Thermal Transition and Mechanical Properties of Magnetite and Wollastonite Filled Rigid Polyurethane Foams

Doğan Berkay Altınel¹, Meral Akkoyun²*

¹ Bursa Technical University, Faculty of Engineering and Natural Sciences, Department of Polymer Materials Engineering, Bursa, Turkey (ORCID: 0000-0001-5804-336X)
² Bursa Technical University, Faculty of Engineering and Natural Sciences, Department of Polymer Materials Engineering, Bursa, Turkey (ORCID: 0000-0002-8113-5534)

(International Symposium on Multidisciplinary Studies and Innovative Technologies (ISMSIT) 2020 – 22-24 October 2020)

(DOI: 10.31590/ejosat.819855)

ATIF/REFERENCE: Altınel, D. B. & Akkoyun, M. (2020). Thermal Transition and Mechanical Properties of Magnetite and Wollastonite Filled Rigid Polyurethane Foams. European Journal of Science and Technology, (Special Issue), 138-145.

Abstract

Polyurethane (PU) foams, despite their low mechanical and thermal conductivity properties, are preferred materials in applications such as automotive, insulation and adhesives because of their ease of processing and their possibility to be produced as rigid/flexible materials. Rigid polyurethane foams are materials used in the automotive, ship and construction industries due to their low density and closed cell structure. In recent years, various properties of polyurethane foams reinforced with different additives, such as morphological, mechanical and conductive properties, have been extensively investigated. However, the effect of magnetite/wollastonite hybrid systems on thermal transition and mechanical properties of rigid PU foam composites was not studied yet. The aim of this work is to explore thermal transition temperatures and mechanical properties of wollastonite (W) and magnetite (M) filled rigid polyurethane foams. The relationships between mechanical and thermal transition properties of the foams and in particular, the effect of the weight ratio of magnetite/wollastonite (1:3, 1:1 and 3:1) hybrid systems on the PU foam properties were studied. The foams produced were characterized by a Fourier transform infrared spectrometer, differential scanning calorimeter and tensile test device. As a result of the studies, it has been determined that the chemical structure of polyurethane foams is not affected by additives (magnetite and wollastonite). Thermal transition results revealed the presence of two main behaviors. In the first case an overall increase of the glass transition temperature of hard segments is observed and this behavior can be explained by the diminution of the mobility of polyurethane chains with the inclusion of magnetite and wollastonite particles between polymer chains. In the second case a general decrease tendency of the glass transition temperature of soft segments is obtained probably due to the presence of magnetite or wollastonite into the polymer matrix which hinders the formation of entanglements of polymer chains. A more important negative impact of wollastonite is observed in tensile properties of rigid PU foams compared to magnetite.

Keywords: Rigid Polyurethane Foam, Wollastonite, Magnetite, Thermal Transition, Mechanical Properties.

Vollastonit ve Manyetit Katkılı Rijit Poliüretan Köpüklerin İslık Geçiş ve Mekanik Özellikleri

Öz

Poliüretan (PU) köpüklerin sahip olduğu düşük mekanik ve termal iletkenlik özelliklerine karşın işleme kolaylığı ve sert/esnek olarak üretilenlikli dehşetlere dolaylı otomotiv, yalıtım ve yapıştırıcı gibi uygulamalarında tercih edilen malzemeleridir. Sert poliüretan köpük ise sahip oldukları düşük yoğunluk ve kapalı hücre yapısı özelliklerinden dolayı otomotiv, gemi ve inşaat sektörlerinde kullanılan malzemelidir. Son yıllarda, farklı katkılarla takviye edilmiş olan poliüretan köpüklerin morfolojik, mekanik ve iletkenlik özellikleri gibi çeşitli özellikleri yoğun bir şekilde araştırılmaktadır. Ancak manyetit/vollastonit hibrit sistemlerin sert PU köpük kompozitlerin termal geçiş ve mekanik özellikleri üzerindeki etkisi henüz araştırılmamıştır. Bu çalışmamız amacı vollastonit (W) ve manyetit (M) 

