CSCanada
Advances in Petroleum Exploration and Development
Vol. 7, No. 1, 2014, pp. 1-6
DOI:10.3968/j.aped.1925543820140701.1962

ISSN 1925-542X [Print]
ISSN 1925-5438 [Online]
www.cscanada.net
www.cscanada.org

Morphological and Physico-Thermal Properties of Soy-Based Open-Cell Spray Polyurethane Foam Insulation Modified With Wood Pulp Fiber

Mustafa Khazabi[a],*; Mohini Sain[a]

[a] Faculty of Forestry, University of Toronto, Canada.
*Corresponding author.

Supported by NSERC Collaborative Research and Development, thank FPInnovations and Mr. Bob Knudson, Ruijun Gu, Koumbi-Mounanga Thierry and Govindarajan Sankar for their support.

Received 6 January 2014; accepted 24 March 2014

Abstract

Replacing polyether and polyester polyols with soy-based vegetable oil, using water as a blowing agent, would provide environmentally friendlier spray foam insulations, making buildings safer places to live in. The objective of this work was to produce sustainable open-cell spray polyurethane foam insulation from soy-based polyol and enhance its properties by incorporation of wood pulp fiber. The effect of wood fiber in composite foam was investigated in terms of its morphology by Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM), and Thermo-gravimetric Analysis (TGA). The changes in foam properties such as bulk density, compressive strength, water vapor permeability and thermal resistance were observed. Addition of fiber as reinforcement improved bulk density, moisture permeability and thermal degradation, but slightly reduced the comprehensive strength and thermal resistance of the insulation foam.

Key words: Spray foam; Polyol; Isocyanate; Wood fiber; Hydrogen bonding; Polyurethane; Urethane; Urea; Hard segment; Open-cell

Khazabi, M., & Sain, M. (2014). Morphological and physico-thermal properties of soy-based open-cell spray polyurethane foam insulation modified with wood pulp fiber. *Advances in Petroleum Exploration and Development*, *7*(1), 1-6. Available from: http://www.cscanada.net/index.php/aped/article/view/j.aped.1925543820140701.1962
DOI: http://dx.doi.org/10.3968/j.aped.1925543820140701.1962

INTRODUCTION

High petroleum prices over the last two decades, along with sustainability of resources have prompted the researchers to look for alternative renewable resources to produce eco-friendly insulation foam to be used in buildings. Soy oil, palm oil, and castor oil - to name a few, exist in plenty to be considered as potential replacements for petrochemical polymers. Soy-based polyol generated from soy bean oil is gradually gaining industrial importance as it contains high O-H value make it more suitable for obtaining good quality spray foam insulation.

Soy-based polyurethane (PU) foams are produced by the reaction of isocyanate with soy polyol. For water blown polyurethanes, foaming process involves two basic reactions where isocyanate reacts with a) polyol to generate the urethane linkages leading to curing and b) water to form urea and carbon dioxide to expand the polymer. Rigid and flexible foams are the two main categories in polyurethane industry. Open-cell spray polyurethane foam (SPF) is a rigid type of foam, widely used as wall insulation in residential and commercial buildings. It has the ability to reduce heat loss and provide a good air/moisture barrier with respect to traditional fiber glass insulation, and to save energy for home owners. Two main components, component 'B' as isocyanate and component 'A' as polyol, mixed with catalysts including blowing agents, come together at the nozzle of a gun and are sprayed between the struts of the wall. It expands many times of its liquid volume and solidifies in seconds sealing the wall.

In general, the performance of PU foam depends on hard and soft segment ratio in copolymers. Hard segments are those formed by the reaction of di-isocyanate with short-chain diols. They contain high density urethane groups of high polarity, and for that reason, the foam becomes rigid. On the other hand, soft segments are shaped by the reaction of di-isocyanate with the long-chain diols, having low density urethane groups and polarity, and therefore, are flexible. They usually have a phase separation due to the incompatibility between the hard and soft segments. The high polarity of hard segments generates a strong attraction between them which forms a high concentration and order in this phase, generating crystalline regions within flexible matrix[1]. The crystalline areas have high levels of elasticity and act as cross linkers, whereas the flexible or soft chains are more chain extenders and give longitudinal strength to the polymer. When a load is applied to the foam material, the soft segment phase would stretch while the hard segment would carry the load and release it when the stress is removed.

