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Preparation and Characterization of Selected Rigid Polyurethane Foam Formulations

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Abstract

Density of rigid polyurethane foam (RPF) has a major effect on its mechanical properties which, in turn, determine the performance level in different applications. Several RPF samples were prepared through free and non-free rise foaming with different densities by changing the weight percent of its major chemical constituents. Moreover, some additives were used to change the density in the range of 40-900 kg/m^3. Stress-strain curves of selected samples showed clearly the effect of density on the mechanical properties (such as elastic modulus and plateau stress values), effect of load direction on resistance of samples to the applied load, and effect of preparation method (in high density samples) on the mechanical properties. Finally, Stress-strain curves were used to assess the rigidity level change due to chemical formulation nature change.

Key Words

Rigid Polyurethane Foam, Stress-Strain relation, Elastic modulus.

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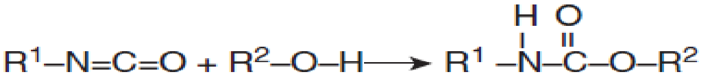
1. Introduction

The discovery of polyurethane [PU] dates back to the year 1937 by Otto Bayer and his coworkers at the laboratories of I.G. Farben in Leverkusen, Germany. The initial studies focussed on PU products obtained from aliphatic diisocyanate and diamine forming polyurea, till the interesting properties of PU obtained from an aromatic diisocyanate and polyol, were realized [1]. Some of the properties common to both polyether and polyester urethane rigid foams are the foaming ability on spot, wide range of physical properties, combination of high strength and light weight, good heat resistance properties, and excellent adhesion to several surfaces.

For a given polyol system, the foam properties can be varied by merely changing the density. Properties such as compressive, tensile, shear, flexural stress and modulus of elasticity depend to a considerable degree on foam density [2].

Made of a skeleton of more or less regular open or closed cells, polymer foams have a high capacity of energy absorption which is useful for shock attenuation, acoustic and thermal insulation in some cases, filtering applications, etc. For these reasons, polymer foams are widely used in aircraft structures, automobile, buildings, and packaging industry. Combining good mechanical properties with a low density, rigid polyurethane foam can also be used as sacrificial material to partially mitigate the blast wave hazards [3].

The urethane linkages can be produced by different routes. The most common are through reactions of the isocyanate groups with compounds bearing hydroxyl groups, e.g.



$$R^1{-}N{=}C{=}O + R^2{-}O{-}H \longrightarrow R^1{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R^2$$

Also, the water origin reacts with isocyanate to form carbamic acid, which is unstable, and decomposes forming carbon dioxide (the foaming agent) and an amine.

$$R\text{-}N{=}C{=}O + H_2O \longrightarrow R\text{-}NH\text{-}COOH \longrightarrow R\text{-}NH_2 + CO_2$$

The amine reacts with more isocyanate to give a substituted urea.

$$R_1\text{-}N{=}C{=}O + R_2\text{-}NH_2 \longrightarrow \text{-}R_1NH\text{-}CO\text{-}NH\text{-}R_2\text{-}$$

Produced urea is not strongly soluble in the reaction mixture and tends to form separate hard segment phases consisting mostly of polyurea which have a significant impact on the RPF properties [4, 5].

The choice of polyol type (functionality) has a major influence on the physical properties of the resultant foam at which it determines whether the foam will be rigid flexible, brittle or ductile, and the extent of its permeability to gas and moisture. The choice of the isocyanate type for PU production is governed by the required properties for end-use applications. To prepare RPF, aromatic isocyanates are chosen, however, PU produced from these isocyanates shows lower oxidative and UV stabilities .The most commonly used diisocyanates in production of rigid foam are toluene diisocyanate TDI and methylene di-para-phenylene isocyanate MDI [2].