http://dergipark.gov.tr/ejosat
Polyurethane is one of the most popular polymers which is used for most applications such as automobile, electronic, adhesion and insulations. These polymers are synthesized by a step-growth polymerization reaction of disocyanate with polyether polyols and polyurethane foams are mainly classified into three different types such as rigid, flexible and semi-rigid materials. Rigid polyurethane foams, instead of their low mechanical and thermal properties, are used for most applications such as adhesion and insulation because of their low density and moisture permeability properties. At the same time, these materials are durable, comfortable and light (Ghosh, et al., 2018; Akkoyun & Akkoyun, 2019; Akkoyun & Suvaci, 2016; Usman, et al., 2016; Sattar, et al., 2015).

Magnetite is a preferred material in the development of advanced nanotechnologies for their applications in electronic devices, medical diagnostics and treatment, imaging and production of magnetic nanocomposite materials. Magnetite brings highest insulation into foams. The notable magnetic, thermal and mechanical properties of magnetite allowed this material to be used in rigid PU foam composites for numerous applications (Alavi Nikje, et al., 2015; Akkoyun & Suvaci, 2016; Moghaddam & Naimi-Jamal, 2018; Silva, et al., 2020). Wollastonite, thanks to its properties such as high brightness and white coloration, low moisture and oil absorption, low volatile content and high electrical resistivity is a useful additive which is mainly used for electrical, radio engineering, low-voltage electric insulators. Wollastonite generally affects mechanical properties of polymers (Azarov, et al., 1995).

Nowadays, various properties such as morphological, mechanical and conductivity properties of polyurethane foams reinforced with various fillers are intensively researched (Norshahi, et al., 2018; Król, et al., 2015; Paciorek-Sadowska, et al., 2012; Akkoyun & Akkoyun, 2019; Akkoyun & Suvaci, 2016). However, the effect of magnetite/wollastonite hybrid systems on the thermal transition and mechanical properties of rigid PU foam composites was not investigated yet.

This study aims to explore the impact of wollastonite, magnetite and magnetite/wollastonite hybrid systems on the mechanical and thermal transition properties of rigid polyurethane foams. The relationships between mechanical and thermal transition properties of the foams and in particular, the effect of the weight ratio of magnetite/wollastonite (1:3, 1:1 and 3:1) hybrid systems on the PU foam properties were studied.

2. Materials and Methods

2.1. Materials

Magnetite (Fe₃O₄) was purchased from KIAŞ/Turkey as macro size and was milled within 30 minutes to reduce the mean particle size from 70 µm to 5 µm. Wollastonite (CaSiO₃) was supplied by Quarzwerke GmbH as the supplier reference of TERMIN939 and is a surface-treated filler (iron-free grinding and coating with an organo-silicon compound). In addition to these, isocyanate and polyol were supplied by Kimpur Polyurethane (Istanbul, Turkey) through the supplier reference of Izokin RD 001 and KIMrigid RD 057 respectively. The NCO content and viscosity properties of isocyanate are 30.5±2.5% and 200±40 mPa.s respectively. The polyol used in this work has a viscosity of 400 mPa.s. All materials were used as received.

2.2. Preparation of PU/M/W foam composites

PU/M, PU/W and PU/M/W rigid foam composites were obtained at various filler amount in polyol (10, 15 and 30wt.%). Furthermore, in the case of hybrid systems PU/M/W, to detect the effect of the weight ratios on the final properties of the foams, foam samples were prepared at various M/W weight ratios (1:3, 1:1 and 3:1) for 10wt.% and 30wt.% total filler content in polyol. The filler was first introduced in the polyol and then, the polyol/filler blend was stirred with an ultrasonic sonicator (Bandelin, UW 3200) during 10 min in a water bath. Afterwards, a mechanical mixer (DLAB, OS20–PRO) was used in order to mix the PU/filler suspension for an additional 1 minute at 2000 rpm. Then, the isocyanate was immediately included into the polyol/filler suspension and the mixture was stirred for extra 5 seconds. At the final stage, the mixture was poured into an aluminum mold with the dimensions 30x30x4cm. Table 1 presents the formulations of the PU foam samples prepared in this study.
Table 1. Compositions of the different magnetite and wollastonite filled rigid PU foam composites.