The objective of this study was to develop an optimum formulation to produce open-cell soy-based SPF insulation in the laboratory and to introduce wood fiber into it as reinforcement. The fiber was incorporated in 13%, 26%, and 40% per hundred grams of polyol (php). Many research studies have demonstrated that fiber has strength and its addition would enhance foam properties. Though this effect has been reported for flexible and rigid foaming, little is known about introducing fiber in spray foam insulation. In this study an attempt has been made to incorporate fiber in open-cell spray foam insulation and try to understand the fiber-polyurethane interactions at morphological level, as well as its effect on the physio-chemical properties of spray foaming. The benefits would be to encourage the use of sustainable and green materials, to reduce CO_2 emissions, and to increase safety and comfort in buildings.

1. EXPERIMENTAL

1.1 Materials

Bi-functional soy-based polyol (Soyol R-2101) was obtained from Urethane Soy Systems, Volga, USA. Its viscosity @ 25° C was 2040 cps with hydroxyl value 69 mg KOH/g. The aromatic polymeric diphenylmethane di-isocyanate (Robinate M) was donated by Huntsman PU Geismar, LA, USA having functionality of 2.7, NCO content 31.5%, and viscosity @ 25° C 190 cps. The surfactant and catalysts I & II were also donated by Air Products and Chemicals, Allentown, USA. Distilled water was used as blowing agent. Mechanically pulped medium density wood fiber with average 1600 μm in length was donated by FPInnovations, Canada. It was grinded to 400 μm in length to reduce the impact of viscosity. The aspect ratio was estimated to be around 8.

1.2 Foam Preparation

Spray foam specimens were prepared by mixing soy-based polyol and other ingredients with isocyanate at room temperature in the laboratory, which was poured into a mould for free rise. After two hours, the samples were removed from the mould and left for 48 hours for full curing under ambient temperature. It may be mentioned that the quantity of all ingredients used in the formulation was expressed as part per hundred grams of polyol (php). In case of composite foam, at first fiber was mixed thoroughly with polyol and then other ingredients and isocyanate were added.

The first set of experiments was carried out to obtain neat foam. Many samples were prepared trying out different catalysts and surfactants of varying quantities to arrive at the optimum formulation. The amount of water had significant influence on the blowing behavior and formation of cell sizes. Then wood fiber was incorporated as reinforcement in 13%, 26%, and 40% php. Attempt has been made to increase the concentration of wood fiber as much as possible to reduce the amount of raw materials and make the Biofoam more environmentally friendly. At least four scenarios were prepared - one for neat foam and the others for fiber foam at the above quantities.

Foam has been characterized by Fourier transform infrared (FTIR) spectroscopy to determine the behavior of different functional groups present in the polymer structure. Brucker infrared spectrometer with resolution of 4 cm^{-1} and 32 scans for signal averaging was used to record the spectra of the samples. Cellular structural observations have been made with Hitachi S-2500 as well as Hitachi TM-1000 Table-top scanning electron microscopy (SEM). Thermal degradation of neat and composite foam samples have been investigated using Thermo-gravimetric Analyzer Q 500 at heating rate of 10 °C/min. in nitrogen atmosphere. Decomposition temperatures at different weight loss percentages have been recorded. The Brookfield Viscosity Test (BVT) was utilized to measure the viscosity of polyol with added ingredients known as component ‘A’. The ingredients were catalysts, blowing agent, surfactant and fiber (where applicable). The mixture was poured into a glass jar and placed under a viscometer. The tests were performed for 30 seconds at ambient temperature with spindle number 64 and running speed of 50 and 100 RPM and averaged.

