0002)	0.0077 (0.0004)	2.5 (0.1)	1.54 (0.04)	67.9 (6.9)	80.6 (7.1)	110.7 (8.3)	334.2 (23.5)
10% 251-20	43.2 (0.9)	15.5 (2.5)	0.035 (0.005)	0.0032 (0.0004)	0.0049 (0.0006)	0.0080 (0.0008)	2.5 (0.1)	1.54 (0.04)	83.7 (2.9)	91.1 (3.4)	123.9 (8.7)	357.7 (23.5)
20% 251-20	43.6 (1.3)	22.7 (3.9)	0.036 (0.003)	0.0034 (0.0004)	0.0051 (0.0004)	0.0083 (0.0004)	2.5 (0.2)	1.54 (0.07)	87.2 (5.3)	88.9 (6.6)	142.9 (11.9)	419.5 (24.9)
30% 251-20	45.1 (1.8)	30.6 (5.7)	0.052 (0.008)	0.0043 (0.0003)	0.0067 (0.0004)	0.0110 (0.0009)	2.6 (0.3)	1.56 (0.08)	103.4 (4.0)	99.5 (4.0)	171.3 (18.7)	515.2 (44.0)
50% 251-20	44.3 (2.9)	42.1 (2.4)	0.061 (0.006)	0.0049 (0.0003)	0.0073 (0.0003)	0.0125 (0.0005)	2.6 (0.2)	1.50 (0.09)	108.8 (7.1)	100.9 (7.5)	206.9 (22.5)	563.4 (43.4)
0% 351-30	44.2 (1.0)	14.3 (3.5)	0.036 (0.004)	0.0033 (0.0003)	0.0051 (0.0004)	0.0081 (0.0005)	2.5 (0.1)	1.55 (0.04)	81.4 (4.5)	88.5 (6.3)	131.4 (7.0)	361.8 (29.1)
10% 351-30	43.3 (1.8)	17.2 (3.4)	0.043 (0.010)	0.0035 (0.0002)	0.0056 (0.0004)	0.0092 (0.0012)	2.6 (0.3)	1.60 (0.10)	78.6 (7.4)	82.2 (5.8)	143.8 (6.6)	390.1 (32.4)
20% 351-30	42.3 (0.6)	19.8 (3.0)	0.048 (0.005)	0.0046 (0.0003)	0.0070 (0.0004)	0.0094 (0.0041)	2.4 (0.1)	1.52 (0.04)	88.5 (6.7)	91.0 (8.9)	150.0 (12.4)	387.4 (12.4)
30% 351-30	44.9 (1.3)	28.3 (2.8)	0.067 (0.008)	0.0055 (0.0005)	0.0085 (0.0006)	0.0142 (0.0011)	2.6 (0.3)	1.53 (0.07)	99.5 (6.7)	82.7 (4.6)	232.4 (23.2)	484.6 (27.5)
50% 351-30	45.5 (3.3)	42.9 (2.0)	0.121 (0.018)	0.0108 (0.0006)	0.0164 (0.0010)	0.0268 (0.0020)	2.5 (0.2)	1.52 (0.08)	116.8 (11.4)	85.7 (8.8)	301.3 (17.59)	574.9 (48.2)

Parentheses indicate standard deviation.