| Samples          | Magnetite content (wt.%) | Wollastonite content (wt.%) | Magnetite/Wollastonite content (wt.%) |
|------------------|--------------------------|-----------------------------|---------------------------------------|
| PU_0             | 0                        | 0                           | 0                                     |
| PU/M_10          | 10                       | 0                           | 0                                     |
| PU/M_15          | 15                       | 0                           | 0                                     |
| PU/M_30          | 30                       | 0                           | 0                                     |
| PU/W_10          | 0                        | 10                          | 0                                     |
| PU/W_15          | 0                        | 15                          | 0                                     |
| PU/W_30          | 0                        | 30                          | 0                                     |
| PU/MW_10_1:3     | 2.5                      | 7.5                         | 10                                    |
| PU/MW_10_1:1     | 5                        | 5                           | 10                                    |
| PU/MW_10_3:1     | 7.5                      | 2.5                         | 10                                    |
| PU/MW_30_1:3     | 7.5                      | 22.5                        | 30                                    |
| PU/MW_30_1:1     | 15                       | 15                          | 30                                    |
| PU/MW_30_3:1     | 22.5                     | 7.5                         | 30                                    |

2.3. Characterization methods

2.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

A ThermoFisher Nicolet IS50 Fourier Transform Infrared (FTIR) spectrometer was used for the characterization of the chemical bonds characteristic of the prepared rigid PU foams. These measurements were performed between a wavelength range of 4000-400 cm\(^{-1}\).

2.3.2. Differential Scanning Calorimetry (DSC)

These measurements were realized using a TA Instrument Discovery DSC25 Differential Scanning Calorimeter (DSC). All samples were characterized under nitrogen atmosphere and between -70°C and 270°C with a heating rate of 10°C/min.

2.2.4. Tensile Test

Specimens of each rigid PU foam samples were prepared according to ASTM D638 (Type V specimen) and the tensile test was performed with a 5kN load cell and a crosshead speed of 5mm/min.

3. Results and Discussion

3.1. Effect of magnetite/wollastonite weight ratio on FTIR spectra of rigid PU foam composites

FTIR spectra of unfilled and magnetite/wollastonite added rigid PU foams prepared at various filler content (10, 15 and 30wt.%) and different magnetite/wollastonite weight ratios (1:3, 1:1 and 3:1) were given in Figure 2. From this Figure 2, it can be seen that the main specific adsorption peaks of PU foams appear with the presence of the vibration bands for isocyanurate ring in the wavelength range of 1710 - 1690 cm\(^{-1}\) and 1410 cm\(^{-1}\) but also the presence of the vibration bands for urethane group in the wavelength range of 1742 - 1700 cm\(^{-1}\). All the results were well correlated with the literature (Norshahli et al. 2018; Sri-ngo 2008). In addition, from these FTIR spectra it could be depicted that spectra of PU foam composites exhibit similar peaks as the unfilled rigid PU foams. As a result, it can be concluded that the chemical structure of polyurethane foams were not really affected by the fillers (magnetite and wollastonite). In this case, no reaction occurs between fillers and polyurethane molecule.
3.2. Effect of magnetite/wollastonite weight ratio on thermal transitions of rigid PU foam composites

DSC measurements were conducted on unfilled PU foam and magnetite/wollastonite filled rigid PU foam composites in order to detect the effect of the presence of fillers on the thermal transitions of rigid PU foams. These polymeric materials display two different thermal transitions with the presence of two different glass transition temperatures corresponding to two distinct behaviors of soft segments ($T_g^1$) and hard segments ($T_g^2$) of polyurethane molecules. The thermal transition observed for low temperatures (0-50°C) represents the glass transition temperature of soft segments whereas the one obtained for higher temperatures (80-150°C) represents the glass transition temperature of hard segments. The thermal transitions determined from DSC traces (Figures 3-6) were gathered in Table 2.

