ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

ACOUSTIC PROPERTIES OF STYRENE BUTADIENE RUBBER- ISOCYANTE COMPOSITION REINFORCED WITH CARBON NANOTUBES AND SILICON OXIDE NANO-POWDER

M.Sc. THESIS

Alkan SANCAK

Department of Nanoscience and Nanoengineering

Nanoscience and Nanoengineering Programme

JUNE 2017

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

ACOUSTIC PROPERTIES OF STYRENE BUTADIENE RUBBER-ISOCYANTE COMPOSITION REINFORCED WITH CARBON NANOTUBES AND SILICON OXIDE NANO-POWDER

M.Sc. THESIS

Alkan SANCAK
(513141001)

Department of Nanoscience and Nanoengineering

Nanoscience and Nanoengineering Programme

Thesis Advisor: Prof. Dr. Levent Trabzon

JUNE 2017

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

SİLİKON OKSİT NANO TOZLARI VE KARBON NANOTÜPLERİ İLE GÜÇLENDİRİLMİŞ STİREN BÜTADİEN KAUÇUK- İZOSİYANAT KOMPOZİSYONUNUN AKUSTİK ÖZELLİKLERİ

YÜKSEK LİSANS TEZİ

Alkan SANCAK
(513141001)

Nano-Bilim ve Nano-Mühendislik Ana Bilim Dalı

Nano-Bilim ve Nano-Mühendislik Programı

Tez Danışmanı: Prof. Dr. Levent TRABZON

HAZİRAN 2017

Alkan SANCAK, a M.Sc. student ITU Graduate School of Science Engineering and Technology of student ID 513141001, successfully defended the thesis/dissertation entitled "ACOUSTIC PROPERTIES OF STYRENE BUTADIENE RUBBER-ISOCYANTE COMPOSITION REINFORCED WITH CARBON NANOTUBES AND SILICON OXIDE NANO-POWDER",which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Levent Trabzon** .....
Istanbul Technical University

Jury Members : **Assoc. Prof. Dr. Elif Ülkü Arıcı** .....
Istanbul Technical University

Assoc. Prof. Dr. Fikret Yıldız .....
Gebze Technical University

Date of Submission : 09.05.2017
Date of Defense : 12.06.2017

To my family,

FOREWORD

I would like to express my gratitude to my thesis supervisor, Prof. Dr. Levent TRABZON for his continuous effort, labor, encouragement, guidance, helpful critics and discussions in my studies.

I would like to give special thanks to Prof Dr. Nilüfer Eğrican, Prof Dr. Haluk Erol, and Asst. Prof. Hikmet İskender from İstanbul Technical University, for their guidance and help, and special thanks to my laboratory friends Dr. Ayber YILDIRIM, Kemal Baran YILDIRIM, Amir NAVİDFAR and Sertaç TORÖZ for his collaborative. We happily exchanged experience and benefited from each other.

Most of all, I would like to thanks my relative. For all those times they stood by me and heartedly supported. I was able to accomplish everything in my life thanks to their eternal love.

Finally, I would like to thank all of my other friends for all their emotional assists and motivation during this extremely difficult accomplishment.

May 2017

Alkan SANCAK
(Chemical Engineer)

TABLE OF CONTENTS

Page

FOREWORD ..... **xi**
TABLE OF CONTENTS ..... **xiii**
ABBREVIATIONS ..... **xv**
SYMBOLS… ..... **xvii**
LIST OF TABLES ..... **xviiix**
LIST OF FIGURES ..... **xxii**
SUMMARY ..... **xxiiiiii**
ÖZET…… ..... **xxiiiv**
1. INTRODUCTION **1**
1.1 Purpose of Thesis 1
1.2 Literature Review 1
2. THEORITICAL PART **5**
2.1 Physics of Sound 5
2.2 General Information about Sound Transmission 6
2.3 Styrene Butadiene Rubber(SBR) 9
2.4 Isocyanate 11
2.5 Glass Transition Temperature 12
3. EXPERIMENTALS **15**
3.1 CNTs 17
3.2 Nano-Silica 18
3.3 CNT preparation 19
3.4 Preparation of samples with CNTs 19
3.5 SiO2 Nano-Particle Preparation 20
3.6 Cutting the Samples 21
4. RESULTS AND DISCUSSION **25**
4.1 Impedance Tube 25
4.2 Sound Transmission Loss(STL) 27
4.3 Sound Absorption Coefficient(α) 32
5. CONCLUSION **37**
REFERENCES **39**
CURRICULUM VITAE **43**

ABBREVIATIONS

SBR	: Styrene butadiene rubber
CNTs	: Carbon nanotubes
Iso	: Isocyanate
RI	: Rubber-Isocyanate
MWNTs	: Multi-walled carbon nanotubes
S-type	: Spherical type
P-type	: Porous type
PP	: Polypropylene
Rpm	: Revolotions per minute
Wt.	: Weight
STL	: Sound Transmission Loss
dB	: Decibels

SYMBOLS

τ : Transmission Coefficient
Wt : Transmitted power
Wi : Power incident on the surface
R : Sound reduction index
p : Pressure
v : Velocity
W : Acoustical Power
S : Surface

LIST OF TABLES

Page

Table 3.1 : Properties of H 1710/06 styrene butadiene rubber and isocyanate components..... **15**
Table 3.2 : Percentage of the additives of the RI composite samples. **16**
Table 3.3 : Properties of Silicon Oxide Nanopowder **19**
Table 4.1 : Sound Transmission Loss of the Samples..... **27**
Table 4.2 : Physical Properties of the Samples **27**

LIST OF FIGURES

Page

Figure 2.1 : Sound transmission paths between a room containing a noise source and adjacent rooms **7**
Figure 2.2 : When sound strikes a partially absorbing partition between two rooms, some is reflected back into room, some transmits into adjacent room ... **7**
Figure 2.3 : Chemical formula of SBR **10**
Figure 2.4 : MDI (diphenylmethane 4,4 - diisocyante) chemical formula **11**
Figure 2.5 : Isocyanate used for production of the RI composites **11**
Figure 2.6 : A heat vs. temperature plot for an crystalline polymer, on the left; and a amorphous polymer on the right. **12**
Figure 3.1 : A representative picture of used CNTs taken during RI production **17**
Figure 3.2 : A representative image of measurements **18**
Figure 3.3 : Overhead stirrer used for mixing the composites **20**
Figure 3.4 : Hydraulic Press **20**
Figure 3.5 :Water jet machine is used for shaping the samples……**21**
Figure 3.6 : 1 cm thickness and 100 mm diameter **22**
Figure 3.7 : A photograph of a RI sample **23**
Figure 4.1 : Testing equipment for determining the sound transmission loss **25**
Figure 4.2 : Testing equipment for determining the sound absorption coefficient ... **26**
Figure 4.3 : Sample in an impedance tube **26**
Figure 4.4 : Sound Transmission Loss Measurments **28**
Figure 4.5 : Compare of reference sample and the best STL samples **29**
Figure 4.6 : Compare of sound transmission loss of nano adicted samples and the reference sample at low frequencies **30**
Figure 4.7 : Sound transmission loss diffrences by percentage at 200 Hz **31**
Figure 4.8 : Compare of Sound Absorption Coefficients **32**
Figure 4.9 : Compare of Best Samples at significant frequencies **33**
Figure 4.10 : The samples which have the highest sound absorption coefficient **33**
Figure 4.11 : The difference in α up to 600 Hz **34**
Figure 4.12 : Evaluation of the best sample at 100Hz, 125Hz, 250Hz and 500Hz .. **35**

ACOUSTIC PROPERTIES OF STYRENE BUTADIENE RUBBER-ISOCYANTE COMPOSITION REINFORCED WITH CARBON NANOTUBES AND SILICON OXIDE NANO-POWDER

SUMMARY

In this study, the main aim is about enhancing acoustic properties of styrene butadiene rubber with small amount of carbon-nanotubes and silicon oxide nanopowders which were added to the styrene butadiene rubber -isocyante composition. The acoustic properties are tested with the additon of small amount of carbon-nanotubes and silicon oxide nanopowders (S-type, P-Type) to the rubber-isocyante composition. By adding CNTs and/or nano-silica in the form of powder at different concentrations up to 5% within the rubber-isocyante composition to improve the sound absorption were investigated in the frequency range up to 1250Hz. In this thesis, both CNT and nano-silica particles are added with different quantities to the rubber-isocyante composition. The properties, specially the sound transmission loss and sound absorption, are studied for all the prepared samples and results are investigated to come up with the best nanocomposites that can be applied for our sound absorption application at the desired operating frequency. For rubber-isocyante nanocomposites, a fixed weight percentage of CNTs (up to 5 wt%) was first mixed with the rubber at 2000 rpm for 10 min using an overhead stirrer equipment. Mixing was started from a speed of about 100 rpm and it was gradually increased to 2,000 rpm for 10 min when the CNT is added to rubber-isocyante solution. The amount of CNT added was 0.25, 0.5, 0,75 and 1 percent of the total weight. Same procedure is applied fot the silicon oxide nano-powder. The small amount of silicon oxide nanopowders (S-type, P-Type) added was 0.25, 0.5, 0,75, 1 percent of the total weight.

Firstly, the isocyanate was added to the styrene butadiene rubber which has granul diamater smaller than 2mm and stirred for 5 min at 2000 rpm at room temperature in plastic mould. The rubber-isocyante mixture, which were molded into another cylndrical plastic volume and were pressurized in that volume, were screwed, and were kept at room temperature for 1 day before characterization.Secondly, sound transmission loss (STL), determined with an impedance tube, was used to characterize our fabricated samples soundproofing properties. The testing was performed according using a Brüel & Kjaer 4206 acoustic test system comprising an impedance tube, speaker, three microphones and a digital frequency analyzer to measure the sound tranmission loss. Sound transmission loss measurement of the samples were determined using large impedance tube. The basic test results showed that addition of 1 wt.% s-type Silicon Oxide Nano-powder and 1 wt.% p-type Silicon Oxide Nano-powder composition improved sound transmission loss up to %20 percent than that of pure rubber-isocyante sample. The accumulation of excess CNTs and nano-silica aggregate in void space of a cell can act as a barrier to influence the movement of the sound wave inside a cell. It should be stressed that the presence and distribution of

nano-particles has a huge role to play in the nanocomposite especially at the higher particle loading.

SİLİKON OKSİT NANO TOZLARI VE KARBON NANOTÜPLERİ İLE GÜÇLENDİRİLMİŞ STİREN BÜTADİEN KAUÇUK- İZOSİYANAT KOMPOZİSYONUNUN AKUSTİK ÖZELLİKLERİ

ÖZET

Ses iletim kaybı özelliğini arttırmak için nano partikül olarak CNTs (karbon nanotüp) kullanılması daha önce de araştırılmış ve CNTs (karbon nanotüp) eklenmesinin sistemin akustik absorpsiyonun bütün aralık değerlerinde pozitif yönde katkı sağladığı görülmüştür. Çok düşük oranlarda, örneğin % 0.01 gibi değerlerde dahi CNTs eklenmesi görece olarak çok düşük bir etkiye sahip olurken, % 0.1 gibi CNTs eklenmesi akustik özelliklerin kayda değer bir şekilde yükselmesini sağlamaktadır.

Ses dalgaları iki ana mekanizma ile absorbe edilmekte olup bunlardan bir tanesi mekanik sürtünme ile, diğeri de direkt termal enerji dağılımına maruz kalmasıdır. Polimerler içerisinde nano partikül bulunması, özellikle de CNTs bulunması, mekanik enerji dağılımında ve özellikle loss modülünde kayda değer artış ile birlikte kuvvetli bir sönümleme etkisine sahip olacağı bilinmektedir.

Bu tez çalışmasında özellikle silikon oksit nano tozları ve karbon nanotüpler ile güçlendirilmiş kauçuk-izosiyanat kompozisyonunun akustik özellikleri araştırılmış olup % 5'i geçmeyecek şekilde farklı oranlara sahip 10'dan fazla numunenin birbirleri ile kıyaslanacak şekilde akustik ölçümleri yapılmıştır. Araştırmanın başında kauçuk-izosiyanat oluşumunu sağlşayacak şekilde stiren bütadien ve izosiyanat malzmeleri temin edilmiştir.

Birinci bölümde, deney aşamasında kullanılan karbon nanotüpler 40 ile 60 μm çapında ve 200 μm uzunuğunda olup 85-90 % saflık değerine sahip olmaktadırlar. Deney sırasında kullanılacak olan karbon nanotüplerin etkileşimini arttırmak için hidrojen peroksit (H_2O_2) kullanılarak ultrasonik banoyoya sokulmuştur. İlk aşamalarda 1.5 gram karbon nanotüp 35% H_2O_2'nin 500 ml'si ile ultrasonik banyoya sokulmuştur. Fonksiyonalitesi arttırılan karbon nanotüpler daha sonra oluşan solüsyon hidrojen peroksit'ten arındırılacak şekilde iki kez saf su ile yıkanıp filtreden geçirilmiştir. Bu kısımda filtreden geçirme işlemi sırasında hassas filtreler dikkatli bir biçimde kullanılmış ve hem soluma hem de temas yoluyla oluşabilecek tüm zararlı durumlar önceden saptanmış ve engellenmiştir.