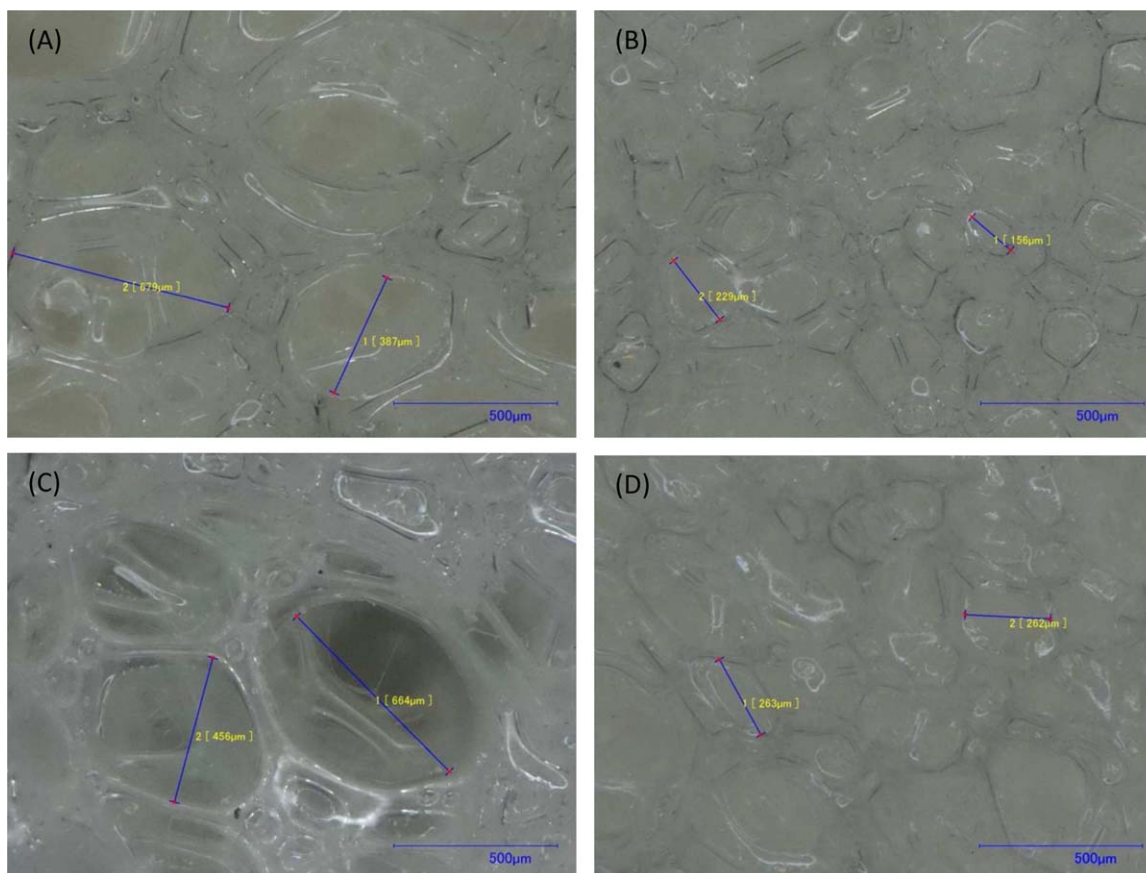


Figure 1. Optical images of (A) 0% polyol D 251-20, (B) 50% polyol D 251-20, (C) 0% polyol D 351-30, and (D) 50% polyol D 351-30. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

set for seat applications (cushions and backs) and underbody thermal and/or sound absorbing insulators should be in the range of 5–30% and 50%, respectively. Wet compression set values for constant deflection of 50% of the foams are shown in Table III. There is an increase in the wet compression set values as the concentration of CO₂-based polyol increases. The wet compression set increased from 13% to 42% for polyol D 251-20 and from 14% to 43% polyol D 351-30. In foams containing 50% CO₂-based polyol, wet compression set properties are 200% greater than the 100% petroleum-based sample for both polyol types. The increase in wet compression set can be explained by the smaller average cell size observed in foams with increasing concentrations of CO₂-based polyol which is caused by the higher viscosity of the CO₂-based polyol reducing cell drainage by gravity during the initial foaming stage.^{27,28} Images of 0% and 50% polyol D 251-20 and 0% and 50% polyol D 351-30 showing cell size can be seen in Figure 1. Foams containing 100% petroleum-based chemicals have cell sizes between about 350–700 µm while foams containing 50% CO₂-based polyol have cell sizes less than 300 microns. CO₂-based foams also create cells with uniform size because CO₂-based polyols act as an additional surfactant.²⁴ Similar phenomena also observed for palm oil-based flexible PUFs.²⁴ In addition, the dimensional stability of the cured foam is governed by the fraction of open cells and in the case of CO₂-based PUFs, it is believed that the gas entrapped in the closed cells also resists

compression, reducing the cushioning quality of the final foam product.²⁹ Close cell content of the foams was not measured in this study but Figure 1 suggested too many closed cells in CO₂-based PUFs.