From this Table 2, two main behaviors can be observed. In the first case of hard segments characterized by the apparition of $T_g^2$, an overall increase of the glass transition temperature can be observed with the introduction of fillers into polyurethane matrix with a rise from about 119°C to around 126°C in some cases. This behavior is mainly due to the diminution of the mobility of polyurethane chains with the inclusion of magnetite and wollastonite particles between polymer chains as largely discussed in the literature (Król, et al., 2015; Paciorek-Sadowska, et al., 2019). As a result, the rigidity of hard segments was augmented which induce an increase of the glass transition temperature.

In the second case of $T_g^1$ representing soft segments, a general decrease tendency of the glass transition temperature can be noticed with a drop from about 37°C to a temperature range of 21-29°C for rigid PU foams reinforced with wollastonite and magnetite. This behavior can be understood if the entanglements of polymer chains were take into account. In fact, the presence of magnetite or wollastonite into the polymer matrix will hinder the formation of entanglements of polymer chains leading to the drop of the glass transition temperature of soft segments as mentioned in the literature (Gu, et al., 2014).
Figure 4. DSC thermograms obtained for unfilled and wollastonite filled PU foams

Figure 5. DSC thermograms obtained for unfilled PU and PU/M/W foams prepared at 10wt.% and various M/W weight ratios

Figure 6. DSC thermograms obtained for unfilled PU and PU/M/W foams prepared at 30wt.% and various M/W weight ratios

Table 2. DSC results: glass transition temperatures of unfilled PU and PU/M/W foams (Tg₁ and Tg₂)

| Samples       | Tg₁(°C) | Tg₂(°C) |
|---------------|---------|---------|
| PU_0          | 37.51   | 119.98  |
| PU/M_10       | 26.85   | 122.51  |
| PU/M_15       | 27.27   | 119.82  |
| PU/M_30       | 25.29   | 118.55  |
| PU/W_10       | 23.86   | 119.11  |
| PU/W_15       | 21.42   | 118.56  |
| PU/W_30       | 29.88   | 122.46  |
| PU/MW_10_1:3  | 24.73   | 126.00  |
| PU/MW_10_1:1  | 25.67   | 126.30  |
| PU/MW_10_3:1  | 22.43   | 125.56  |
| PU/MW_30_1:3  | 25.68   | 114.82  |
| PU/MW_30_1:1  | 23.08   | 118.44  |
| PU/MW_30_3:1  | 27.07   | 119.08  |
3.3. Effect of magnetite/wollastonite weight ratio on mechanical properties of rigid PU foam composites

Tensile test results of unfilled and magnetite, wollastonite and magnetite/wollastonite filled rigid PU foam composites were given in Figures 7-10. In particular, the evolution of tensile strength and elongation at break with the filler content of the different foam samples were compared. From Figure 7 and 8, the results revealed a slight decrease of the tensile properties of magnetite added foams whereas a more significant drop of these properties was observed for wollastonite reinforced rigid PU foam composites and more specifically from 15wt.% of wollastonite. Then, it can be concluded that the negative impact of wollastonite in tensile properties of rigid PU foams is more important compared to magnetite. A critical filler content of 15wt.% is visible mainly in the case of PU/W foam composites which can be correlated with the percolation threshold theory where wollastonite particles create agglomerates after this critical point (Akkoyun & Akkoyun, 2019; Yang, et al., 2004). This situation facilitate the formation of local stresses with the diminution of the tensile strength of PU/W rigid foam composites. The effect of M:W weight ratio on the tensile properties of PU foam in hybrid systems was also investigated. The comparison of Figure 9 and 10 showed a reduced tensile strength and elongation at break for PU foams filled at 30wt.% compared to samples prepared at 10wt.%. These results are in correlation with the previous results. Furthermore, as expected, the impact of wollastonite on the mechanical properties can also be observed in hybrid foam composites obtained for lower amount of filler (10wt.%) with reduced tensile strength and elongation at break values for samples prepared at 1:3 M:W weight ratios. Then, the mechanical properties of hybrid rigid PU/M/W foam composites are weakened as the weight of wollastonite increases.