Bir sonraki aşamada ise 80°C sıcaklıktaki fırında yaklaşık 8 saat tutularak kurutulması sağlanmıştır. Hidrojen peroksitten arındırılmış karbon nanotüp içerisinde kalan sudan kurtarılmak amacıyla geniş bir cam kalıba konulmuş ve düzenli olarak kontrol edilerek tam olarak kuruduğundan emin olunana kadar etüv için bekletilmiştir, bu süre optimum olarak 8 saattir. Kuruyan karbon nanotüp ağzı kapalı bir kapta saklanarak herhangi bir kontaminasyona karşı korunmuya alınmıştır

1:10 oranında karıştırılacak izosiyanat ve kauçuk malzemelerinden, kauçuk hassas tartı üzerinde tartıldıktan sonra genel ağırlığa göre sırasıyla %0.25, %0.5, %0,75 ve %1 oranında olacak şekilde karbon nanotüpler karıştırılmıştır. İzosiyanat ve kauçuk ilk

önce mekanik karıştırıcı içerisinde yaklaşık 10 dakika boyunca 2000 dakika devir ile karıştırılmaktadır. Böylece izosiyanat ve kauçuk iyi bir şekilde karıştırılmış olmaları sağlanır. Burada özellikle daha homojen bir karışım için ilk başta yüksek hızda değil daha düşük dakika devir değerlerinden başlanarak karışım hızlandırılmıştır. Bir sonraki aşamada artık iyi bir şekilde karışmış izosiyanat ve kauçuk karışımı içerisine nano malzeme dökülmesidir. Hassas terzide kütlece %0.25, %0.5, %0,75 ve %1 oranında olacak şekilde ayarlanan nano malzeme kauçuk-izosiyanat karışımı içerisine dökülür. Tekrar mekanik karıştırıcıda 10 dakika sürecek şekilde 2000 dakika devir hızında karıştırılır ve karışımın homojen bir şekilde karışması sağlanır. Karıştırma işlemi plastik kaplarda yapılmakta ve daha sonra hidrolik basınç ile pimli silindirik kaplarda sıkıştırılıp 1 gün süreyle basınçlı şekilde bekletilmektedir.

Hidrolik basınç altında pimli kaplarda sıkıştırılarak bekletilen numunler aynı sıcaklık ortamında ve aynı basınç altında bekletilmiştir. Farklı sıcaklılarda ortaya çıkabilecek farklılıklar bu şekilde engellenmiştir.

Benzer şekilde aynı aşamalar nano-silika malzemeler için de gerçekleştirilmiştir. Yüzde bakımında oranları %0.2, %0.5, %0.75 ve %1 olacak şekilde toz formunda nano-silika malzemeler karıştırılmıştır. Deneylar sırasında iki farklı tipte silikon oksit nano tozları kullanılmıştır. Bunlardan bir tanesi p-tipli olarak adlandırılmış gözenekli ve 60-70 μm çapında nano-silika olup bir diğeri s-tipli olarak adlandırılmış küre şeklinde ve bir öncekinden daha büyük çaplı olacak şekilde 15-20 μm çap aralığına sahip nano-silikadır. Her ikisi de toz formunda olup çeşitli kimyasal işlemlerden geçirilmiş ve sıvı formunda getirilmiş nano-silikalar da kullanılmıştır. Özellikle toz formunda nano-silikalar ihtiva eden kauçuk-izosiyanat yapısı deney sırasında çok daha dengeli sonuçlar vermiş olup sıvı formundaki nano-silikalar deney sonuçları dışında tutulmuştur. Karbon nanotüptekinin benzeri bir şekilde toz formundaki p-tip ve s-tip nano-silika tozlar ilk önce kauçuk ile karıştırılmış MDI (izosiyanat)'a eklenerek karıştırılmaktadır. Bir önceki numunelerde de olduğu gibi aynı çap genişliğine sahip olacak şekilde farklı oranlarda kauçuk bazlı malzemeler üretilmiştir.

Her bir üretilen numunenin temiz bir sonuç verebilmesi için ses düzeneği içerisine yerleştirilmeye uygun boyutlara sahip olması gerekmektedir. Bunun için kalıp içerisinden çıkarılan her numune daha sonrasında özel su jeti ile kesilmiştir. Sujeti ile yapılan kesimler öncesinde lazer kesim ve benzeri tüm kesim yöntemleri denenmiş ancak istenen pürüzsüz yüzey elde edilememiştir.

İlk aşamada kalınlık değerlerinin aynı olması sağlanacak şekilde numune miktarı saptanmıştır ve 125gr kauçuk, 12,5 gr izosiyanat ile yaklaşık 10mm kalınlıkta malzemeler basınç alıtnda bekletişmiştir. Sonraki aşamada ise 100 mm çapa sahip numuneler elde edilmesi için su jeti ile kesim yapılmıştır. Böylece 10 mm kalınlığa ve 100 mm çapa sahip pürüzsüz numuneler elde edilmiştir. Bu şekilde elde edilen 12 adet numune daha sonrasında Brüel & Kjaer 4206 akustik test sistemi içerisinde sırasıyla ölçülmüştür.

Ses iletim kaybı (sound tranmission loss) ölçülen her bir numune daha sonra birbirleri ile kıyaslanmıştır. Kıyaslamalar, grafikler üzerinden yapılmıştır ve farklı nano malzeme yüzdelerinde farklı iyileşmeler görülmüştür ancak bu iyileşmeler düzenli olarak artıp azalmak gibi bir eğilim sergilememektedir.

Her bir numune önce akustik test sistemi içerisindeki uygun yere yerleştirilmekte daha sonra sessiz ortamda oluşan ses iletim kaybı ölçülmektedir. Oluşturulan grafikler sonucu üretilmiş farklı oranlardaki 12 numunenin birbiri ile kıyaslanması gerçekleşmiştir. Üretim sırasında karşılaşılan ve sonuçlarda da kendisini belli eden bir durum şu şekildedir. Karıştırılan karbon nanotüp miktarı %0.75'i geçmesiyle birlikte kauçuk ve izosiyanatın birbiri ile etkişelimi kötü yönde olmakta ve yeterli bir şekilde birbirine tutunan bir yapı oluşmamakta ve bunun yanında homojen bir dağılım elde edilememektedir.

Elde edilen grafikler yorumlandığı zaman özellikle 250 Hz değerine kadar kütlece % 0.75 ve % 0.5 karbon naotüpe sahip numunenin daha iyi bir akustik özelliğie sahip olduğu görülmektedir. Diğer yandan kütlece %1, % 2 ve %5 karbon nanotüpe sahip numuneler ise bütünlüklerini koruyamamıştır. Bu durumda daha yüksek karbon nanotüp yüzdeleri için daha yüksek izosiyanat kullanılması durumunda yine bütünleşik yapıda farklı numuneler ortaya çıkabilecektir. En iyi sonuçlar 100hz ve daha sonrasında 200hz'de görülürken 250Hz üstünde katkısız referans numunenin daha iyi sonuç verdiği görülmüştür.

Nano-silikalar, hem p-tip hem de s-tip nano silikalar %0.25, %0.5, %0.75 ve %1 oranında olacak şekilde karıştırılmış olup yapılan akustik testler sonucunda en iyi değerlere kütlece %1 p-tip silikaya sahip karışım ve %1 s-tip silikaya sahip karışım olduğu görülmektedir. %1 üzeri silika eklenmesi yine malzemenin bütünlüğünün bozulmasına yol açmıştır. En iyi sonuçlar 100hz ve daha sonrasında 200hz'de görülürken 250Hz üstünde katkısız referans numunenin daha iyi sonuç verdiği görülmüştür.

Ek olarak ses yutma katsayısı ile ilgili yapılan ölçümler de hem karbon nanotüp hem de nano silikalar için yapılmıştır ve yine kauçuk-izosiyanat kompozisyonunun ses yutma katsayısını geliştirdiği gözlemlenmiştir. Ses yutma katsayısı hali hazırda kauçuk-izosiyanat kompozisyonu için ölçülen değerin 2 katından da fazlasına çıkması, nano malzemelerin yüksek etkisini farklı bir akustik özellik ile de doğrulamıştır.

Sonuç olarak karbon nanotüp ve nano silikalar ile yapılan çalışmalar ile görülmektedir ki nano malzemeler, kauçuk-izosiyanat tabanlı malzemelerin hem ses iletim kaybı özelliğine hem de ses yutma katsayısına önemli derecede iyileştirme yapmıştır.

1. INTRODUCTION

In this thesis, acoustic properties of the styrene butadiene rubber - isocyante compositions reinforced with carbon nanotubes and silicon oxide nano-powder were investigated. Both CNTs and nano-silica particles are added with different quantities to the rubber-isocyante compositions. By adding CNTs and/or nano-silica in the form of powder at different concentrations up to 5% within the RI composition to improve the sound absorption were investigated in the frequency range up to 1250Hz. All the prepared samples and results are investigated to come up with the best nanocomposites that can be applied for sound absorption application at the desired operating frequency.

1.1 Purpose of Thesis

Adding small amounts of nanoparticles in a polymer matrix can considerably improve the desired properties of the composite. The properties, especially the sound absorption, are studied for all the prepared samples and results are investigated to come up with the best nanocomposites that can be applied for our sound absorption application at the desired operating frequency. Carbon nanotubes and nano-silica incorporation on sound absorption of rubber - isocyante compositions were investigated. Effects of different parameters such as quantities, mass per unite area and percentage of nanoparticles on RI compositions were also investigated. Main purpose of the thesis is that determine the acoustic effects of CNTs and Nano-Silica added rubber - isocyante compositions.

1.2 Literature Review

In order to enhance the RI properties, attempts have been made to incorporate appropriate reinforcements into the matrix material [1]. Adding small amounts of nanoparticles in a polymer matrix can considerably improve the desired properties of the composite. However, the extent of success in enhancing the properties depends strongly on the uniform dispersion of particles at the nanoscale as well as good

interaction between the matrix material and nanoparticles. It appears that fibrillar nanoparticles, particularly carbon nanotubes (CNTs), have great potential in the enhancement of RI composites properties. It was shown that by incorporation of only 0.1 wt% CNTs, a significant improvement in acoustic damping can be achieved [2]. SiO2 nanoparticles have also been widely introduced into polymers to improve the heat resistance, radiation resistance, mechanical and electrical properties of polymer materials [3]. However, current studies concerning various aspects of these nanoparticles in RI materials are very limited, and thus further investigations are required.

There are also few studies in the literature regarding the use of nanoclay [4], titania nanoparticles [5, 6] multi-walled carbon nanotubes (MWNTs) reinforced material for giving rise to considerable improvement in sound absorption. Especially CNTs having promising mechanical properties were used as a filler to improve sound absorption properties of the PU-based composites [7]. Additionally, nano-silica have been widely introduced into polymers to improve the heat resistance, radiation resistance, mechanical and electrical properties of polymer materials [8, 9]. Nano-silica compositions have remarkable improvement in materials properties. [10]. Nano-silica has the features of small particle size, narrow particle size distribution, porous, large surface area [11].

In an experimental study with polyurethane foams, with increasing density of the foams, their cell size decreases, and the sound absorption ratio of foams increases. This confirms that foams with small cell size absorb sound better than the foams with large cell size. The sound waves lead to the vibration of the thin cell walls and air inside cells. The sound energy is dissipated through vibration damping of the cell walls and air. Better sound absorption ability of foams with small cell size could be due to the high cell density resulting in more dissipation through vibration damping of the cell walls and air. Up to a certain loading of CNT and nano-silica, the absorption of sound is noted to increase substantially. Very high loading can result in aggregate formation leading to no improvement in the stiffness of the cell wall. At very high loading, the uneven distribution of silica can affect the stiffness of the cell wall in such a way as to reduce the modulus and tensile strength of the foam. Besides, the accumulation of excess CNT and nano-silica aggregate in void space of a cell can act as a barrier to influence the movement of the sound wave inside a cell. It should be stressed that the

presence and distribution of nano-particles has a huge role to play in the nanocomposite especially at the higher particle loading[19].