Compression Strength

The compression modulus is a measure of stiffness of the foam and therefore, provides information on the deflection of the foam under load. Foams with higher compression moduli are stiffer and have low deflections when loaded. Table III shows the compression modulus of each concentration of both CO₂-based polyols. The compression modulus in foams containing 50% polyol D 251-20 is 89% greater than the 100% petroleum-based polyol sample, while the compression modulus with inclusion of 50% polyol D 351-30 polyol is 240% greater. The difference in compression modulus with the inclusion of 50% of the two CO₂-based polyol types is likely because of the higher molecular weight and viscosity of polyol D 351-30 as compared to polyol D 251-20. In addition to compression modulus, compression stress can also be measured at different strain levels which provide an indication of the way the foam behaves with different amounts of force applied to it. In vehicle applications, this is applicable to determining the properties of foams used for seating when people with varying weight sit on them. As shown in Table III, the compression stress at 25% strain, 50% strain, and 65% strain show an increasing trend in

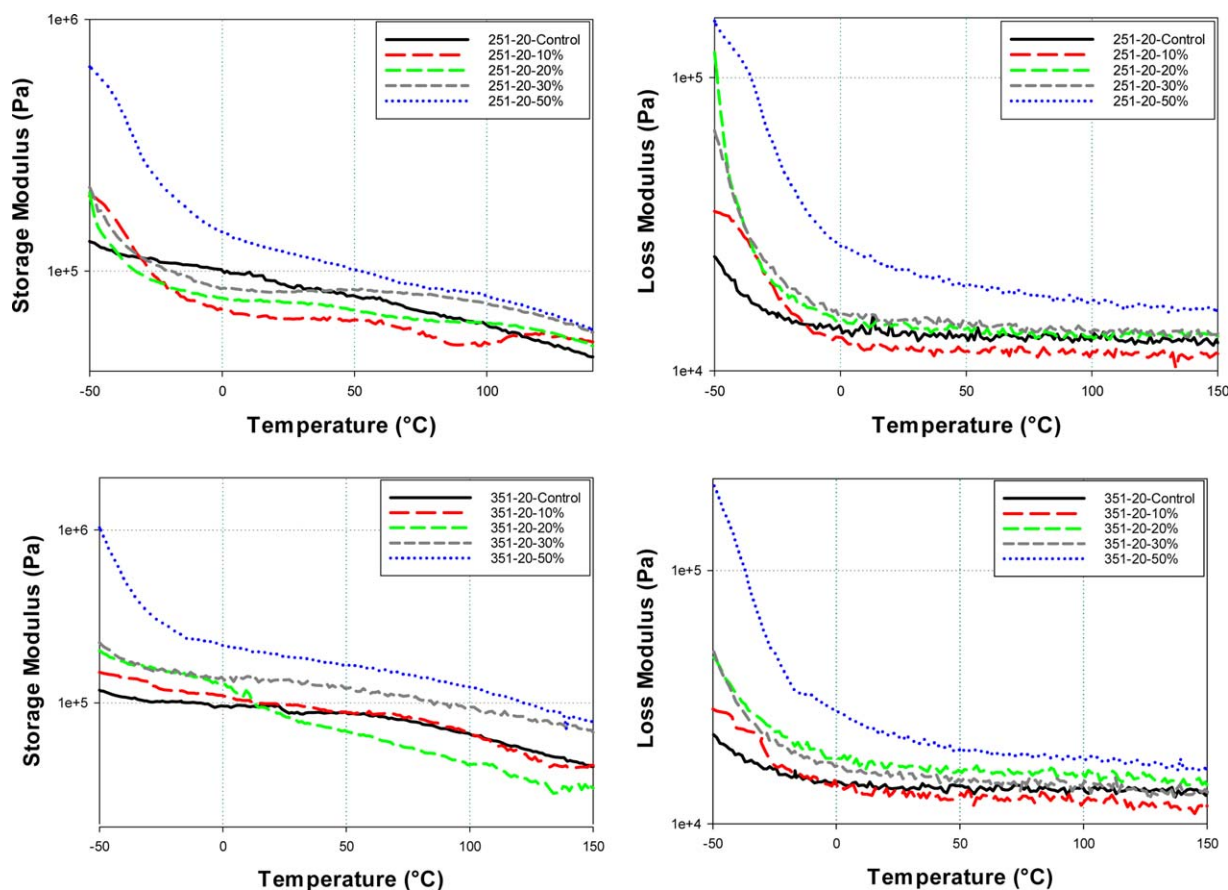


Figure 2. DMTA data for (A) polyol D 251-20 and (B) polyol D 351-30 CO₂-based polyol samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compression stress with increasing concentrations of CO₂-based polyol with only slight increases in stress with increasing concentration with the exception of the highest CO₂-based polyol concentration of the polyol D 351-30 polyol where the compression stress increases dramatically. Fifty percent inclusion of polyol D 251-20 shows up to 60% greater compression stress for each strain value compared to the 100% petroleum-based sample while polyol D 351-30 shows 220% greater compression stress than the 100% petroleum-based samples for each strain value. The compression properties are related, among others, to the density, cross-linking density, and foam structure and increased with both higher cross-link density and greater foam density.