Figure 7. a) Tensile strength and b) elongation at break of unfilled PU and magnetite filled PU foams

Figure 8. a) Tensile strength and b) elongation at break of unfilled PU and wollastonite filled PU foams
Figure 9. a) Tensile strength and b) elongation at break of unfilled PU and PU/M/W foams prepared at 10wt.% and various M/W weight ratios

Figure 10. a) Tensile strength and b) elongation at break of unfilled PU and PU/M/W foams prepared at 30wt.% and various M/W weight ratios

4. Conclusions

The impact of wollastonite, magnetite and magnetite/wollastonite hybrid systems on the mechanical and thermal transition properties of rigid polyurethane foams was realized and in particular, the effect of the filler content and the weight ratio of magnetite/wollastonite (1:3, 1:1 and 3:1) hybrid systems on the PU foam properties was studied. From the results, it has been determined that the chemical structure of polyurethane foams is not affected by additives (magnetite and wollastonite). Thermal transition results revealed the presence of two main behaviors. In the first case, an overall increase of the glass transition temperature of hard segments is observed with a rise from about 119°C to around 126°C in some cases. This behavior can be explained by the diminution of the mobility of polyurethane chains with the inclusion of magnetite and wollastonite particles between polymer chains. In the second case a general decrease tendency of the glass transition temperature of soft segments is obtained with a drop from about 37°C to a temperature range of 21-29°C for rigid PU foams reinforced with wollastonite and magnetite. This behavior is probably due to the presence of magnetite or wollastonite into the polymer matrix which hinders the formation of entanglements of polymer chains. A more important negative impact of wollastonite in tensile properties of rigid PU foams compared to magnetite is observed. Furthermore, the mechanical properties of hybrid rigid PU/M/W foam composites are weakened as the weight of wollastonite increases.

5. Acknowledgement

Kimpur Polyurethane (Turkey) is acknowledged for the supply of isocyanate and polyol.

References

Akkoyun, M., & Akkoyun, S. (2019). Blast furnace slag or fly ash filled rigid polyurethane composite foams: A comprehensive investigation. Journal of Applied Polymer Science, 136, 47433.
Akkoyun, M., & Suvaci, E. (2016). Effects of TiO2, ZnO, and Fe3O4 nanofillers on rheological behavior, microstructure, and reaction kinetics of rigid polyurethane foams. Journal of Applied Polymer Science, 133, 43658.
European Journal of Science and Technology

Alavi Nikje, M. M., Akbar, R., Ghavidel, R., & Vakili, M. (2015). Preparation and Characterization of Magnetic Rigid Polyurethane Foam Reinforced with Dipodal Silane Iron Oxide Nanoparticles Fe3O4@APTS/GPTS. *Cellular Polymers, 34*(3), 137-156.

Alavi Nikje, M. M., Farahmand Nejad, M. A., Shabani, K., & Haghshenas, M. (2013). Preparation of magnetic polyurethane rigid foam nanocomposites. *Colloid Polym Sci, 291*, 903–909.

Alavi Nikje, M. M., Noruzian, M., & Moghaddam, T. S. (2015). Novel Polyurethane Rigid Foam/Organically Modified Iron oxide Nanocomposites. *Polymer Composites, 38*(5), 877-883.

Azarov, G. M., Maiorova, E. V., Oborina, M. A., & Belyakov, A. V. (1995). Wollastonite raw materials and their applications (a review). *Glass and Ceramics, 52*, 237-240.

Ghosh, S., Ganguy, S., Remanan, S., Mondal, S., Jana, S., Maji, P. K., & Das, N. C. (2018). Ultra-light weight, water durable and flexible highly electrical conductive polyurethane foam for superior electromagnetic interference shielding materials. *Journal of Materials Science: Materials in Electronics, 29*, 10177.