Thermal (λ= thermal conductivity) and acoustic (TL= Transmission Loss at normal incidence) properties of granular silica aerogels for building insulation are investigated, taking into account the impact of granules size (small, medium, and large granules) on the performance of the bed. The experimental results reveal that the small granules (granules size in the 0.01-1.2 mm range), which have the highest density (80-85 kg/m3), have the best performance both in terms of thermal and acoustic properties. Depending on the granules size, λ varies in the 19-22 mW/mK range at 10°C, whereas TL value equal to13 dB at about 6400 Hz for 20 mm thickness was obtained for small granules. Very good acoustic performance is in general achieved: the best sound insulation properties are observed for small granules (TL=19 dB at about 6400 Hz for 40 mm thickness), whereas for medium and large granules maximum values are in the 10-14 dB range[20].

Sound absorption coefficient measurements show that the resonant frequency of the nanofibrous membrane decreases with increasing area density of the membrane and increases with decreasing average diameter of the nanofibers. Comparing results from the examination of both acoustic characteristics (transmission loss L (dB) and the sound absorption coefficient α) shows that the resonant frequencies are not in agreement. The peaks occurring under each measurement are formed at different frequencies. The transmission loss measurement shows that 530 Hz and 2700 Hz would be the resonant frequencies of the measuring apparatus during transmission loss measurement[21].

PU foams filled with two different fillers, NanoSilica and NanoClay at different loading levels were prepared and characterized for thermal, mechanical and sound absorption properties in the low frequency range of 100 – 200Hz. Maximum sound absorption coefficient value of 0.80 with improved properties was obtained at 1.4% of NS and NC filled PU foam at a thickness of 15mm while the same alpha was obtained at 60mm thickness for unfilled PU foam . On the other hand alpha of 0.88 was obtained in PU/NS-GF cloth hybrid at thickness of about 20 mm. The increase in alpha has been attributed to pore size, uniform distribution of filler and porosity. Nanosilica and glass fiber contribute towards improvement in sound absorption even at low thickness of the material. Thus maximum sound absorption is achieved in low frequency range (100-

200Hz) even with lower thickness of PU by incorporating nano fillers and also with glass and polyester cloth in hybrid composite foams[22].

2. THEORETICAL PART

Transmission of sound through structures, glass temperature of materials, physics of sound, styrene butadiene rubber and isocyanates are investigated.

2.1 Physics Of Sound

Sound can propagate through a medium such as air, water and solids as longitudinal waves and also as a transverse wave in solids. The sound waves are generated by a sound source, such as the vibrating diaphragm of a stereo speaker. The sound source creates vibrations in the surrounding medium. As the source continues to vibrate the medium, the vibrations propagate away from the source at the speed of sound, thus forming the sound wave. At a fixed distance from the source, the pressure, velocity, and displacement of the medium vary in time. At an instant in time, the pressure, velocity, and displacement vary in space.

During propagation, waves can be reflected, refracted, or attenuated by the medium [29].

The behavior of sound propagation is generally affected by three things:

- A complex relationship between the density and pressure of the medium. This relationship, affected by temperature, determines the speed of sound within the medium.
- Motion of the medium itself. If the medium is moving, this movement may increase or decrease the absolute speed of the sound wave depending on the direction of the movement. For example, sound moving through wind will have its speed of propagation increased by the speed of the wind if the sound and wind are moving in the same direction. If the sound and wind are moving in opposite directions, the speed of the sound wave will be decreased by the speed of the wind.

- The viscosity of the medium. Medium viscosity determines the rate at which sound is attenuated. For many media, such as air or water, attenuation due to viscosity is negligible.

Although there are many complexities relating to the transmission of sounds, at the point of reception (i.e. the ears), sound is readily dividable into two simple elements: pressure and time. These fundamental elements form the basis of all sound waves. They can be used to describe, in absolute terms, every sound we hear.

However, in order to understand the sound more fully, a complex wave such as this is usually separated into its component parts, which are a combination of various sound wave frequencies (and noise)[30].

Sound waves are often simplified to a description in terms of sinusoidal plane waves, which are characterized by these generic properties:

- Frequency, or its inverse, wavelength
- Amplitude, sound pressure or Intensity
- Speed of sound
- Direction

Sound that is perceptible by humans has frequencies from about 20 Hz to 20,000 Hz. In air at standard temperature and pressure, the corresponding wavelengths of sound waves range from 17 m to 17 mm. Sometimes speed and direction are combined as a velocity vector; wave number and direction are combined as a wave vector [30].

2.2 Transmission of Sound through Structures

A typical noise control application involves a combination of absorption of sound and transmission of sound energy by a variety of airborne and stucture-borne paths[23]. It is shown in Figure 2.1.

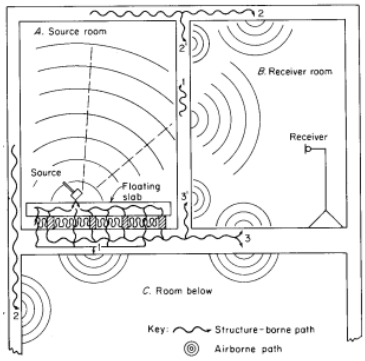

Figure 2.1 : Sound transmission paths between a room containing a noise source and adjacent rooms[23].

Transmission Coefficient τ, for walls

$$\tau = \frac{I_{Transmitted}}{I_{Incident}}$$ (τ is a frequency-dependent physical property of the material) (2.1)

Sound Transmission Loss STL = the log ratio of the incident energy to the transmitted energy

$$STL = 10 \log 1/\tau$$ (2.2)

In Figure 2.2, the sound transmission loss is shown.

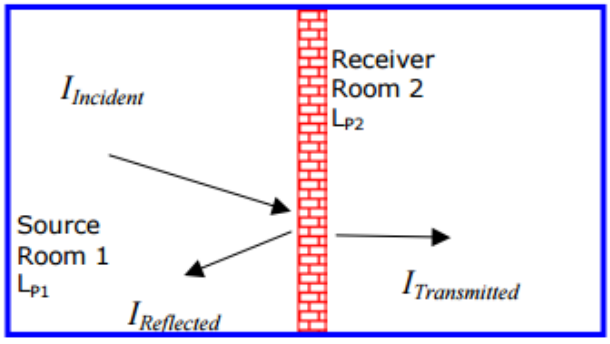

Figure 2.2 : When sound strikes a partially absorbing partition between two rooms, some is reflected back into room, some transmits into adjacent room[23].

A perfectly reflecting material has a transmission coefficient of 0 (STL = ∞), while the transmission coefficient of an opening is 1.0 (STL=0). It should be noted that typical materials tend to be better at blocking higher frequencies.

Transmission loss can be measured directly (but not easily) by mounting a test panel between two reverberation rooms and measuring the sound pressure levels on each side. Other commonly used metrics to describe sound transmission include:

NR = Noise Reduction = LP1-LP2 (easy to measure) but NR ≠ STL,

IL = Insertion Loss = change in sound levels with and without the barrier or treatment in place (easy to measure)[23]

The power transmission factor τ of a surface is defined as the ratio of the transmitted power Wt and the power incident on the surface Wi .

$$\tau = \frac{W_t}{W_i} \tag{2.3}$$

The sound reduction index (sometimes called transmission loss) is defined in dB as

$$R = 10 \log \frac{1}{\tau}. \tag{2.4}$$

With p denoting the pressure and v the particle velocity, the acoustical power is defined as

$$W = \frac{1}{2}\Re\{p^* v\} = \frac{|p|^2}{2}\Re\{1/Z_c\} \tag{2.5}$$

where * denotes the complex conjugate, and Zc the characteristic impedance of the medium, Zc = p/v. The power transmission factor can therefore be written as

$$\tau = \left|\frac{p_t}{p_i}\right|^2 \tag{2.6}$$

provided that the medium is the same on the input and output side [24]. The power transmission factor can be seen as the ratio between the amplitude of the transmitted and incident wave.

Another way to approach the power transmission factor is to consider two rooms separated by wall. Assume that the sound field in both rooms are diffuse. The sound intensity at the wall in the sending room is given by

$$W_i = \frac{\tilde{p}_S^2}{4\rho_0 c_0} S \tag{2.7}$$

where pS denotes the sound pressure in the sending room and S the surface of the separating wall. The power transmitted through the wall is

$$W_t = \frac{\tilde{p}_R^2}{4\rho_0 c_0} A_R \tag{2.8}$$

where ˜pR and AR denotes the pressure and total absorption area of the receiving room. Combining equation 2.7 and 2.8 gives an expression for the transmission factor,

$$\tau = \frac{\tilde{p}_R^2}{\tilde{p}_S^2} \frac{A_R}{S} \tag{2.9}$$

And the sound reduction index

$$R = L_S - L_R + 10 \log \frac{S}{A_R} \tag{2.10}$$

The power transmission factor can therefore also be seen as the difference in sound pressure level with a correction due to absorption in the receiving room. [25]

2.3 Styrene Butadiene Rubber(SBR)

Styrene-butadiene or styrene-butadiene rubber (SBR) describe families of synthetic rubbers derived from styrene and butadiene . These materials have good abrasion resistance and good aging stability when protected by additives. In 2012, more than 5.4 million tonnes of SBR were processed worldwide. [12] About 50% of car tires are made from various types of SBR. The styrene/butadiene ratio influences the properties of the polymer: with high styrene content, the rubbers are harder and less rubbery [13]. SBR is not to be confused with a thermoplastic

elastomer made from the same monomers, styrene-butadiene block copolymer is shown in Figure 2.3.

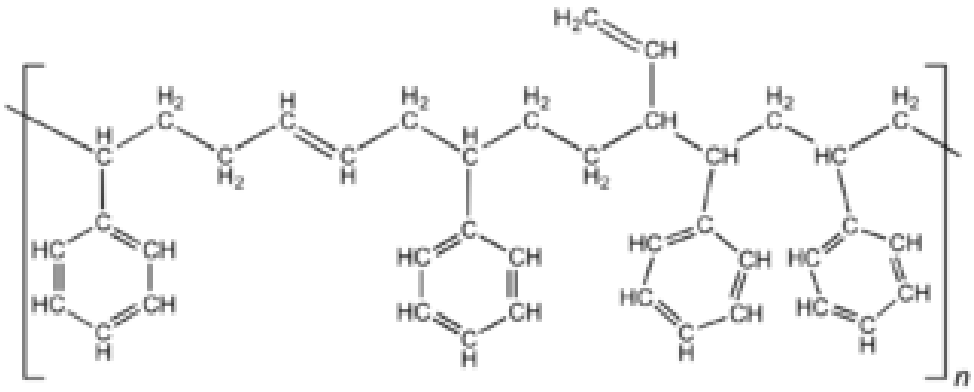

Figure 2.3 : Chemical formula of SBR

It is a commodity material which competes with natural rubber. The elastomer is used widely in pneumatic tires. This application mainly calls for E-SBR, although S-SBR is growing in popularity. Other uses include shoe heels and soles, gaskets, and even chewing gum [13].

Latex (emulsion) SBR is extensively used in coated papers, being one of the cheapest resins to bind pigmented coatings.

It is also used in building applications, as a sealing and binding agent behind renders as an alternative to PVA, but is more expensive. In the latter application, it offers better durability, reduced shrinkage and increased flexibility, as well as being resistant to emulsification in damp conditions.

SBR is often used as part of cement based substructural (basement)waterproofing systems where as a liquid it is mixed with water to form the Gauging solution for mixing the powdered Tanking material to a slurry. SBR aids the bond strength, reduces the potential for shrinkage and adds an element of flexibility.

It is also used by speaker driver manufacturers as the material for Low Damping Rubber Surrounds. Additionally, it is used in some rubber cutting boards.

SBR is also used as a binder in lithium-ion battery electrodes, in combination with carboxymethyl cellulose as a water-based alternative for, e.g. polyvinylidene fluoride [14].

2.4 Isocyanates

Many commercial grades of isocyanates used for making PUs are aromatic in nature. Each isocyanate will give different properties to the end product, requiring different curing systems and, in most cases, different processing systems. An important property of an isocyanate is its functionality, i.e. the number of isocyanate groups (-NCO) per molecule. For cross linked PU applications the average functionality of the isocyanate is usually a little over two. The higher functionality isocyanates are used for special applications. When a di-functional isocyanate is used with a di-functional polyol a long linear PU molecule for elastomeric applications is formed. The common isocyanates used to make PUs are shown in Figure 2.4 [15].

Figure 2.4 : MDI (diphenylmethane 4,4 - diisocyante) chemical formula

A fundamental feature of isocyanates is their high reactivity. The reaction of the isocyanate groups with one another or with small NCO-reactive molecules (for example water or short-chain mono- or polyhydric alcohols) is utilized in the modification reaction for the preparation of polyisocyanates, the crosslinking agents for coatings [16]. In our experiment the isocyanate component includes difenilmetan diisocyanate mixture (ISO PMDI 92140) which is shown in Figure 2.5.

Figure 2.5 : Isocyanate used for production of the RI composites

2.5 Glass Transition Temperature

The glass–liquid transition or glass transition for short is the reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a hard and relatively brittle "glassy" state into a viscous or rubbery state as the temperature is increased [26]. An amorphous solid that exhibits a glass transition is called a glass. The reverse transition, achieved by supercooling a viscous liquid into the glass state, is called vitrification.