^{5,7} Since density remains relatively constant when compared to the 100% petroleum-based sample, the increase in compressive stresses can be explained by different cross-linking densities of the obtained CO₂-based foams. In addition, the CO₂-based polyol has a 100% polycarbonate backbone with perfectly alternating CO₂ and epoxide units which yields 100% carbonate and zero ether linkages. It is believed that this imparts distinct properties such as load building, tensile, tear strength, and compression properties in flexible foam due from the high-density carbonate backbone. The higher molecular weight and branched network of polyol D 351-30 compared to polyol D 251-20 likely causes the increase in the load bearing properties of the foam. Chemical compositions and variables (isocyanate content, functionality of the isocyanate, etc.) can affect load

bearing properties of flexible PUF foams.³⁰ The improvement in load bearing properties in PU foams resulting from the use of the polycarbonate polyols in the mixture. High load bearing flexible foams also exhibit increased stiffness in Table III. SAG factor is another indicator of cushioning quality in foam. Higher values indicate resistance to “bottoming out” which is important in automotive applications as comfort necessitates that the foam supports people and the support structure under the foam is not felt.³¹ SAG factor is given as a ratio of compression stress at two different amounts of strain. Two different SAG factors were considered in this study. The ratio of compression stress at 65% strain to compression stress at 25% strain is shown in Table III, and the ratio of compression stress at 50% strain to compression stress at 25% strain shown in Table III. The SAG factors remain constant for each concentration of CO₂-based polyol at approximately 2.5 and 1.5 for SAG factors of 65% and 50% respectively. There is a slight increase in the standard deviations of foams containing higher concentrations of CO₂-based polyol. The high consistent SAG factor values indicate that increasing CO₂-based polyol concentration continues to provide comfortable support for foam applications.

Tensile Strength and Tear Resistance

Maximum tensile strength and tear resistance were measured to understand the overall strength of the foam. Maximum tensile strengths of the flexible PUFs containing CO₂-based polyols are