The American Society for Testing and Materials (ASTM) procedures were utilized to evaluate the effect of fiber on physical and mechanical properties of foam samples. At least five samples were considered for each test with ±3% error. The bulk density of the foam was estimated by direct measurement of volume and weight of the samples according to ASTM-D1622. The compressive strength was determined in accordance with ASTM-D1621. The test was carried out using INSTRON 3367 equipment with crosshead speed of 2.5 mm/min. and cell load of 2 kN. The square specimens of 50 mm x 50 mm cross-sectional dimensions and 25 mm thickness were used for both tests. Water vapor transmission property plays an important role in assessing moisture permeability of foam insulation. The test method is specified in ASTM-E96. A foam specimen of 25 mm thickness, was sealed to the open mouth of an impermeable dish containing water and placed in a desiccator containing saturated calcium nitrate (as desiccant) to maintain a relative humidity of 50% at all times. The whole assembly was placed in atmospheric temperature. The test dish was filled with water to a level 25 mm from the specimen having a mouth area of 12.6 cm X 12.6 cm. and defined as the area of the specimen exposed to the water vapor. Periodic weighing of dish assembly determined the rate of water flow through the specimen. As foam insulations are rated in terms of their resistance to heat flow, the thermal resistance and R-value of foam samples were determined in accordance with ASTM-C518, by means of the heat flow meter apparatus and in conjunction with ASTM-C1045 standard practice for calculating thermal transmission. Laser Comp FOX314 Heat Flow Meter instrument was used.

1.3 Results and discussions

A series of neat and wood fiber SPF samples were prepared to evaluate the effect of wood fiber on physical and mechanical properties. They are summarized in Table 1. The same formulation was used in preparation of all samples including fiber foam. It was observed that addition of fiber delayed foam creaming compared to the neat foam and increased the bulk density as fiber content was raised. During foaming process fiber could be acting as a heterogeneous nucleating agent producing smaller cell sizes, thereby increasing the foam density[2, 3]. To verify this reduction due to addition of fiber, the average cell diameters of samples were measured utilizing SEM images and Image J software. It was determined that it had decreased from 184 µm for the neat foam to 170 µm for the fiber foam. On the other hand, compressive strength of fiber foam was reduced compared to neat foam. The strength reduction was about 7% to 28% depending on fiber content. Higher fiber content resulted in lesser reduction in strength. The presence of fiber as nucleating agent not only generated smaller cell sizes, but also reduced the cell wall thicknesses and lowered the compressive strength.

Table 1
Physico-Thermal Properties of Neat and Composite Polyurethane Spray Foams

Foam type	Average density (kg/m^3)	Average compressive strength (KPa)	Water vapor transmission ($g/h \cdot m^2$)	Thermal resistance at 25mm thickness ($K \cdot m^2/W$)	R-value (US) ($h \cdot ft^2 \cdot {}^\circ F/Btu$)
Neat foam	20.99	23.70	3.77	0.604	3.43
13% php wood fiber foam	20.60	17.02	2.50	0.535	3.05
26% php wood fiber foam	24.80	18.35	2.25	0.550	3.11
40% php wood fiber foam	26.97	22.10	2.18	0.500	2.85

The performance of PU foam also depends on the quantity and quality of cross-links formed within the polymer network. Higher cross-links give rise to higher compressive strength[4]. Reaction of di-isocyanate with multifunctional polyol and water leads to the formation of urethane and urea linkages that are highly cross-linked network. Urethanes are elastomers with combination of hard and soft segments whereas urea polymers are hard short chains and bridge urethane units. In a more balanced and stable polyurethane structure, urethane chain formations are greater or equal to that of urea production in order to create a good hydrogen bonding between N-H groups (acceptors) and C=O groups (donors) within the network[5]. They are cross-linked together into a single networked molecule that is hard to break and can withstand the pressure in a more effective manner[6].