Regarding to compressive strength, most of rigid urethane foams have an elastic region in which the stress is nearly proportional to the strain. However, they do not entirely follow Hook's law, because the curve is slightly S shaped. In compression, the elastic region varies from 5 to 10% of the initial deflection (strain). Beyond the yield point, the foam has small elastic recovery. If a foam is compressed beyond that point, the cell structure is crushed. The stress required to crush the foam cell structure is about the same as the yield point stress. In the plateau region, strain increases with little or no increase in stress. The plateau behavior can extend to about 70-80% strain compression, Figure (1). At higher strain rates, higher values of stress and smaller plateau ranges may be obtained. Most rigid foams are anisotropic in that they are stronger in the direction of foam rise. In molded items, the directional properties of the foam can be minimized by overloading the mold, but then higher density foam is produced [2].

The aim of this work is to prepare several rigid polyurethane foams through different combinations of polyol and isocyanate compounds, study the foam composition-density relationship, and determination of stress-strain behavior of these foams.

2. EXPERIMENTAL WORK

2.1 Preparation method

Preheated (70^0C for five minutes) Polyol [Voracor($(C_4H_6)_{50}H_2O_2$)(commercial), triethanol amine (TEA)(commercial) or glycrol (sigma-aldrich)] were mixed with preheated (70^0C for five minutes) diisocyanate (methylene di-para-phenylene isocyanate MDI (sigma-aldrich) or toluene diisocyanate TDI (sigma-aldrich)) using mechanical stirrer until homogeneous blend was obtained (450 rpm within 5-10seconds). The product was derived immediately prior to injection into the shaping mold. Eighteen RPF samples were prepared with compositions shown in the following tables. Measurement of stress-strain were carried on parallel to the direction of foam rise.

2.2 Effect of density on RPF mechanical properties

Densities of Samples (1, 2, and 3) were controlled by variation of the mass in a constant mold volume (non-free rise foaming), while densities of samples (4 and 5) were varied by changing the weight percentages of MDI and voracor, Table (1).

Table (1). Composition and density of samples containing voracor and MDI

Sample no.	**Total mass (g)**	**voracor (Wt %)**	**MDI (Wt %)**	**Density (kg/m^3)**	**Type of rise**
1	64	50	50	60	Non-free rise
2	80	50	50	75	Non-free rise
3	96	50	50	90	Non-free rise
4	96	66	34	50	Free rise
5	96	34	66	90	Free rise

Compression stress- strain curves for Samples 1, 2, 3, and 5 were obtained using tension-compression machine to evaluate the mechanical properties of these selected samples, and variation of load direction was carried out for sample 2.

2.3 Effect of isocyanate type on RPF mechanical properties

Samples (6, 7, and 8) were prepared with the same density and curing ratio as samples (2, 3, and 5 respectively), since the latter will be used as reference, Table (2).

Table (2). Composition and density of samples containing voracor and TDI

Sample no.	**voracor (Wt %)**	**TDI (Wt %)**	**Density (kg/m^3)**	**Type of rise**
6	58.80	41.20	75	Non-free rise
7	58.80	41.20	90	Non-free rise
8	41.46	58.54	90	Free rise

Then, stress- strain curves for Samples 6, 7, and 8 were obtained and compared to their analogous in MDI system (samples 2, 3, and 5 respectively).

2.4 Effect of polyol type on RPF density

Through taking sample no.5 as reference, samples no. (9 and 10) were prepared with insertion of TEA as a part of polyol. Samples no. (11, 12, and 13) were prepared with insertion of buffered TEA (TEA + HCl) as a part of polyol. Finally, samples no. (14 and 15) were prepared with insertion of glycrol as a part of polyol, Table (3).

Table (3). Composition of samples containing different polyols and MDI

Sample no.	voracor (Wt %)	MDI (Wt %)	TEA (Wt%)	HCl (Wt%)	Glycrol (Wt%)	Type of rise
9	25.75	66	8.25	0	0	Free rise
10	17.0	66	17.0	0	0	Free rise
11	17.0	66	15.75	1.25	0	Free rise
12	17.0	66	14.5	2.5	0	Free rise
13	17.0	66	12.0	5.0	0	Free rise
14	25.75	66	0	0	8.25	Free rise
15	17.0	66	0	0	17.0	Free rise

To calculate the density of these prepared samples, the mass is normally determined with a balance; while the volume was calculated directly from the geometry of the sample or by the displacement of a fluid.