The glass-transition temperature, T_g, of a material characterizes the range of temperatures over which this glass transition occurs. In Figure 2.6, the diffrence is shown. It is always lower than the melting temperature, Tm, of the crystalline state of the material, if one exists[27].

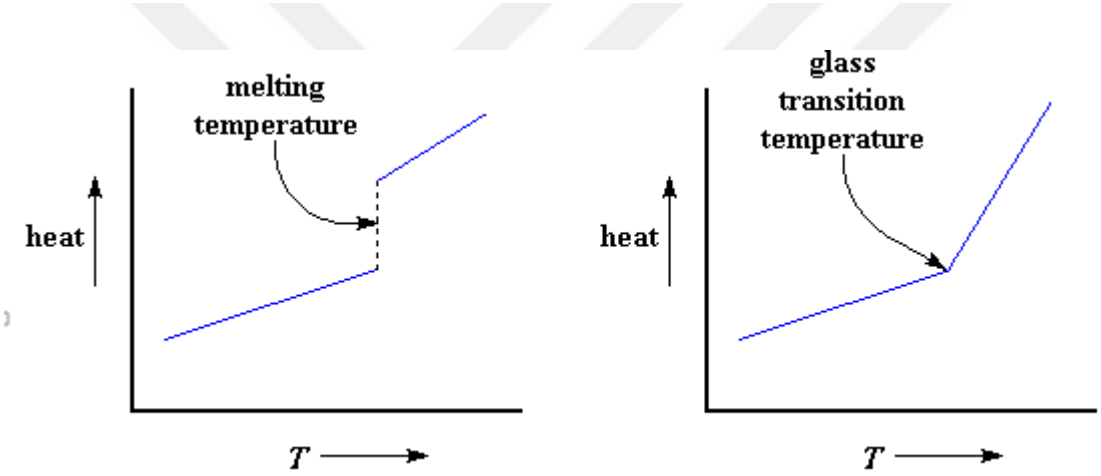

Figure 2.6 : A heat vs. temperature plot for an crystalline polymer, on the left; and a amorphous polymer on the right.

There are a lot of important differences between the glass transition and melting. Melting is something that happens to a crystalline polymer, while the glass transition happens only to polymers in the amorphous state. A given polymer will often have both amorphous and crystalline domains within it, so the same sample can often show a melting point and a T_g. But the chains that melt are not the chains that undergo the glass transition.

There is another big difference between melting and the glass transition. When you heat a crystalline polymer at a constant rate, the temperature will increase at a constant

rate. The heat amount of heat required to raise the temperature of one gram of the polymer one degree Celsius is called the heat capacity [27].

A study for glass transition temperature is about nano silica fillers for styrene butadiene rubber is done. The mechanical behaviour of a styrene-butadiene rubber, containing 23.5% styrene and filled with up to 55% by weight with silica nanoparticles, has been examined. The tan d spectra of these composites show a second relaxation of relatively low intensity located about 40.8 °C above the main a relaxation, the glass transition T_g; which occurs at 34.5 °C in the unfilled polymer. This is attributed to an interfacial layer of polymer molecules whose chain relaxation dynamics have been altered by interaction with the filler surface [28]. It is possbile to say that nano silica increased the glass temperature of styrene-butadiene rubber.

3. EXPERIMENTALS

Polymer foams are a group of lightweight materials, which are made up of a gaseous phase distributed uniformly within a polymeric matrix. Rubber-Isocynate (RI) composites are known to be the most widely used in sound insulation and thermal insulation of constructions. They are important and versatile materials due to their outstanding strength-to-weight ratio, their resilience, thermal, and acoustic insulating properties, amongst other characteristics. The composite is produced by the mix of Styrene Butadiene Rubber and Isocynate. After the mixing step the mixture is molded to the pressure volume because of the importance of the shape and the fast drying of the compound. Table 3.1 represents the properties of the materials.

Table 3.1: Properties of H 1710/06 styrene butadiene rubber and isocyanate components

Physical properties	Unit	SBR	Isocyante	Standards
Density (20°C)	g/cm3	0,94	1.230	DIN 51 757
Viscocity (20°C)	Mpa.a	-	210	DIN 53 018
NCO content	H2O	-	31,5	ASTM D 5155-96 A
Storage life	Month		6	

The surface modification which is appropriate on nanoparticles, not only leads to better dispersion and compatibility of nanoparticles in polymer matrix, but also can form chemical and physical interactions with polymer matrix, which guarantee a durable chemical junction between the two incompatible phases [3]. Recipes for obtaining RI

with CNT and nano-silica particles can be modified to include some additives that might improve the properties of the mixture.

Nanoparticles tend to aggregate and show very poor dispersion in polymers, the aggregation is more and more serious with the particle size reduced. To achieve good dispersion of nanoparticles and yield better compatibility between nanoparticles and polymer matrix, the use of various modification agents, such as trialkoxy silane, stearic acid, and CTAB are recommended.

CNTs and Silicon Oxide Nano powder were added to the rubber and isocyanate composition to improve sound insulation efficiency. Prior to the synthesis of RI composites, four different weight ratios (0.25, 0.5, 0.75, %1 wt%) of CNTs were mixed with H 1710/6 RI composite (table 3.1) at 2000 rpm for 10 min by using an mechanical stirrer equipped with a stirrer tip (figure 3.2 (b)). The stirrer tip made from polymer material for preventing any kind of reaction with the composition. Table 3.2 shows the percentage of the additives of the samples used for producing RI composites.

Table 3.2 : Percentage of the additives of the RI composite samples

MIXTUIRE	RI		
CNTS	0.25, 0.5, 0.75, %1 wt%		
NANO-SILICA S-TYPE		0.25, 0.5, 0.75, %1 wt%	
NANO-SILICA P-TYPE			0.25, 0.5, 0.75, %1 wt%

3.1 Carbon Nanotubes (CNTs)

The diameters of CNTs used in the experiment are vary from 40 to 60 nm with a length of around 200 μm and purity %85-90. CNTs were first chemically-treated with a 3:1 concentrated sulphuric–nitric acid mixture followed by three times filtering and washing with distilled water [17].

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. In our study, as mentioned before, .CNTs were added to the RI mixtures, (0.25, 0.5, 0.75, %1 wt%). When the RI mixture sample is synthesized at high speed, these additives do not disperse homogeneously and they are aggregating each other. Therefore, the mixing speed should start of about 200 rpm and it gradually increase to 2,000 rpm for 10 min when the nano-particles is added to the solution. Picture of CNT and the measurment materials are shown in Figure 3.1 and Figure 3.2.

Figure 3.1 : A representative picture of used CNTs taken during RI production

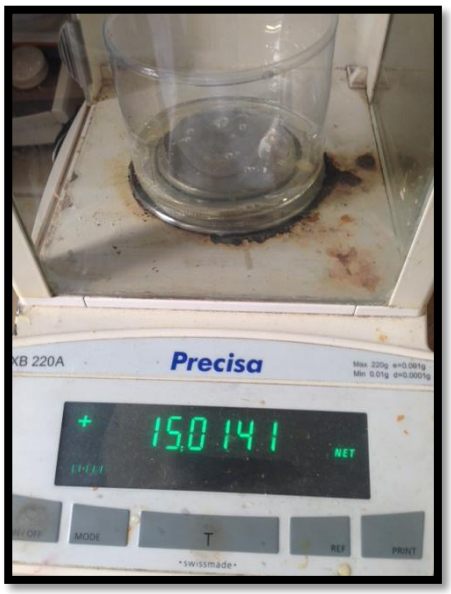

Figure 3.2 : A representative image of measurements

After added rubber and isocyanate is calculated, predetermined amount of the CNTs are added to the mixture for mixing. What we observed is that increasing amount of the CNTs cause to decreasing homogeneity of the composition.

3.2 Nano-Silica

Silicon dioxide nanoparticles, also known as silica nanoparticles or nanosilica, are the basis for a great deal of biomedical research due to their stability, low toxicity and ability to be functionalized with a range of molecules and polymers [18].

Nano-silica particles according to their structure are mainly divided into two types: P-type (Porous particles) and S-type (Spherical particles). P-type nano-silica surface contains a number of nano-porous with the pore rate of 0.611ml /g;. In our experiment, two different type of nano-silica were used (Table 3.3).

One of them is Silicon Oxide Nanopowder (SiO2, 99.5+%, S-type (Spherical), 15-20 nm, amorphous) and the other one is Silicon Oxide Hollow Micron Powder (SiO2, 99%, P-type (Porous), 60-80nm, amorphous).

Table 3.3 : Properties of Silicon Oxide Nanopowder

Materials	Characteristics
Silicon Oxide Nanopowder (S-Type)	(SiO2, 99.5+%, S-type (Spherical), 15-20 nm, amorphous)
Silicon Oxide Hollow Micron Powder (P-Type)	(SiO2, 99%, P-type (Porous), 60-80nm, amorphous)

3.3 CNT preparation

The CNT was functionalized by treating with the hydrogen peroxide (H2O2). A 1.5 g sample of CNT was sonicated with 500 mL of 35% H2O2 at room temperature for 90 min. The solution was then filtered and washed twice with DI water to remove any H2O2 and dried in the oven at 80^{o}C for 8 hours.

3.4 Preparation of samples with CNTs

For RI Nano-composites, a fixed weight percentage of CNTs (up to 2 wt%) was mixed with RI mixture at 2000 rpm for 10 min using an overhead stirrer equipment, as shown in Figure 3.3. No surfactant, catalyst nor distilled water was added to the CNT/RI mixture at this stage. When the RI sample is synthesized at high speed, the CNT additives do not disperse homogeneously. Therefore, the mixing was started from a speed of about 100 rpm and it was gradually increased to 2,000 rpm for 10 min when the CNT is added to polyol solution. The amount of CNT added was 0.25, 0.5, 0.75, and 1percent of the total weight.

Figure 3.3 : Overhead stirrer used for mixing the composites

Finally, the mixture is moulded into pressure volume and dried for 1 day as shown in Figure 3.4. This part is including the hydraulic press, screw down in cylindrical volume. After the pressure part, samples are kept for 1 day for drying.

Figure 3.4 : Hydraulic Press

3.5 Preperation of samples with SiO_2 Nano-Particle

Nano-SiO2 used in this experiment has two different diameters of about 10-15 nm and 60-80 nm. Same procedure with CNT's is done. For RI Nano-composites, a fixed weight percentage of SiO_2's (up to 2 wt%) was mixed with RI mixture at 2000 rpm for

10 min using an overhead stirrer equipment same with the CNT's. No surfactant, catalyst nor distilled water was added to the SiO_2/RI mixture at this stage. When the RI sample is synthesized at high speed, the SiO_2 additives do not disperse homogeneously. Therefore, the mixing was started from a speed of about 100 rpm and it was gradually increased to 2,000 rpm for 10 min when the CNT is added to polyol solution. The amount of CNT added was 0.25, 0.5, 0.75, and 1 percent of the total weight.

3.6 Cutting the Samples

After the pressure step, samples are kept in the cylindrical volumes for 1 day and end of the time the samples are taken out from the volume and packaged for water jet. Water jet is needed for smooth surface which is shown in Figure 3.5. A lot of different cutting method is tried but the volume of the sample is changed or the cutting method failed for the sample. Only the water jet method became successful for cutting the samples. For getting perfect cylindrical shape all the dimensions are important but the mating surface of the samples with the impedance tube is the most important part that is why the water jet is suitable for the cutting of samples. The thickness of the every sample was optimized at production step with determining the weight of the each materials.

Figure 3.5 : Water jet machine is used for shaping the samples

After all process was done, all samples were shaped to be in a 1 cm thickness and 100 mm diameter which are shown in Figure 3.6.

Figure 3.6 : 1 cm thickness and 100 mm diameter samples

As mentioned before, every sample was shaped and sliced to be in a perfect desired size for acousticg tests. It was very important that every sample was in a same shape for consistency.

As it is shown above, the samples were cut and sliced to be in a form cylinder having 100 mm diameter and 10 mm thickness. Porous form also can be seen top and bottom faces of the sample. More than 50 samples have been produced and shaped as mentioned above for determine acoustic properties. But this is done in 5 different step and with the 5^{th} and the final step, 12 samples which are suitable for impedance tube, are obtained. For decent measurement, one of the most important points was that shaping of the form. It is clear that all the samples should have the same diameter and thickness for a decent comparison as shown in Figure 3.7.