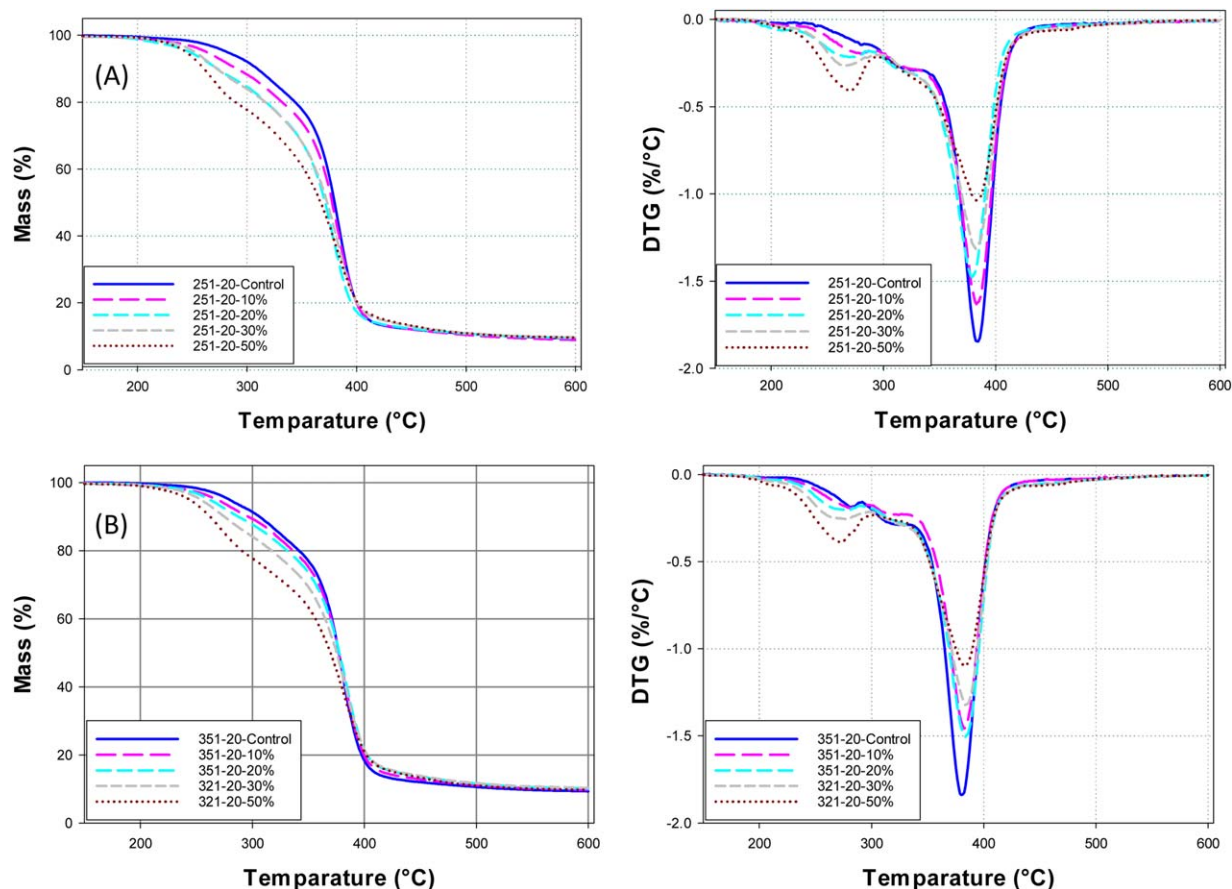


Figure 3. TGA and DTG of polyurethane foams containing (A) polyol D 251-20 and (B) polyol D 351-30 CO₂-based polyol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shown in Table III. Increasing concentrations of CO₂-based polyols correlates with an increase in maximum tensile strength. Compared to petroleum-based polyol alone, the maximum tensile stress is 60% greater in foams using 50% polyol D 251-20 and 43% greater in foams using 50% polyol D 351-30. Elongation at maximum load is a measure of the extent to which the foam can be stretched before it breaks and the results can be seen in Table III. The addition of polyol D 251-20 lead to an increase in elongation at maximum load as the concentration of CO₂-based polyols increased. Foams containing 50% polyol D 251-20 exhibited elongation at maximum load that was 25% greater than petroleum-based polyol alone. Polyol D 351-30 had neither a significant increase nor decrease in elongation at maximum load with increasing CO₂-based polyol concentration as compared to petroleum-based polyol. Young's modulus values are shown in Table III. The Young's moduli increased with increasing concentrations of CO₂-based polyols. Inclusion of 50% polyol D 251-20 resulted in moduli values 87% greater than the 100% petroleum-based sample. Concentrations of 50% polyol D 351-30 show moduli values of 129% greater than the petroleum alone. Modulus for seat cushions and backs should be in the range of 50–120 kPa. For automotive applications, tear resistance is important for releasing the foam material from the mold in which it is made. Tear resistance for seat applications (cushions and backs) and underbody thermal and/or

sound absorbing insulators should be in the range of 200–350 and 250 N/m, respectively. Increasing concentrations of CO₂-based polyols resulted in an increase in tear resistance as shown in Table III. At 50% concentration levels of polyol D 251-20 and polyol D 351-30, the tear resistances of the foams are 69% and 59% greater than the 100% petroleum-based foams, respectively.

Dynamic Mechanical Thermal Analysis

Foam materials in automobiles are routinely exposed to desert or arctic temperatures. It is necessary to determine any changes to the mechanical properties at extremely hot and extremely cold temperatures. DMTA results for foams containing various concentrations of CO₂-based foams are shown in Figure 2. Storage (E') and loss (E'') modulus shows two plateau regions, the one from -50°C to 0°C corresponding to glass transition region and the one from 0°C to 150°C corresponding to rubbery state of the foam.¹¹ The sharp decrease in the E' and E'' curves can be seen until 0°C and then the curves flatten out. The foams containing 50% CO₂-based polyols show a similar behavior and have a higher modulus over the entire temperature span compared to the petroleum-based polyol. This result indicates that 50% CO₂-based foams have better energy absorption than petroleum-based foam.³² Because of the porous nature of foams, it is very difficult to obtain reliable modulus