2.5 Effect of blowing agent percentage on density

Samples (16, 17, and 18) were prepared with addition of different amounts of distilled water to the system containing voracor polyol and MDI, Table (4).

Table (4). Composition of samples containing voracor, MDI, and blowing agent

Sample no.	voracor (Wt %)	MDI (Wt %)	Dist. H_2O (Wt %)	Type of rise
16	48.75	50	1.25	Free rise
17	47.5	50	2.5	Free rise
18	45	50	5	Free rise

Then, the density was measured for these samples.

3. RESULTS AND DISCUSSION

3.1 Effect of density on RPF mechanical properties

Mechanical properties determination tests have shown the dependence of plateau stress and elastic modulus on foam density, Figure (2). These mechanical properties are major factors in some applications of rigid PU foams particularly that related to shock absorbance applications. Also In Figure (2), stress-strain curves show the effect of rise type during preparation. In case of high density (90 kg/m^3), it is clear that preparation of high densities through overloading the mold has a negative effect on the mechanical properties of foam. The influence of the load direction is obvious in Figure (3); resistance of the foam to load was higher when that load was parallel to the direction of foam rise during preparation.

3.2 Effect of isocyanate type on RPF mechanical properties

Reflection of the benzene rings number (with constant density for the compared samples) on the rigidity of the foam structure is clear in Figures (4 and 5), since decreasing the number of benzene rings (using of TDI instead of MDI) the structure becomes less rigid. The difference is not too large for 90 kg/m^3 prepared by non-free rise foaming as there was defects in both samples due to overloading the preparation mold, as shown in Figure (6).

3.3 Effect of polyol type on RPF density

Sample 5 is taken as reference for the following results. Decreasing the percentage of isocyanates in the formulation, sample (4), decreased the value of density due to decrease of the crosslinking degree in the structure, Figure (7). Incorporating triethanol amine as a part of the polyol system (samples 9), firstly, increased the crosslinking degree due to the presence of third OH group in triethanol amine acing as a crosslinking tool between the polyurethane chains. Moreover, the presence of amine group has more catalytic effect on the urethane reaction rate building the skeleton of the foam (than the foaming reaction rising the foam) leading to higher density (120 kg/m^3). The balance between the rates of the two reactions could be lost by increasing the concentration of these amine groups and very high density could be reached (sample 10).

When buffered triethanol amine was used (samples 11, 12, and 13) the catalytic effect was reduced leading to lower densities than in samples 9 and 10 as shown. Through these results, the sharing percent of triethanol amine or buffered triethanol amine in the polyol system was used as a means to control the density. In the same way the presence of glycrol as a part of polyol system (samples 14 and 15) could increase the amount of crosslinking leading to higher densities compared to samples containing voracor alone (sample 5).

3.4 Effect of blowing agent percentage on density

Reversely, the density of rigid polyurethane foam could be reduced by increasing the concentration of water as a blowing agent (Figure 8) in the formulation system (samples 16, 17, and 18). In this case, the rate of foaming reaction (producing CO_2) exceeds that of the urethane formation reaction.

4. CONCLUSION

- Density of rigid polyurethane foam has a major effect on its mechanical properties. The higher the density, the higher the values of plateau stress and modulus of elasticity.
- Rigidity of the foam structure can be changed through variation the number of benzene rings in the formulation structure. Increasing the number of benzene rings increases the foam rigidity (using MDI instead of TDI).
- Using different concentrations of tertiary amine polyols successfully controls Density of rigid polyurethane foam because of its effect on urethane reaction rate.
- Density of rigid polyurethane foam can be controlled through foaming reaction rates, by using different concentrations of blowing agent.