To understand the chemistry between these two hard segment groups, foam samples were analyzed by FTIR spectroscopy. Figure 1 represents peak absorptions of urethane carbonyl groups at 1740 cm^{-1} and urea carbonyl groups at 1660 cm^{-1}. It was observed that for the neat foam the concentration of urethane carbonyl groups had increased, while that of urea carbonyl groups had decreased. This is an enhancement to the foam. The addition of fiber had reversed this process by decreasing the absorbance of urethane carbonyl groups followed by increasing the urea carbonyl groups. For an unknown reason, fiber hysterically hindered the reactivity of isocyanate with polyol causing less formation of urethane linkages and promoted the blowing reaction increasing the urea. They did not interact in an efficient manner. Thus the fiber foam network did not generate enough urethane elastomers to support a strong network to carry the applied stress and thus lowered the compressive strength[7, 8]. It may be noted that this slight reduction in compressive strength is less important in spray foam as wall insulation.

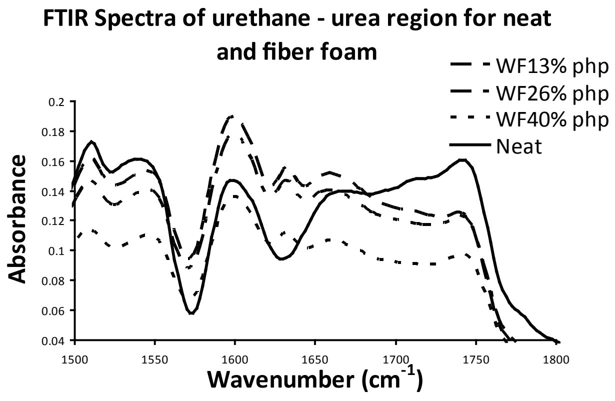

Figure 1
FTIR Spectra Peak of Urethane Carbonyl at 1740 cm^{-1} and Urea Carbonyl at 1660 cm^{-1}

Thermal resistance and degradation of sample materials have been investigated to observe the behavior of fiber in foaming. According to the US Department of Energy, insulations are rated in terms of their resistance to heat flow (also known as R-value). The higher the resistance, the greater is the insulating effectiveness. The analysis revealed that thermal resistance of the foam has decreased slightly when fiber was embedded. The lower reactivity of polyol with isocyanate has diminished the foam cell strength and formed a weaker three-dimensional structure of cell walls. The cross-linkages in polyurethane solid structure were weakened to such extent that less carbon dioxide could be trapped inside the foam during foaming process. Thermal resistance of foam would be greatly improved if more diffused gas could get trapped inside. As more air replaced the escaped carbon dioxide, the thermal conductivity of the material was increased and resulted in lower thermal resistance and R-value[9]. However, both thermal resistance and R-value measurements of open-cell spray foam with or without fiber matched the commercial foam values and were in accordance with minimum requirements specified by CAN/ULC-S706-09.

Thermal gravimetric analysis determined degradation behavior of Biofoam. Temperatures at different percentages of weight loss were recorded as shown in Table 2. Both neat and composite foams experienced a two-stage weight loss behavior supplemented by two major endothermic peaks representing urethane and urea bond degradation. The initial degradation of foam started at about 250 °C (at 5% weight loss, T5), and was delayed slightly at higher levels of fiber content. As temperature was increased, urethane linkages and urea bonds started to decompose, as indicated by two endothermic peaks[10]. The recorded data indicated that degradation temperatures have been delayed at 50% and 75% weight losses (T50 & T75) for the fiber foam. All samples experienced significant weight losses at 600° C at relatively same percentage. Hence, it was obvious that the fiber had positively influenced thermal behavior of the foam and delayed its degradation temperature. This effect increased as fiber content was increased. This suggested that some O-H groups on the surface of fiber must have reacted with N-C-O groups of isocyanate, increasing urethane formation beyond polyol and isocyanate reaction. FTIR spectra in Figure 2 also revealed that free N-C-O group peaking at 2270 cm^{-1} were diminished in fiber foam system. Therefore, fiber foam system had more thermal stability than the neat foam.