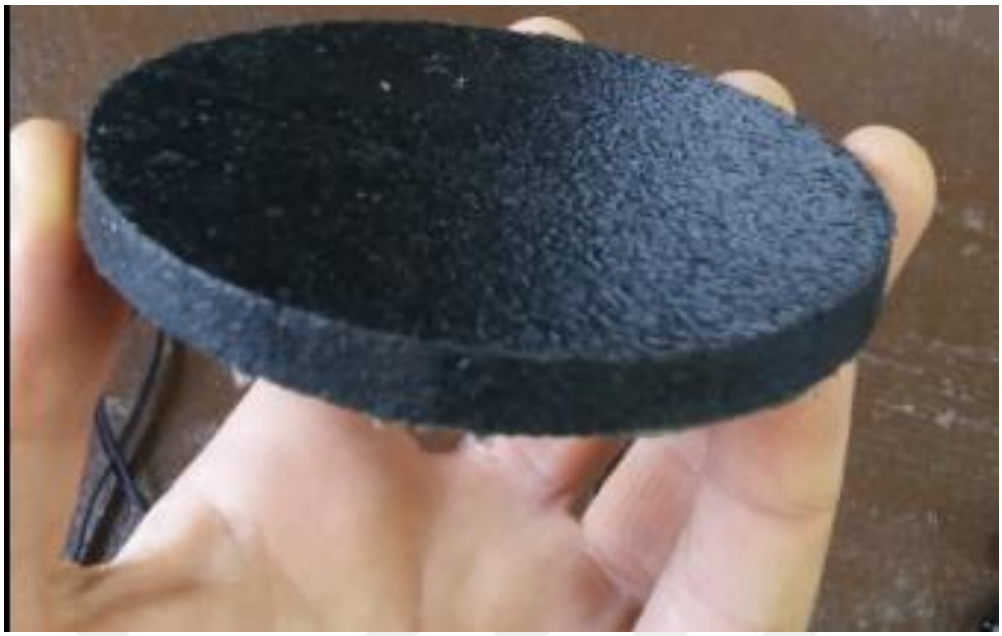

Figure 3.7 : A photograph of a RI Sample

As a result of the experiment the %wt of CNTs must be lower than %1 for RI (1:10). When more than %1 wt is added. The sample always lost the unity as a result of high CNT percentage

This can be explained by the reaction between CNT and isocynate with higher ratios.

4. RESULTS AND DISCUSSION

Sound transmission loss and sound absorption coefficient results are investigated here.

4.1. Impedance Tube

Measurment are done between 50-1250 Hz frequency range. Temperature is 23ºC and the rate of the humidity is 50% during the measurment. The experimental setup is suitaible to international standard “ISO 10534–2 Acoustics-Determination of sound absorption coefficient and impedance in impedance tubes - Part 2: Transfer-function method”.

The testing equipment which is determining the sound transmission loss depending on frequency is shown in Figure 4.1.

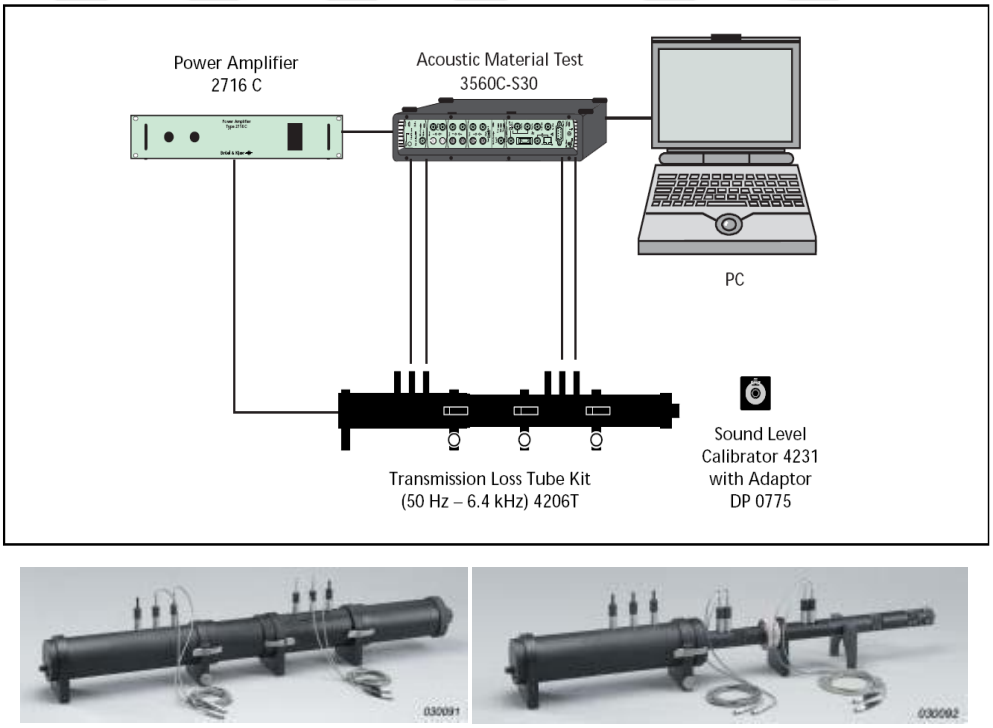

Figure 4.1 : Testing equipment for determining the sound transmission loss

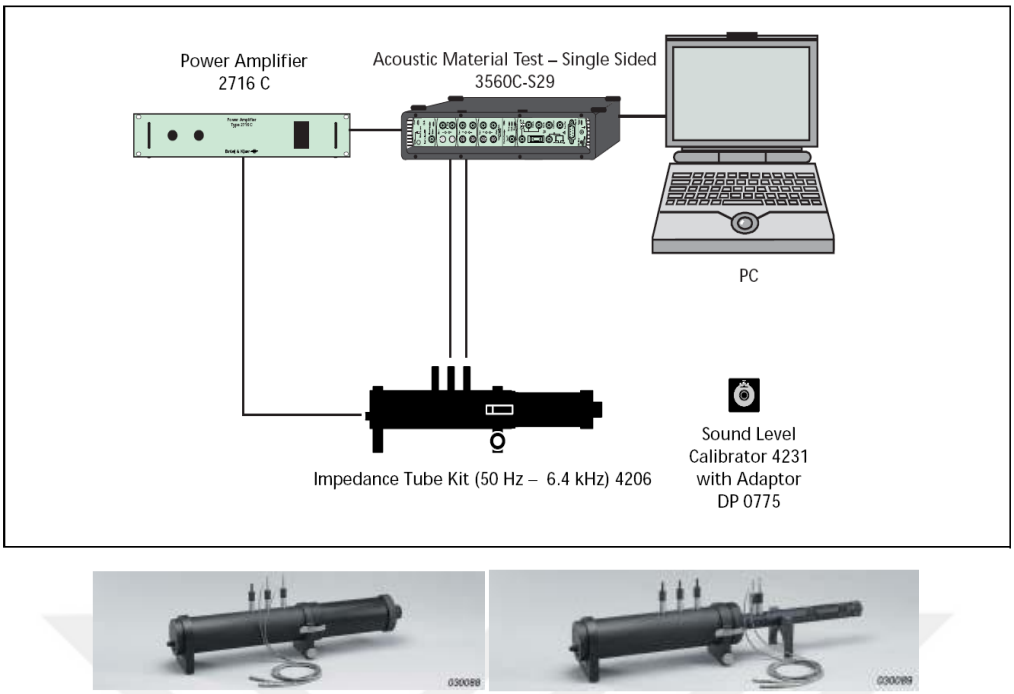

Figure 4.2 : Testing equipment for determining the sound absorption coefficient

The testing equipment which is determining the sound absorption coefficient based on frequency is shown in Figure 4.2.

Acoustic Measurments are done in impedance tube with the samples which are cut 100mm diameter. An example of a sample which is placed in impedance tube, is shown in Figure 4.3.

Figure 4.3 : Sample in an impedance tube

4.2. Sound Transmission Loss

Sound transmissionloss of the samples are determined and all the dates are shown in Table 4.1.

Table 4.1.: Sound Transmission Loss of the Samples

	TL [dB ref, 1,0]											
Frekans [Hz]	S-Silica%025	S-Silica%050	S-Silica%075	S-Silica%100	P-Silica%025	P-Silica%050	P-Silica%075	P-Silica%100	CNT%075	CNT%050	CNT%025	Referans
63	36,1	40,1	36,9	37,4	37,7	36,0	40,2	42,7	37,8	38,3	38,3	36,4
80	33,7	37,1	36,3	36,3	35,1	34,4	38,7	38,6	35,8	34,6	38,0	32,2
100	30,9	33,8	34,5	34,6	33,3	31,8	35,9	36,2	33,5	33,0	34,0	29,9
125	27,8	31,3	31,7	31,4	29,6	28,6	33,6	34,8	30,3	31,1	30,7	26,3
160	22,8	28,0	27,6	27,3	27,3	24,0	30,0	31,1	26,3	26,6	26,8	21,1
200	16,2	21,7	21,8	21,1	20,6	17,4	25,2	26,2	20,1	19,8	20,5	16,1
250	21,5	19,2	19,7	20,0	19,0	21,2	19,0	19,6	19,8	19,4	19,1	22,7
315	27,6	26,6	27,0	27,3	26,4	27,6	25,5	25,0	27,2	26,9	26,6	28,3
400	31,8	31,7	31,7	32,1	31,5	32,0	31,1	30,7	31,9	31,8	31,7	32,6
500	35,4	35,7	35,9	36,0	35,6	35,8	35,5	35,4	36,0	35,8	35,8	36,3
630	38,5	39,9	39,8	39,8	39,7	39,8	39,5	39,6	39,8	39,7	39,8	39,3
800	37,0	40,9	41,7	41,6	39,8	39,6	42,3	42,6	40,4	40,4	40,1	37,6
1000	37,1	37,9	37,9	38,1	37,6	37,8	38,5	38,9	37,7	37,7	37,4	38,3
1250	39,9	39,3	42,4	41,8	43,0	39,4	41,3	41,5	40,3	42,9	42,3	41,1
STC [dB]	33	33	34	34	33	34	33	34	33	33	33	33

As a result of Sound Transmission Class, the samples which have 0.75% S-Silica, 1% S-Silica, 0.5% P-Silica, 1% P-Silica gave better results.

The physical properties of the samples are given in table 4.2. Rubber granüle diameter is selected as <2mm and the weight of the rubber is 125gr. Binder ratio which is 10%, equal to 12,5 gr and the ratio of nano materials are between 0.25%- 1% which is equal to 312,5mg -1250mg. Samples molded into 125mm diameter plastic volumes and after that cut with water jet, that's why the final weights are smaller then the first weight. The pressure part represents the hydraulic pressure which is done by hydraulic pressure equipment.

Table 4.2. Physical Properties of the Samples

No	Rubber Granules Diameter (mm)	Rubber Weight	Binder Ratio	CNT (%)	P-Silica (%)	S-Silica (%)	Weight (gr)	Volume (cm^3)	Density (gr/cm^3)	Average Thickness (cm)	Pressure (Pa)
1	< 2	125	10%	-	-	-	83,02	83,6	0,99	1,065	60
2	< 2	125	10%	0,5%	-	-	86,99	79,1	1,10	1,0078	60
3	< 2	125	10%	-	0,5%	-	84,54	77,8	1,09	0,9905	60
4	< 2	125	10%	-	-	0,5%	87,33	80	1,09	1,0188	60
5	< 2	125	10%	0,25%	-	-	84,1	77,8	1,08	0,9908	60
6	< 2	125	10%	-	0,25%	-	84,73	80,2	1,06	1,0208	60
7	< 2	125	10%	-	-	0,25%	84,99	80,2	1,06	1,0218	60
8	< 2	125	10%	0,75%	-	-	87,13	80,8	1,08	1,0288	60
9	< 2	125	10%	-	0,75%	-	87,79	78	1,13	0,9935	60
10	< 2	125	10%	-	-	0,75%	87,08	79,1	1,10	1,0075	60
11	< 2	125	10%	-	-	1%	88,03	82	1,07	1,044	60
12	< 2	125	10%	-	1%	-	88,24	81,8	1,08	1,0415	60

It is possible to say that the STL result of each sample has similar tendency an it is shown in Figure 4.4.