6. References

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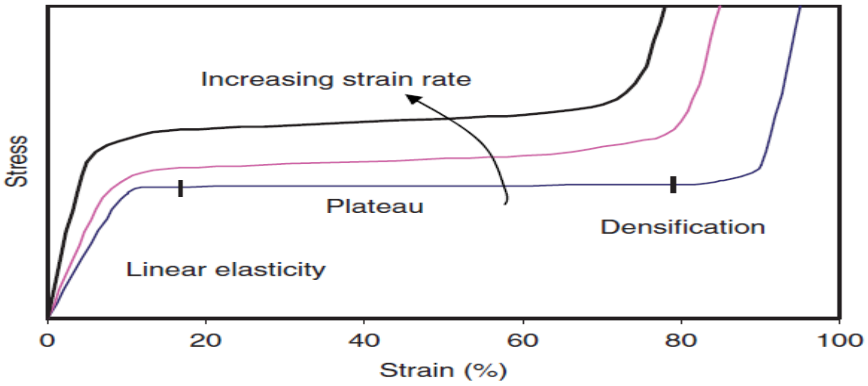

Figure (1) General compressive stress strain behavior of polymeric foam

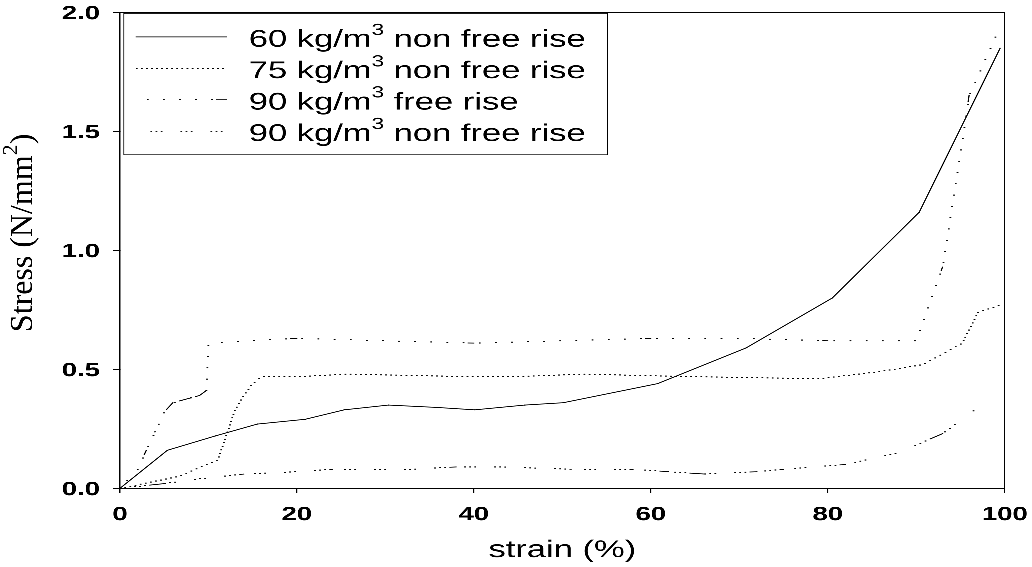

Figure (2) Stress-strain curves for PU foam at different densities

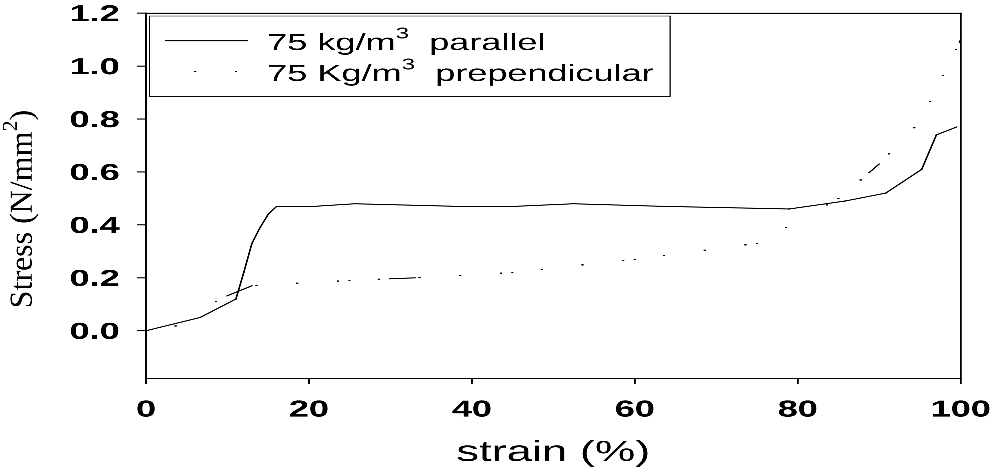

Figure (3) Stress-strain curves for non-free rise PU foam of different load direction