Table 2
Thermal Degradation Analysis of Spray Foam Insulation

Foam Type	Degradation Temperature (°C)			Residue in % @ 600 °C
	T5	T50	T75	
Neat Foam	253	376	458	12.27
Fiber Foam WF13% 400	250	370	458	12.75
Fiber Foam WF26% 400	247	380	460	11.50
Fiber Foam WF40% 400	261	384	462	12.91
Wood Fiber only	206	353	380	12.04

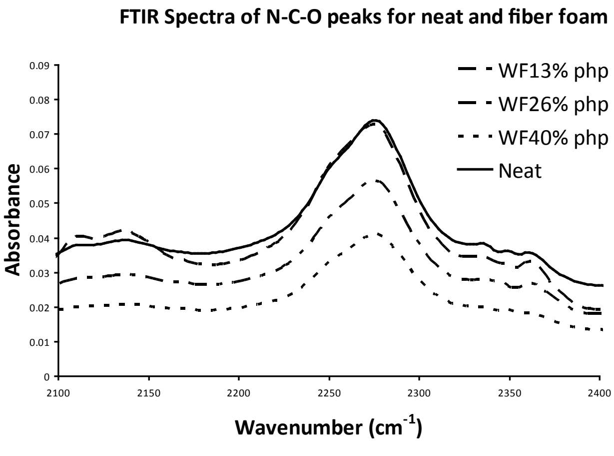

Figure 2
FTIR Spectra of Free N-C-O Absorption Peak at 2275 cm^{-1}

Water vapor transmission property plays an important role in assessing moisture permeability of foam insulation. This is the rate of water vapor flow through unit area of a flat material of unit thickness under specified temperature and relative humidity conditions[11]. As water vapor moves from a warm interior through the insulation material to a cooler surface, it gets condensed as liquid water. The condensed water not only reduces the thermal effectiveness of the insulation but also damages the foam structure[12]. In order to measure water permeability through each foam samples, an apparatus was constructed and the flow of water vapor was measured during different time intervals. The effect of moisture permeability on various foam samples were determined and tabulated in Table 1. It was demonstrated that presence of wood fiber in foaming would enhance the foam quality by restricting the flow of water vapor through the foam. The permeability was decreased with increase in fiber content suggesting that fiber acted as moisture barrier in foam insulation.

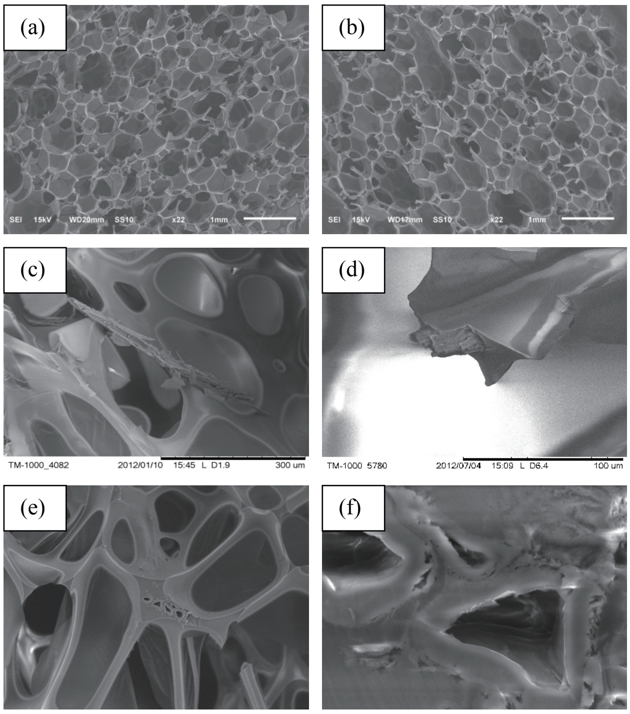

Figure 3
SEM Foam Cell Structure (a) 13% Php Fiber Foam, (b) Neat Foam, (c) Fiber Detection, (d) Fiber Compatibility With Matrix, (e-f) Fiber Embedded in Foam