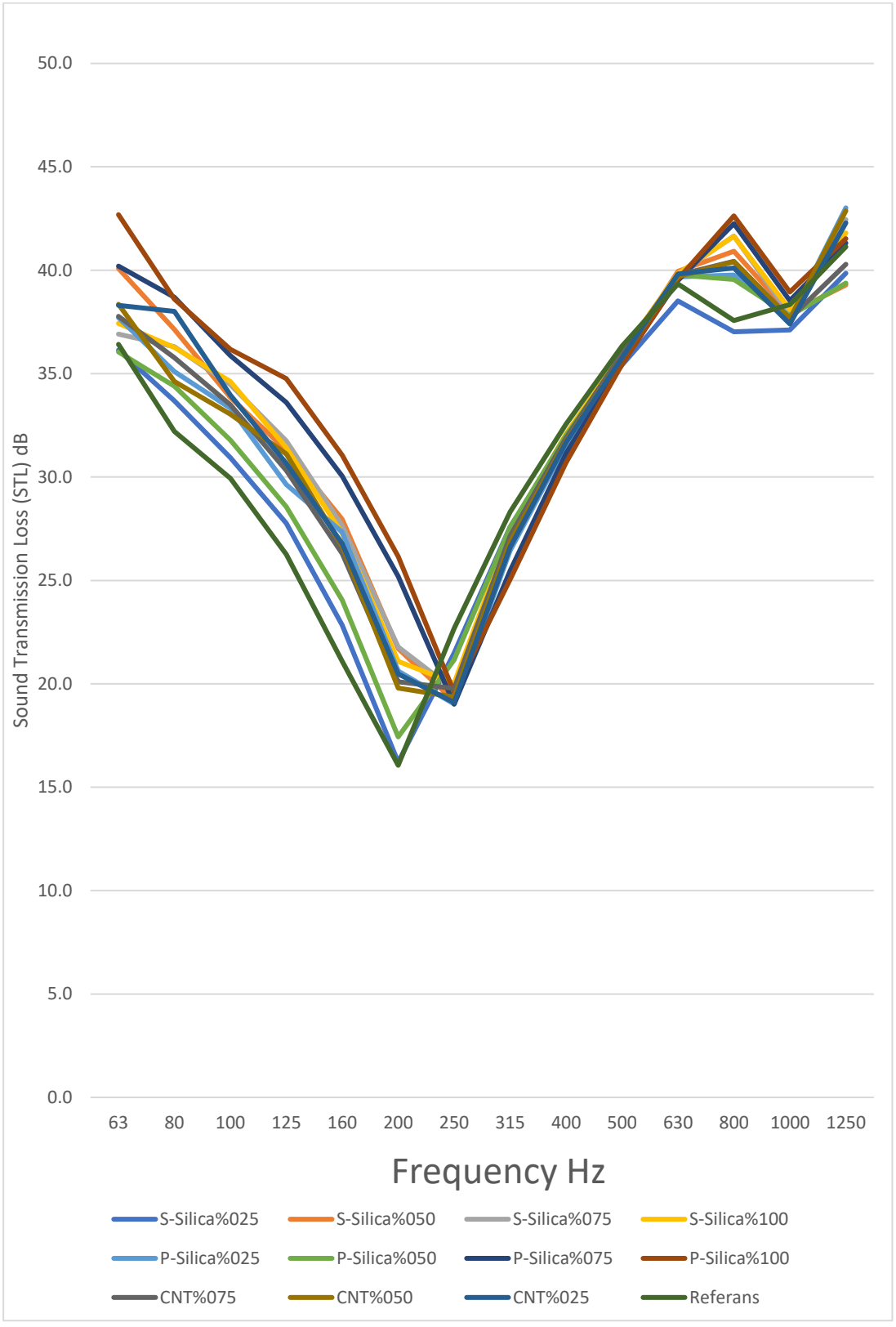

Figure 4.4 : Sound Transmission Loss Measurments

But for the sound transmission loss, 0.25% S-Silica, 0.50% S-Silica, 0.25% CNT, 0.75 P-Silica and 1% P-Silica including samples gave the best results. In Figure 4.5. reference sample is compared with these best samples

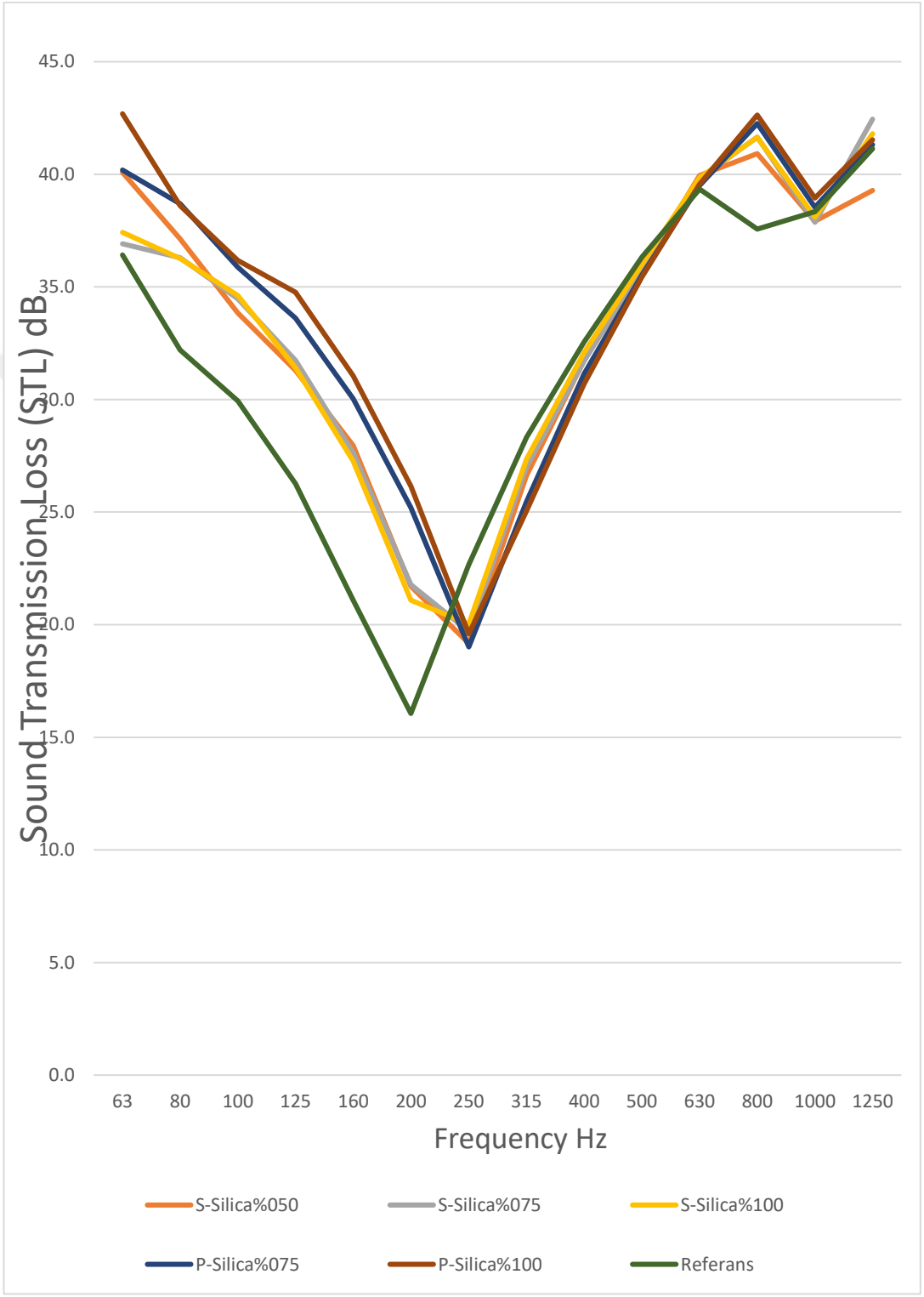

Figure 4.5 : Compare of reference sample and the best STL samples

At low frequencies 2 types of silica both give better results based on sound transmission loss values. But at high frequencies results are not as good as low frequencies. As a result of that one can say that at low frequencies nano material added samples can intercept the sound as a barrier. It is shown in Figure 4.6.

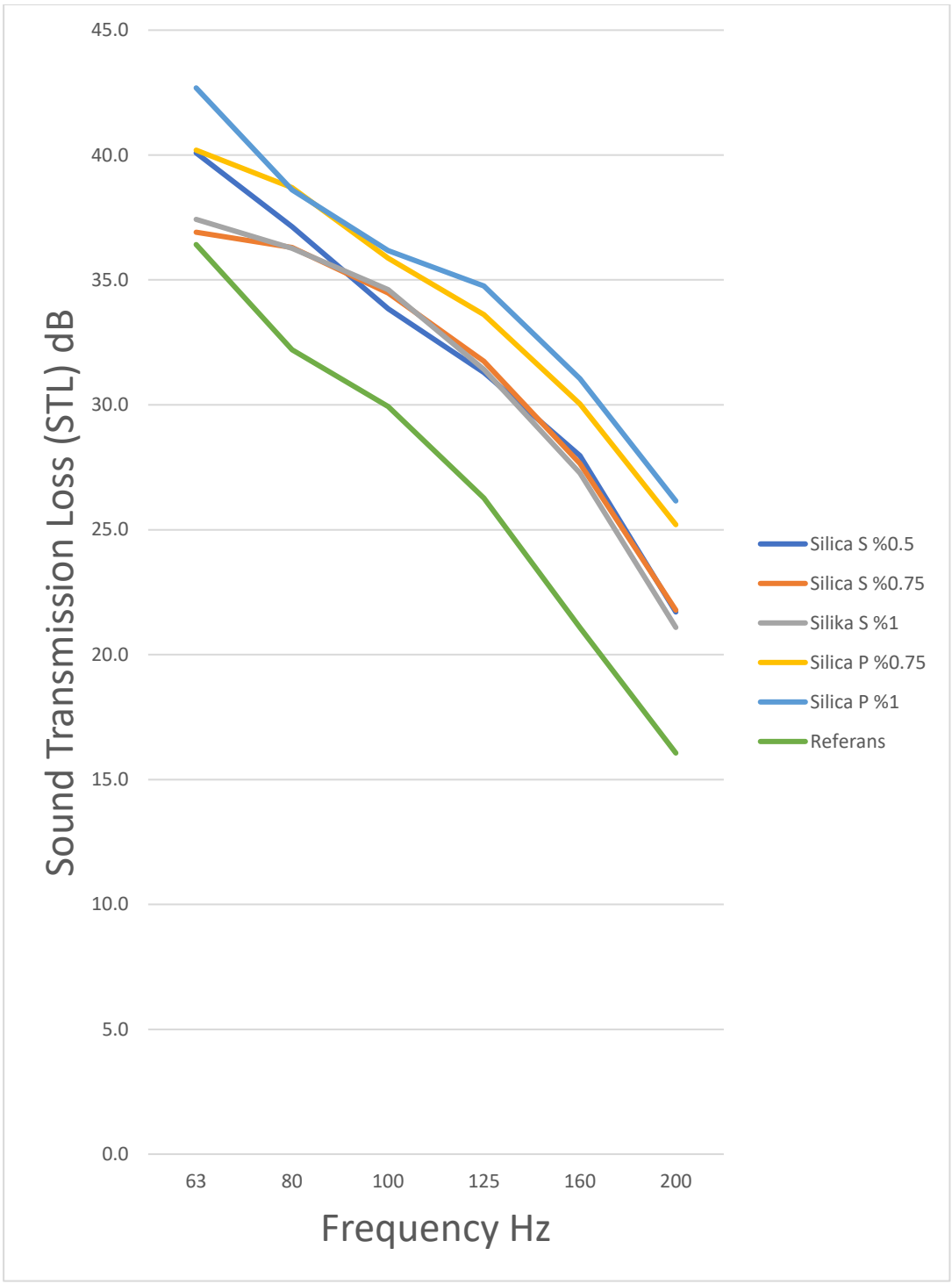

Figure 4.6 : Compare of sound transmission loss of nano adicted samples and the reference sample at low frequencies

It is possible to say that silica added samples can improve the sound transmission loss to 20% like values at low frequencies. If we investigate low freqeuncies more detailed, it is considered that improvements between 3%-20% in sound transmission loss appeared.

At 100 Hz frequency, the biggest diffrences can be seen and it is shown in Figure 4.7. When the best samples are investigated, 15%-21% improvements in sound transmission loss are observed.