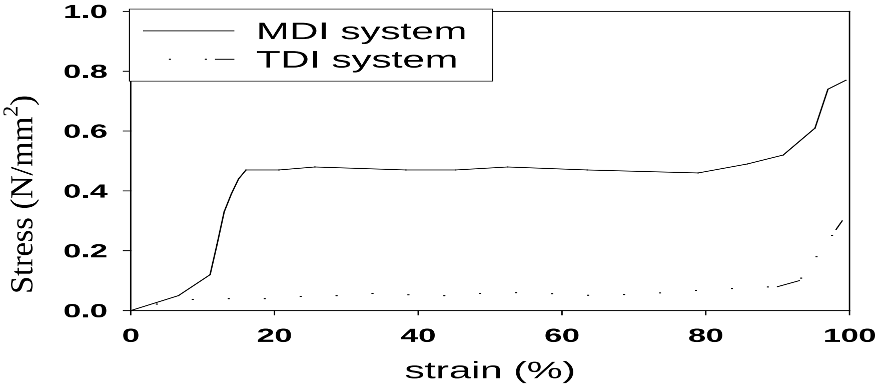

Figure (4) Stress-strain curves for non-free rise PU foam containing different number of benzene rings (density=75 kg/m^3)

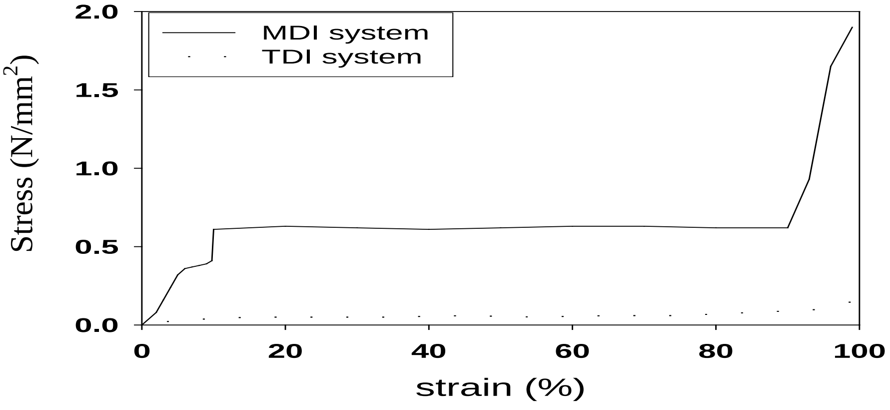

Figure (5) Stress-strain curves for free rise PU foam containing different number of benzene rings (density=90 kg/m^3)

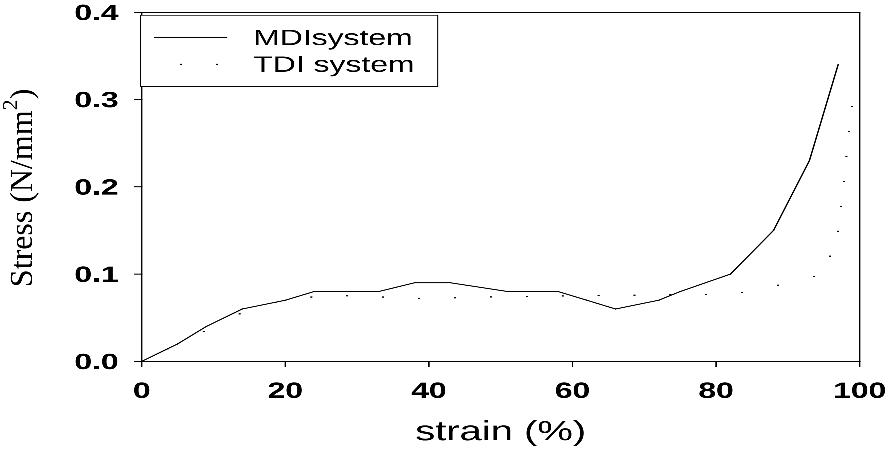

Figure (6) Stress-strain curves for non-free rise PU foam containing different number of benzene rings (density=90 kg/m^3)