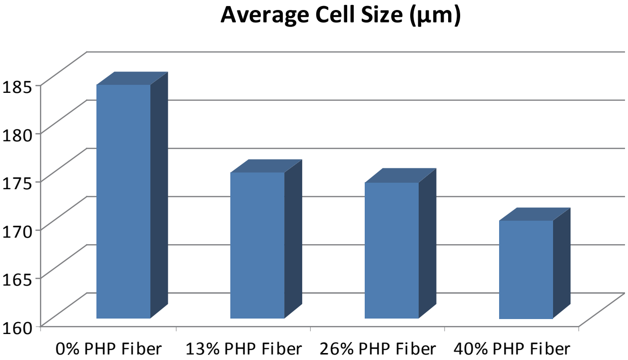

Figure 4
Average Foam Cell Size (Micron)

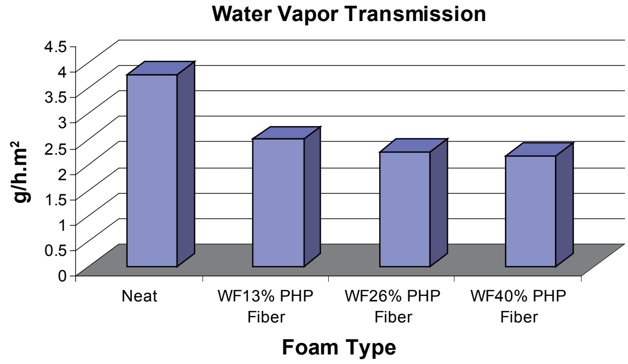

Figure 5
Water Vapor Transmission for the Foam System

To justify the effect of fiber in foaming structure, SEM observations have been made. Figure 3(a) and (b) represents SEM images at 13% and 0% wood fiber content. It was observed that for the neat foam without fiber, cell structures were generated in random and irregular shapes, but as fiber content was progressively increased, cell formation became smaller and more homogeneous. Figure (c) to (f) of SEM images revealed the interaction of fiber with matrix polymer. At some point, fiber was detected free, standing within the foam structure with no interaction, while in another it did so and dispersed within the cell walls. The O-H groups on the surface of the fiber had reactivity with N-C-O groups of isocyanate just like O-H groups of polyol and exhibited some compatibility with the polymer[13]. This effect has been seen by the reduction of free N-C-O groups at 2275 cm^{-1} in FTIR observation. However, the interaction between the fiber and polymer matrix was insignificant, perhaps due to the presence of impurities such as hemi-cellulose and lignin in pulp wood fiber.

Presence of fiber also influenced creaming behavior during the foaming process and reduced slightly the rising height of the foam. This was attributed to the decreased formation of urethane linkages in presence of wood fiber.

Aspect ratio and concentration of fiber play an important role in foam reinforcement. Although longer fiber length would provide better reinforcement, it would create high viscosity problems in polyol component[14] and could not be sprayed with conventional spray guns. Thus, pulp fiber had to be grinded to optimum length of 400 μm to keep viscosity increase of polyol component at minimum. As the fiber content was increased, so was the viscosity. It was observed that the increase in viscosity would be about 10% if fiber concentration remains under 20% php and it could still be sprayed by conventional guns. Incorporation of more fiber percentages in foaming requires modification to present spray foam system, when it would become possible to spray the fiber simultaneously with the polymer matrix.