Gu, S.-Y., Liu, L.-L., & Yan, B.-b. (2014). Effects of ionic solvent-free carbon nanotube nanofluid on the properties of polyurethane thermoplastic elastomer. *J Polym Res, 21*, 356.

Król, P., Król, B., Pieclchowska, K., & Špírková, M. (2015). Composites prepared from the waterborne polyurethane cationomers—modified graphene. Part I. Synthesis, structure, and physicochemical properties. *Colloid Polym Sci, 293*, 421–431.

Liang, K., & Shi, S. Q. (2001). Nano clay Filled Soy-Based Polyurethane Foam. *Journal of Applied Polymer Science, 119*, 857–1863.

Moghaddam, S. T., & Naimi-Jamal, M. (2018). Reinforced magnetic polyurethane rigid (PUR) foam nanocomposites and investigation of thermal, mechanical, and sound absorption properties. *Journal of Thermoplastic Composite Materials, 32*(9), 1224-1241.

Norshahli, M. S., Jun, L. H., & Zubir, S. A. (2018). Mechanical Properties of Palm Oil Polyol based Polyurethane Foam Reinforced Wollastonite Clay. *Journal of Physics: Conference Series* (p. 012041). Penang, Malaysia: IOP Publishing.

Paciorek-Sadowska, J., Borowicz, M., Isbrandt, M., Czuprynski, B., & Apieceonek, L. (2019). The Use of Waste from the Production of Rapeseed Oil for Obtaining of New Polyurethane Composites. *Polymers, 11*, 1431.

Paciorek-Sadowska, J., Czuprynski, B., Liszkowska, J., & Piszczech, K. (2012). Preparation of rigid polyurethane foams with powder filler. *J Polym Eng, 32*, 71-80.

Patcharapon, S., Kalman, M., Timea, L.-K., & Csaba, K. (2018). Polyurethane elastomers with improved thermal conductivity part I: elaborating matrix material for thermal conductive composites. *International Journal of Mechanical and Production Engineering, 6*, 2320-2092.

Pillai, P. K., Li, S., Bouzidi, L., & Narine, S. S. (2015). Metathesized palm oil polyol for the preparation of improved bio-based rigid and flexible polyurethane foams. *Industrial Crops and Products, 83*, 568-576.

Sarier, N., & Onder, E. (2007). Thermal characteristics of polyurethane foams incorporated with phase change materials. *Thermochimica Acta, 454*, 90–98.

Sattar, R., Kausar, A., & Siddiq, M. (2015). Advances in thermoplastic polyurethane composites reinforced with carbon nanotubes and carbon nanofibers: A review. *Journal of Plastic Film & Sheeting, 31*(2), 86–224.

Silva, A. M., Pereira, I. M., Silva, T. I., da Silva, M. R., Rocha, R. A., & Silva, M. C. (2020). Magnetic foams from polyurethane and magnetite applied as attenuators of electromagnetic radiation in X band. *Journal of Applied Polymer Science, 49629.

Sri-mgno, W. (2008). Effects of Calcium Carbonate Fillers on Mechanical Properties of Flexible Polyurethane Foam. Bangkok, Tayland: Chulalongkorn University.

Usman, A., Zia, K. M., Zuber, M., Tabasum, S., Rehman, S., & Zia, F. (2016). Chitin and chitosan based polyurethanes: A review of recent advances and prospective biomedical applications. *International Journal of Biological Macromolecules, 86*, 630–645.

Yang, Z.-G., Zhao, B., Qin, S.-L., Hu, Z.-F., Jin, Z.-K., & Wang, J.-H. (2004). Study on the Mechanical Properties of Hybrid Reinforced Rigid Polyurethane Composite Foam. *Journal of Applied Polymer Science, 92*, 1493–1500.

Zhou, L., Li, G., An, T., & Li, Y. (2010). Synthesis and characterization of novel magnetic Fe3O4/polyurethane foam composite applied to the carrier of immobilized microorganisms for wastewater treatment. *Research on Chemical Intermediates*, 36, pages277–288.