Table IV. Thermogravimetric Data for Polyurethane Foam Containing CO₂-Based Polyol Analyzed from Ambient Temperature to 600 °C

Sample code	Residual Mass (%)	Temp. at 10% ML (°C)	Temp. at 50% ML (°C)
251-20-0%	8.8 (1.0)	305.4 (4.5)	378.6 (1.2)
251-20-10%	8.9 (0.9)	285.2 (2.8)	378.3 (4.9)
251-20-20%	9.4 (0.9)	272.6 (4.9)	371.4 (2.7)
251-20-30%	9.7 (0.4)	272.7 (3.7)	373.2 (2.7)
251-20-50%	9.6 (0.3)	260.9 (1.3)	367.2 (1.1)
351-20-0%	9.3 (0.3)	306.4 (2.9)	377.1 (0.9)
351-20-10%	7.8 (1.6)	295.2 (4.9)	389.4 (0.2)
351-20-20%	10.1 (0.3)	287.3 (2.6)	377.8 (2.1)
351-20-30%	10.3 (0.2)	275.0 (3.7)	375.1 (1.9)
351-20-50%	9.7 (0.5)	262.6 (4.0)	369.5 (1.1)

Parenthesis indicates standard deviation.

values and hence obtained values were also quite similar in Figure 2.9 Figure 2 also shows that E' of foams is much higher than E'' of foams.

Thermogravimetric Analysis

Measurements of thermal stability of the foam materials were also done through TGA analysis. Figure 3 shows TGA decomposition of PUF samples with (A) polyol D 251-20 and (B) polyol D 351-30. As the concentration of CO₂-based polyol increases, the thermal stability of the foam decreases as shown by increasing mass loss at lower temperatures. Table IV provides TGA data for PUFs containing CO₂-based polyols. Temperature at 10% mass loss for the 50% polyol D 251-20 and polyol D 351-30 samples are around 45 °C lower than the 100% petroleum sample. Similarly, as the concentration of CO₂-based polyol increases, the temperature at 50% mass loss decreases as shown in Table III. DTG, which is the derivative TGA, shows that degradation occurs in two steps. The first step is associated with degradation of urea and urethane linkages and the maximum urea and urethane degradation rate for the petroleum-based foams and 50% CO₂-based foams are detected around 280 °C and 265 °C, respectively.³³ The second step is assigned to polyol degradation and the maximum degradation temperature for the petroleum-based foams and 50% CO₂-based foams are detected around 385 °C and 380 °C, respectively.³⁴ Residual mass difference is negligible for CO₂-based foams, with a maximum of 9.7% and 10.3% for 30% polyol D 251-20 and polyol D 351-30 foams.

SUMMARY

CO₂-based polyol show promise for use as an environmentally friendly option in automotive applications. The densities of the foams containing up to 50% CO₂-based polyol are consistent with 100% petroleum-based samples. While wet compression set values increase dramatically with inclusion of greater amounts of both CO₂-based polyol types, foams containing up to 30% CO₂-based polyol which have wet compression set values of approximately 30% will meet standards specified for automotive seating and back applications. Compression

modulus and compression stress at 25%, 50%, and 65% strain all increase with increasing concentrations of both CO₂-based polyols. Most significantly, inclusion of 50% polyol D 351-30 resulted in compression modulus and compression stress at 25%, 50%, and 65% strain values over 200% greater than the 100% petroleum-based sample. Tensile strength at maximum load is 60% and 43% greater than the 100% petroleum-based sample with inclusion of polyol D 251-20 and polyol D 351-30, respectively. Young's modulus was 86% and 129% greater than 100% petroleum-based foam with 50% inclusion of polyol D 251-20 and polyol D 351-30, respectively. Tear resistance was 68% and 58% greater than 100% petroleum-based foam with 50% inclusion of polyol D 251-20 and polyol D 351-30, respectively. DMTA testing shows that the storage modulus increases with increasing CO₂-based polyol concentrations at low temperatures. Thermal analysis by TGA shows that there is less thermal stability with increasing concentrations of CO₂-based polyol in the foams, but the materials remain stable until beyond 200 °C. Inclusion of CO₂-based polyol into seating applications provides a global solution for replacing petroleum-based chemicals with sustainable alternatives. Optimization of the formulation(s) for the various applications should improve performance. Further studies may look into the combination of CO₂-based polyol with other bio-based polyols to try to increase renewable content while improving properties of the final foam simultaneously.

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