CONCLUSIONS

Spray Polyurethane foam was successfully produced in the laboratory with soy-based polyol matrix and water as blowing agent. The neat foam was reinforced with wood fiber as much as possible and its impact as reinforcement was investigated. The Biofoam made by this formulation had comparable properties; same or even better than commercially available spray foams. When fiber was embedded in spray foam, the analysis indicated that pulp wood fiber was less compatible with the matrix, perhaps due to its impurities, and its presence slightly interfered with hydrogen bonding between urethane linkages during foam formation. As cross-linked urethane elastomers were not promoted enough, the comprehensive strength and thermal resistance of the fiber foam were not enhanced in comparison to the neat foam. However, the density of fiber foam was increased as more homogenous and smaller cells were formed as a result of nucleating effect. Addition of fiber also enhanced the foam and delayed the thermal degradation. The moisture permeability was greatly improved in fiber foam system indicating that fiber acted as a good moisture barrier enhancing the foam quality. Though it was possible to achieve high fiber content spray foam of up to 50% php without major impact on foaming reactions, the analysis demonstrated that the fiber content may not exceed more than 20% php in order to achieve optimum viscosity to be able to spray with conventional spray gun system. However, the spraying technology could be improved to accommodate more fiber content in foaming.

REFERENCES

[1] Bagdi, K., Molnar, K., Sajo, I., & Pukanszky, B. (2011). Specific interactions, structure and properties in segmented polyurethane elastomers. *Express Polymer Letters*, *5*(5), 417-427.

[2] Xia, C., Lee, J. L., Widya, T., & Macosko, C. (2005). Polyurethane/clay nanocomposites foams: Processing, structure and properties. *Polymer, 46*, 775-783.

[3] Ema, Y., Ikeya, M., & Okamoto, M. (2006). Foam processing and cellular structure of polylactide-based nanocomposites. *Polymer*, *47*, 5350-5359.

[4] Fan, H., Tekeei, A., Suppes, G. J., & Hsieh, F. H. (2012). Physical properties of soy-phosphate polyol-based rigid polyurethane foams. *International Journal of Polymer Science*. doi: 10.1155/2012/907049.

[5] Zhang, C., Ren, Z., Yin Z., Qian, H., & Ma, D. (2008). Amide II and amide III bands in polyurethane model soft and hard segments. *Polymer*, *60*, 97-101.

[6] McDaniel, P. L., Johnson, G. L., Kniss, J. G., Miller, J. W., & Sabram, K. A. (1999). Fiber optic FTIR: A novel PUR/PIR catalyst development tool. *Plyurethane Expo 1999*, 303-312.

[7] Chen, K. S., Yu, T. L., Lin, T. L., Chen, Y. S. & Liu, W. J. (2001). Soft- and hard- segment phase segregation of polyester-based polyurethane. *Journal of Polymer Research*, *8*(2), 99-109.

[8] Poliuretanos. (2013). *Correlations between structure and properties*. Retrieved October 5, 2013, from http://www.poliuretanos.com.br/Ingles/Chapter1/17Correlations.htm

[9] Federation of European Rigid Polyurethane Foam Association. (2006). *Thermal insulation materials made of rigid polyurethane foam*. Brussels, Belgium: Bing.

[10] Opera, S. (2002). Effect of structure on the thermal stability of curable polyester urethane urea acrylates. *Polymer Degradation and Stability*, *75*, 9-15.

[11] Mukhopadhyaya, P., Kumaran, K., Lackey, J., & Reenen, D. (2007). Water vapor transmission measurement and significance of corrections. *Journal of ASTM International*, *8*(4), 1-12.

[12] Straube, J., & Smegal, J. (2009). *Building America special research project: High-R-walls case study analysis*. Report for Building Science Corporation. Report no. 0903, Somerville, MA: Building Science Press.

[13] Trovati, G., Sanches, E. A., Neto, S. C., Mascarenhas, Y. P., & Chierice, G. O. (2010). Characterization of polyurethane resins by FTIR, TGA, and XRD. *Journal of Applied Polymer Science*, *115*, 263-268.

[14] Widya, T., & Macosko, C. W. (2005). Nanoclay-modified rigid polyurethane foam. *Journal of Macromolecular Science*, *44*, 897-908.