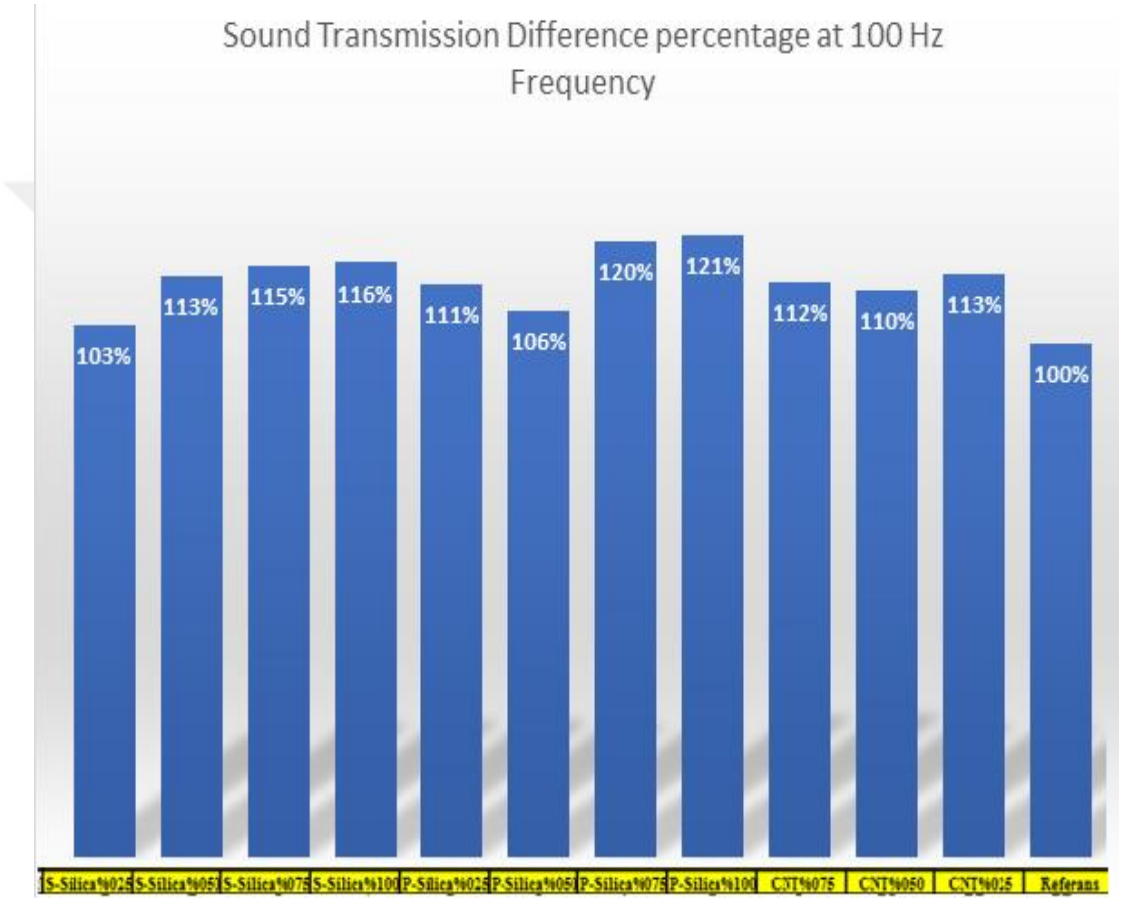

Figure 4.7 : Sound transmission loss diffrences by percentage at 100 Hz

4.3. Sound Absorption Coefficient

Sound Absorption Coefficient measurments are also done with impedance tube. CNT added samples gave better results compared with the other samples. All the sound absorption coefficient measurments of the samples are shown in Figure 4.8.

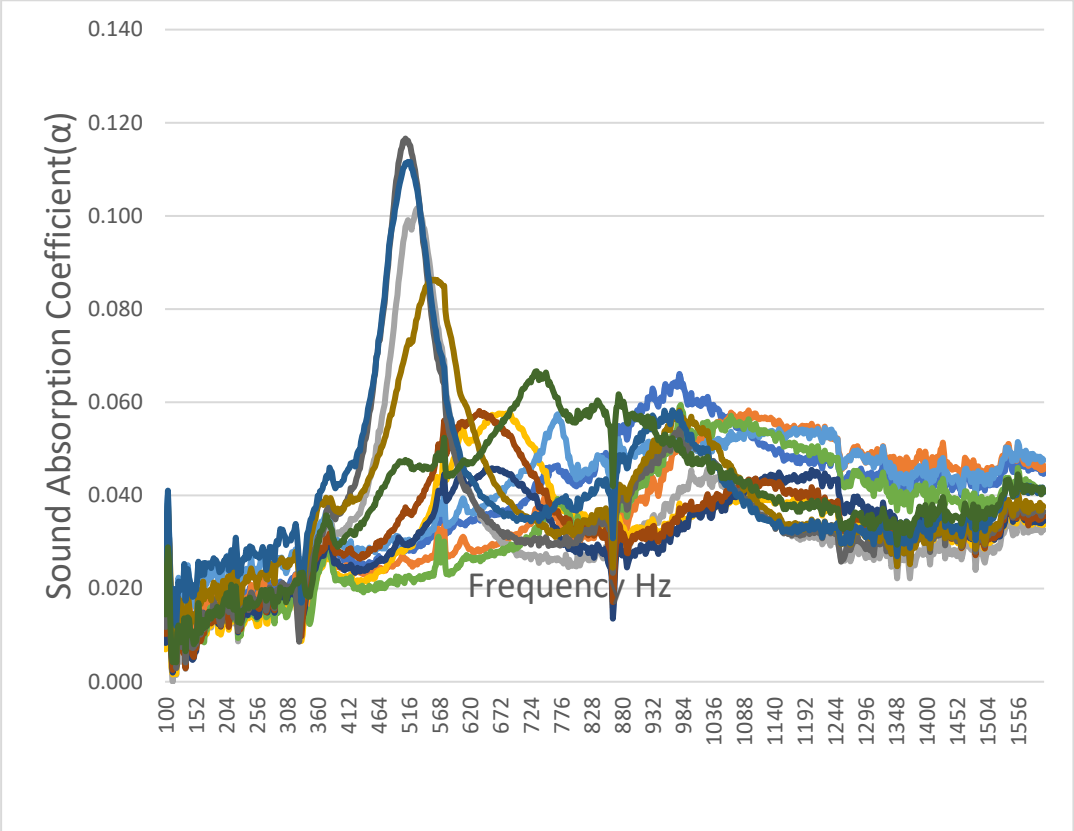

Figure 4.8: Compare of Sound Absorption Coefficients

When the samples are compared at main frequencies again the CNT added samples are again step forward. It is shown in Figure 4.9.

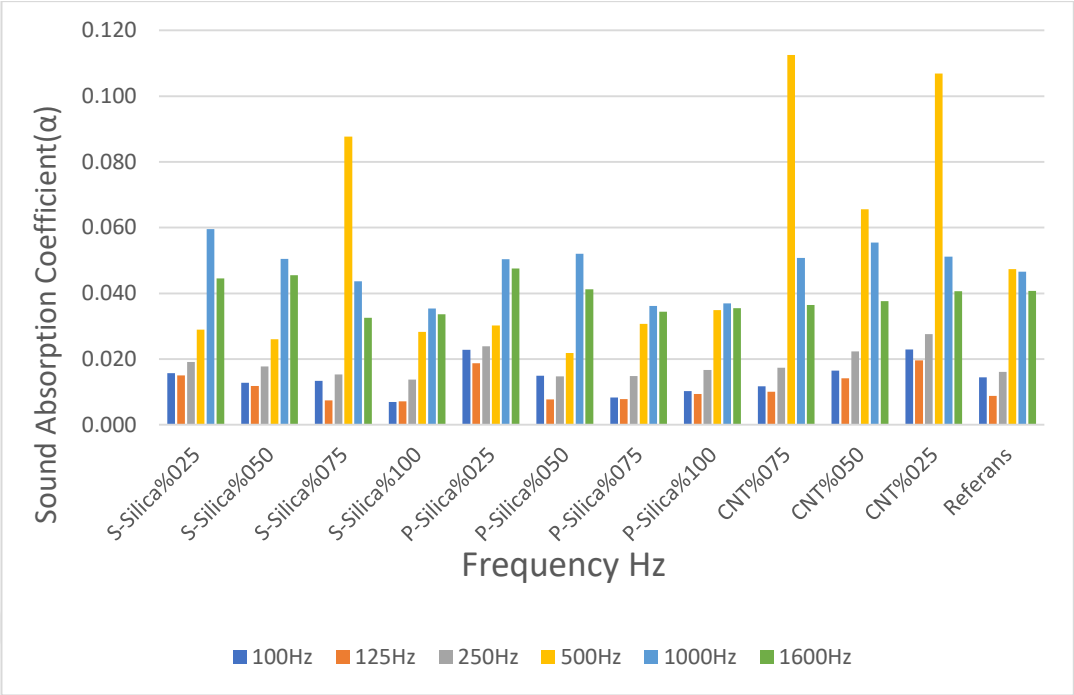

Figure 4.9: Compare of Best Samples at significant frequencies

The samples which have the highest sound absorption coefficient are shown in Figure 4.10. These samples are 0.75% s-silica, 0.75% CNT, 0.5% CNT and 0.25% CNT.

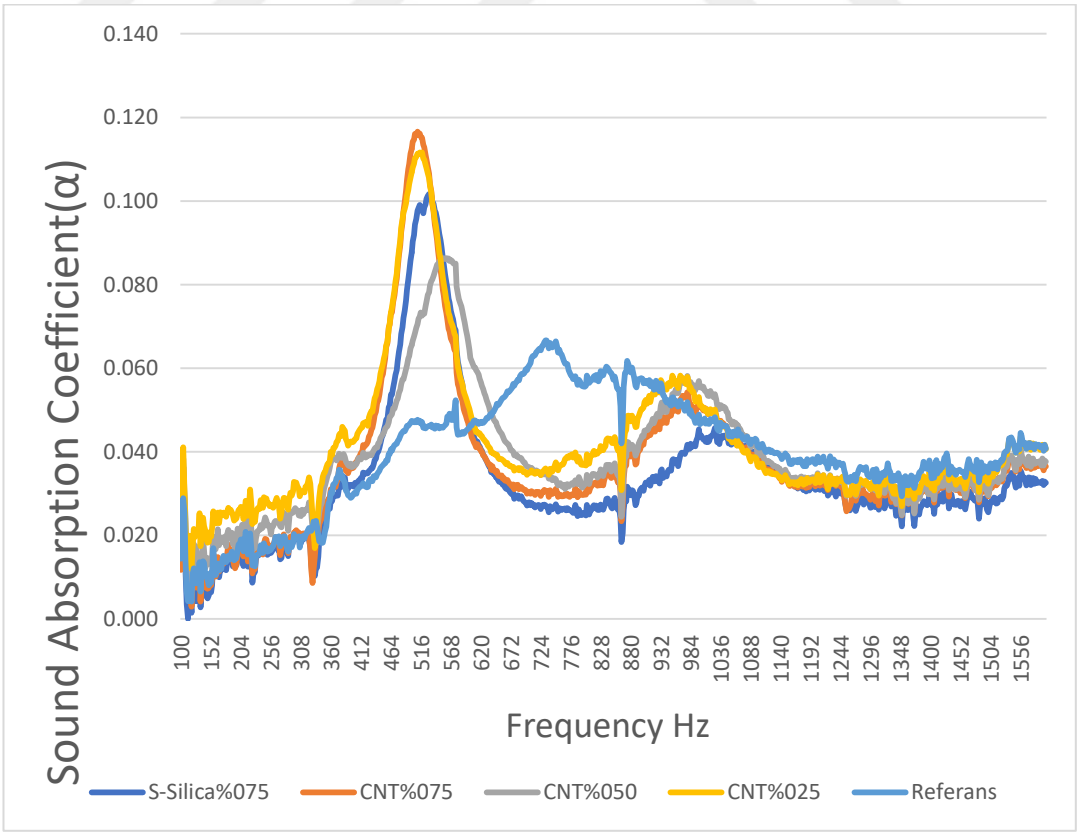

Figure 4.10 : The samples which have the highest sound absorption coefficient

Generally, better effects on sound absorption coefficient is obtained with the Carbon nano tube added samples. Again it is possible to say that, up to 600 Hz frequency, the improvement in sound absorption coefficient is more specific. In Figure 4.11, the difference up top 600Hz is shown.