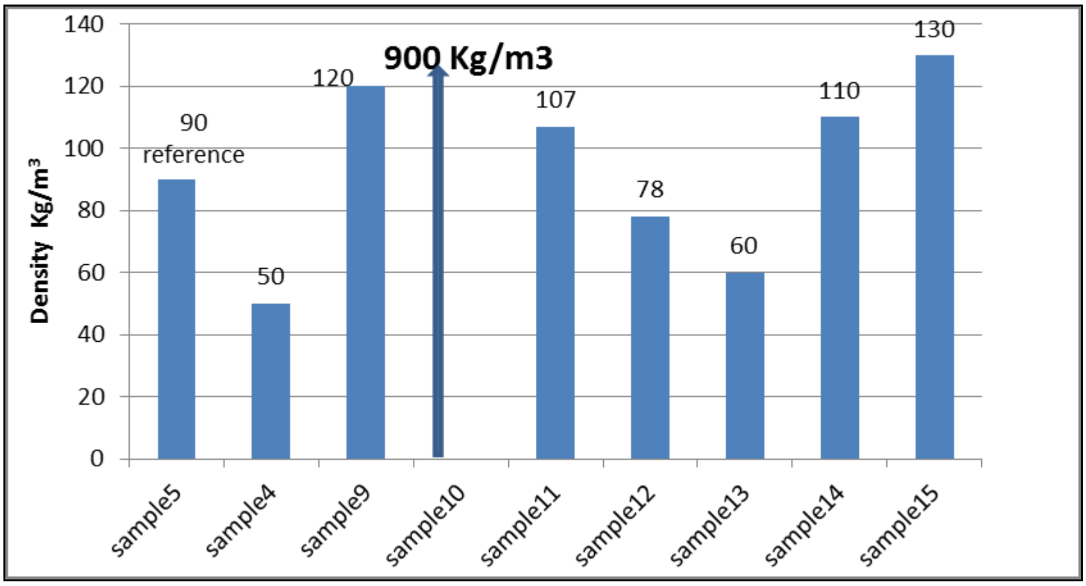

Figure (7) Densities of PU foams with different chemical formulations

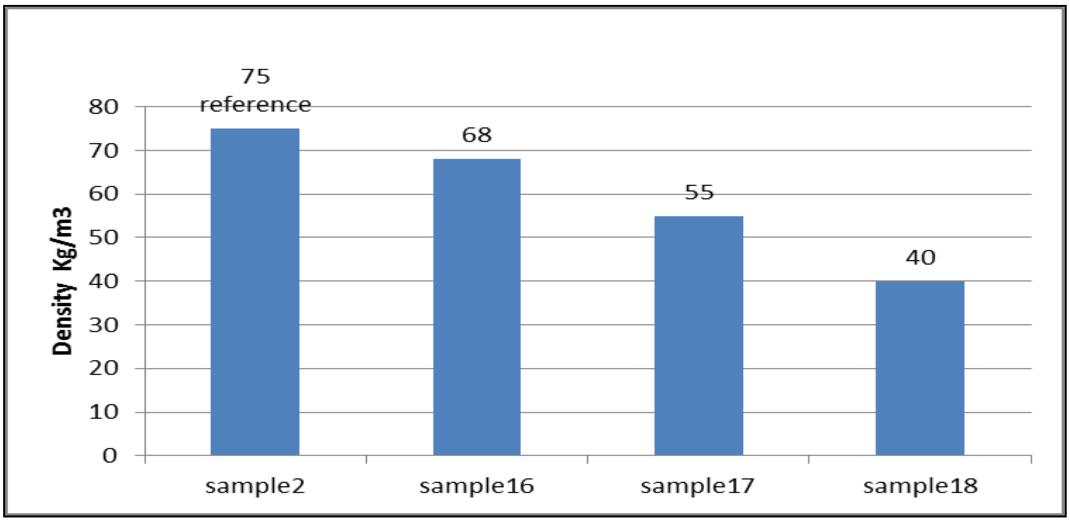

Figure (8) Densities of PU foams containing different concentrations of blowing agent