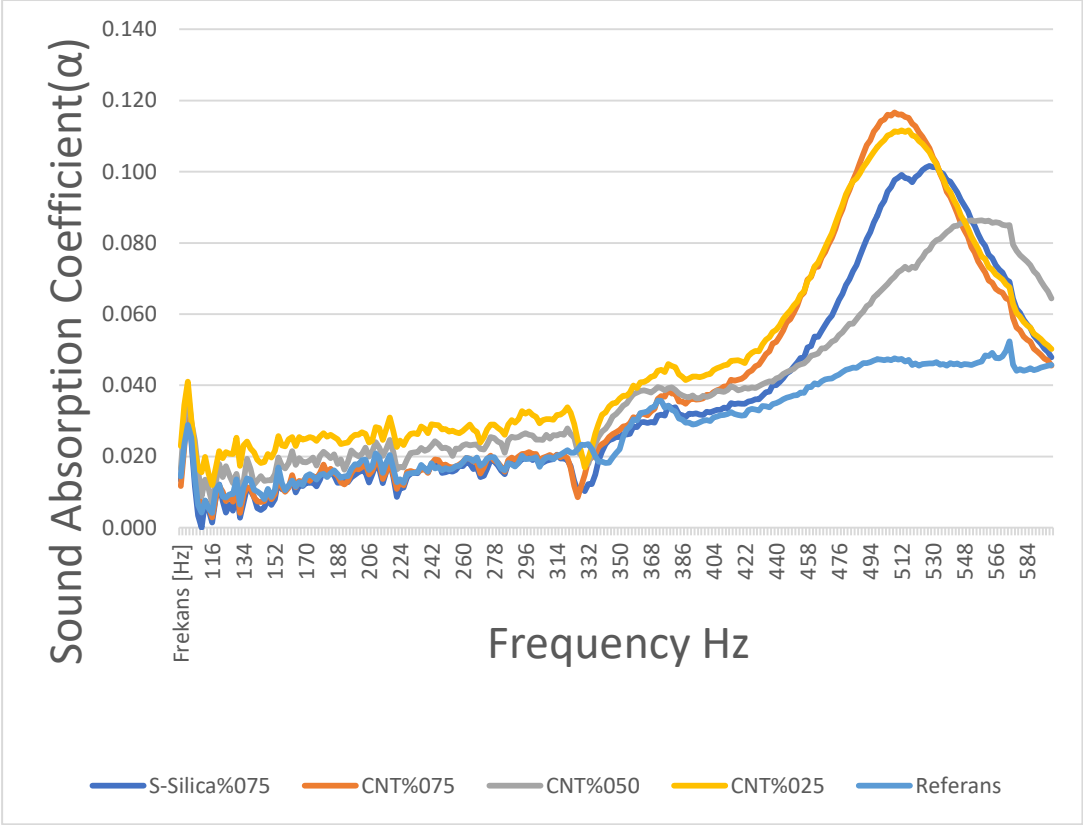

Figure 4.11 : The difference in α up to 600 Hz

When low frequencies are investigated, up to 500 Hz frequency 0.25% CNT added sample is giving the best result based on sound absorption coefficient as we compare with the other nano added samples and the reference sample. Between 500-600 Hz 0.75% CNT, 0.50%CNT and 0.75% S-Silica containing samples are giving the best results.

0.75% CNT, 0.50% CNT, 0.25% CNT and 0.75%S-Silica containing samples are investigated at 100 Hz, 125 Hz, 250 Hz and 500 Hz. The results are shown in figure 4.12.

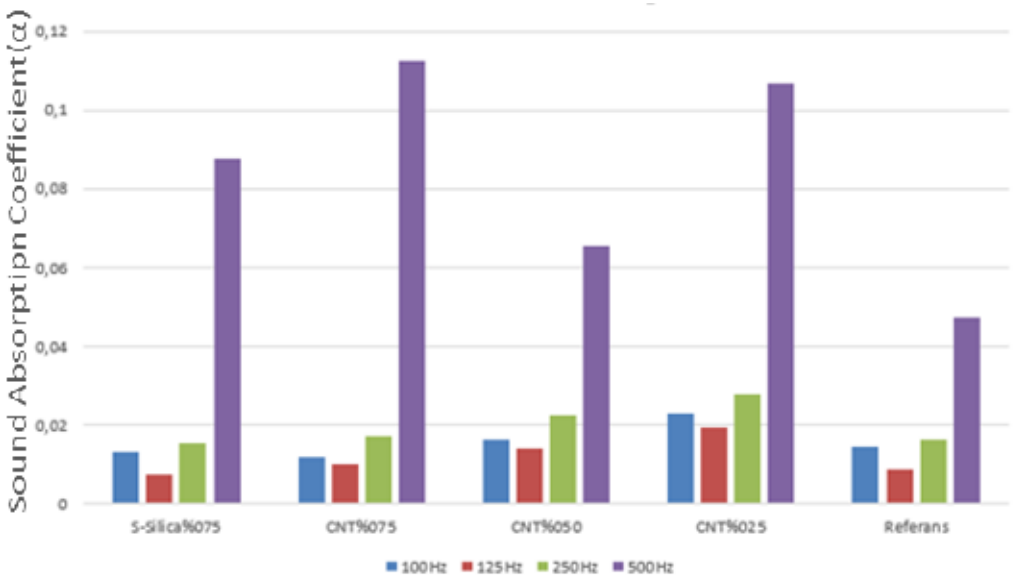

Figure 4.12 : Evaluation of the best sample at 100Hz, 125Hz, 250Hz and 500Hz

Best samples which have better sound absorption coefficient at 100Hz, 125Hz 250Hz and 500Hz are giving the best results at 500Hz. For example, at 500Hz 0.75% CNT containing sample has 0.11 Sound Absorption Coefficient but Reference sample has 0,05. Improvements up to 110% are seen at 500Hz.

5. CONCLUSION

With increasing amount of nano materials, their cell size decreases, and the sound absorption ratio and the sound transmission loss of rubber-isocyanate composites increases but after a peak point the absorption and transmission loss rates decreases. This confirms that rubber-isocyanate composites sound transmission loss and sound absorption properties are related with amount of the nano materials and also have an optimum point. Up to a certain loading of CNT and nano-silica, the absorption of sound and the sound transmission loss are noted to increase substantially. Formation of fine morphology by fillers creates more paths for passing sound waves into the composite structure and thus, they absorb more sound and on the other hand transmission loss of sound also can be seen more efficient. Beyond a certain level, the absorption profile is not improved that much. In fact, after attaining the optimum level, further silica addition results in no change in the absorption characteristics or the sound transmission loss ratio. This has been explained on the basis of distribution profile of the CNT and nano-silica in the composite walls. Very high loading can result in aggregate formation leading to no improvement in the stiffness of the cell wall. At very high loading, the uneven distribution of silica can affect the stiffness of the cell wall in such a way as to reduce the modulus and tensile strength of the composite. Besides, the accumulation of excess CNT and nano-silica aggregate in void space of a cell can act as a barrier to influence the movement of the sound wave inside a cell. It should be stressed that the presence and distribution of nano-particles has a huge role to play in the nanocomposite especially at the higher particle loading. The tests showed that addition of 1 wt.% Silicon Oxide Nano-powder and 0.75 wt.% carbon nanotube to rubber isocyanate composition improved sound transmission loss up to %20 percentage as a dB than that of pure sample. Addition of 0.75 wt.% carbon nanotube to rubber isocyanate composition improved the sound absorption coefficient up to %250 percentage as a dB than that of pure sample.

REFERENCES

[1] Bandarian, M., Shojaei A. and Rashidi, A. (2011). "Thermal, mechanical and acoustic damping properties of flexible open-cell polyurethane/multi-walled carbon nanotube foams: effect of surface functionality of nanotubes," Polymer International, Volume 60, Issue 3, pp. 475–482.

[2] Verdejo, R., Stämpfli, R., Alvarez-Lainez, M., Mourad, S., Rodriguez-Perez, M.A., Brühwiler, P.A. and Shaffer, M. (2009). "Enhanced acoustic damping in flexible polyurethane foams filled with carbon nanotubes," Composites Science and Technology, Vol. 69, pp. 1564–1569.

[3] Gao, X., Zhu, Y., Zhao, X., Wang, Z., An, D., Ma, Y., Guan, S., Du, Y., and Zhou B. (2011). Synthesis and characterization of polyurethane/SiO2 nanocomposites,"Applied Surface Science, Vol. 257, pp. 4719–4724.

[4] Cao X et al., (2005). Polyurethane/clay nanocomposites foams: processing, structure and properties. Polymer 46(3):775–83.

[5] Mahfuz H et al., (2004). Response of sandwich composites with nanophased cores under flexural loading. Compos B Eng 35(6–8):543–50

[6] Mahfuz H et al. (2004). Fabrication**,** synthesis and mechanical characterization of nanoparticles infused polyurethane foams. Compos A Appl Sci Manuf 2004;35(4):453–60.

[7] Chena, C., Taoa, X., and Liua, Y.(2009). Carbon nanotube-reinforced polyurethane composite fibers

[8] Chen, G.D., Zhou, S.X., Gu, G.X., and Wu, L.M. (2007). Modification of colloidal silica on themechanical properties of acrylic based polyurethane/silica composites, Colloids Surf. A: Physicochem. Eng. Aspects 296 29–36.

[9] Leder, G., Ladwig, T., Valter, V., Frahn, S. and Meyer, J. (2002). New effects of fumed silica inmodern coatings, Prog. Org. Coat. 45 139–144

[10] Zhang, K.; Nelson, A. M.; Talley, S. J.; Chen, M.; Margaretta, E.; Hudson, A. G.; Moore, R. B.; Long, T. E. (2016). "Non-isocyanate poly(amide-hydroxyurethane)s from sustainable resources". Green Chemistry. doi:10.1039/C6GC01096B

[11] Url-1 < http://www.nanoparticles-microspheres.com/Products/Nano-SiO2.html >, date retrieved 28.06.2016.

[12] Ceresana. (2013), Market Study Synthetic Rubber.

[13] Obrecht, W., Lambert, J.P., Happ, M., Oppenheimer-

Stix, C., Dunn, J. and Krüger, R. (2012). "Rubber, 4. Emulsion Rubbers" in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim. doi:10.1002/14356007.o23_o01

[14] Url-2 < http://www.jsrmicro.be/emerging-technologies/battery-binder/water-based-anode-binder >, date retrieved 29.06.2016.

[15] Url-3 < http://www.azom.com/article.aspx?ArticleID=218>, date retrieved 29.06.2016.

[16]Url-4 < http:/www.bayercoatings.de/bms/dbrsc/bms_rsc_cas.nsf >, date retrieved 29.06.2016.

[17] Kang, Y.J. and Ahn, **S.H.** (2013) "Soundproofing Properties of Polypropylene/Clay/Carbon Nanotube Nanocomposites," J. Appl. Polym. Sci., Vol. 130, pp. 504–509.

[18] Url-5 < http://www.azonano.com/article.aspx?ArticleID=3398>, date retrieved 30.06.2016.

[19] Yıldırım, B., and Sancak, A. (2015) Acoustic Properties Of Polyurethane Composition Reinforced With Carbon Nanotubes And Silicon Oxide Nano-Powder.

[20] Elisa, M., Merli, F., Cuce, E. and Buratti, C. (2017). "Thermal and Acoustic Properties of Aerogels: Preliminary Investigation of the Influence of Granule Size." Energy Procedia 111 : 472-80.doi:10.1016/j.egypro.2017.03.209.

[21] Kalinová, K. (2011). "Nanofibrous Resonant Membrane for Acoustic Applications." Journal of Nanomaterials 2011: 1-6. doi:10.1155/2011/265720.

[22] Gayathri, R., and R. Vasanthakumari. (2014). "Nanomaterials in PU Foam for Enhanced Sound Absorption at Low Frequency Region." Advanced Materials Research 938: 170-75. doi:10.4028/www.scientific.net/amr.938.170.

[23] Lamancusa, J.S. (n.d.) Noise Control 9. Retrived 17 June 2017 from Transmission of sound through structures.

[24] Munjal, M.L. (1987) Acoustics of ducts and mufflers with application to exhaust and ventilation system design.

[25] Vigran, T.E. (2008). Building Acoustics. Taylor & Francis.

[26] ISO (199) 11357-2: Plastics – Differential scanning calorimetry (DSC) – Part 2: Determination of glass transition temperature.

[27] The Glass Transition. Retrieved 17 June 2017 from Polymer Science Learning Center

[28] Arrighi, V., I.j Mcewen, H. Qian, and Prieto, S. (2003) "The glass transition and interfacial layer in styrene-butadiene rubber containing silica nanofiller." Polymer 44.20 : 6259-266.

[29] "The Propagation of sound". Retrieved 17 June 2017.

[30] Matthews, M. (1999). Introduction to timbre. In P. R. Cook (Ed.), Music, cognition, and computerized sound: An introduction to psychoacoustsic (pp. 79-88). Cambridge, Massachusetts: The MIT press.

CURRICULUM VITAE

Name Surname: Alkan SANCAK

Place and Date of Birth: Kocaeli 21.12.90

Address: Ortaköy Dereboyu Cad. Işık Sk. Başar Apt. No:2 Daire:12 Beşiktaş/Istanbul

E-Mail: sancakaklkan@gmail.com

EDUCATION:

B.Sc : Istanbul Technical University / Chemical Engineer

M.Sc. : Istanbul Technical University / Nano Science & Nano Engineering

Publications

1-**Navidfar, A., Sancak, A., Yıldırım, K.B. and Trabzon, L.** (2016)Influence of multi walled carbon nanotubes and silica nanoparticles on tensile properties of polyurethane- Applied Nanotechnology and Nanoscience International Conference 2016

2- **Sancak, A., Yıldırım, K.B. and Trabzon, L.** (2017)Acoustic properties of polyurethane compositions enhanced with cnts and silica nanoparticles- Journal of Mechanical Science and Technology 2017

3- **Sancak, A. and Dikmen V.** (2016) Innovatıve antibacterial nano additive sound and noise insulation usage at hospital's air conditioning ducts' inside insulation -XII. International HVAC+R&Sanitary Technology Symposium 2016