UTILIZATION OF LOW HYDROXYL CONTENT OF WASTE OIL POLYMER FOAM DOPED WITH WASTE MATERIALS FOR SOUND ABSORPTION APPLICATION

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ABSTRACT

Bio-monomer were named based on the starting vegetable oils as virgin oil monomer (VOM), 'popia' oil monomer (POM), and mixed oil monomer (MOM). MOM has been identified to have the lowest OH index with 0.093 compared to POM and VOM, meanwhile tensile strength for Virgin Oil Polymer (VOP) shows highest result with 5.69 MPa compared to MOP that is 4.48 MPa. The lowest OH formation with low strength of waste oil was used and utilized for sound absorption application. Bio-polymer composites foams were prepared with different ratio of waste tyre rubber (WTR) and wood dust (WD) fillers by opened mould method (OMM) and closed mould method (CMM) with composite and hybrid fillers loading. By OMM, bio-polymer composite with foaming agent for all percentages of fillers shows high α at medium frequency level (Hz). $WTRFMOP_{10}$ and $WDFMOP_{7.5}$ had high potential as an efficient sound absorption material with α approximately equal to 0.95 and 0.9 respectively at 2500 Hz. Bio-polymer composite loading with WTR at different percentages filler loading shows α approximately 1.0 at different frequency level and $WTRMOP_5$ shows the highest α that is 0.99 at 3962 Hz. Bio-polymer composite loading with WD at different percentages filler loading shows α is approximately to 1.0 at high frequency above 4000 Hz and $WDMOP_{7.5}$ shows the highest α that is 0.99 at 5000 Hz. For CMM with composite fillers loading, $WTRFMOP_{10}$ and $WTRFMOP_5$ shows maximum peak of α around 0.8 while $WDFMOP_{10}$ shows maximum peak of α around 0.7 meanwhile $WTRMOP_{7.5}$ and $WDMOP_{2.5}$ gives α around 0.79 and 0.95 respectively. By increasing the percentage loading of waste fillers and foaming agent, at maximum 10% (by wt/wt of bio-monomer) loading for both filler and foaming agent, evidently, the pores size decreases and less uniform structure comprised of large elongated strips-like pores interconnected by smaller pores of different pore sizes take placed. Meanwhile, increasing waste fillers loading without foaming agent shows a decreased and uneven pores size distribution under Scanning Electron Microscope (SEM). This revealed the influence of foaming agent as stabilizer to the polymeric foam while for fillers loading acts as reactive agent for some bubble nucleants and the surplus is prone to agglomerate and isn't efficient for bubble nucleation for pores formation in the system.

CHAPTER 1

INTRODUCTION

1.1 General Introduction

As the oil crisis and global warming deepen, bio- based materials have received particular attention. Agriculture, industry, and the environment will benefit from the use of materials made from renewable resources. Vegetable oils are becoming extremely important as renewable resources for the preparation of polyols required for the polyurethane industry. Polyols from natural oils, such as soybean, castor, and palm oils are increasingly being viewed by industry as a viable alternative to hydrocarbon based feedstocks. These oils are annually renewable, and are cost-competitive as well as environment friendly. According to a market summary published by the United Soybean Board in February 2000, vegetable oil-based polyurethanes are best suited to three markets namely: polyurethane foams, polyurethane binders and agricultural films (Sharma & Kundu, 2008). For the first step in this research, vegetable and waste vegetable oils will converted to bio-monomer and selected to use further in the research for other applications.

According to Chowdhury (2010), during the last few years, a series of works have been done to replace the conventional synthetic fiber with natural fiber composites. For instant, hemp, sisal, jute, cotton, flax and broom are the most commonly fibers used to reinforce polymers. In addition, fibers like sisal, jute, coir,

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oil palm, bamboo, wheat and flax straw, waste silk and banana have proved to be good and effective reinforcement in the thermosetting and thermoplastic matrices his research will focus on fiber-reinforced composites from renewable resources: natural fibers and natural matrix for solid bio-polymer.

In recent years, noise control has received much attention for improving living environments. According to Zulkifli, *et al.* (2010), noise can cause general types negative effects they are; hearing loss, no auditory health effect, individual behavior, effect on sleep, communication interference and effect on domestic animals and wildlife. There are several methods to decrease noise, one of which uses sound absorption materials. Currently, sound absorption materials commercially available for acoustic treatment consisted of glass or mineral-fiber material.

However, when review the issue of safety and health, these fibers when exposed to human can interference human health mainly lungs and eyes. These issues explore an opportunity to look for alternative materials from organic fibers to be developed as noise absorption material. Organic fibers as basis material for absorber materials have several benefit; renewable, nonabrasive, cheaper, abundance and less potential health risks and safety concern during handling and processing (Zulkifli *et al.*, 2010).

According to Ersoy & Kucuk (2009) industrial applications of sound insulation, generally includes the use of materials such as glass wool, foam, mineral fibres and their composites. This research was carried out to study the potential use of bio-polymer foam in replacing synthetic polymer and waste tyre rubber (WTR) and wood dust filler (WD) as the natural composite for sound control applications.

1.2 Problem Statement

Recently, the use of renewable resources has attracted the attention of many researchers because of their potential to substitute petrochemical derivatives. By renewable resource is meant agricultural products mainly from principal crops: soybean, oil palm, rapeseed, sunflower and coconut, where the materials are synthesized by sunlight. The high environmental burden caused by the used of non-

renewable fossil based petrochemical feedstock in the plastic industry has lead to search for renewable materials such as vegetable oil based alternatives. Most of Small Medium Industries (SMI's) in Malaysia has problem of the overloaded waste cooking oil. Cooking oil has proven to be problematic material, with most people don't know how it should be managed. Certainly, it should not be poured down the drain of the kitchen sink or into toilet. It can clog the sanitary sewer system, causing costly backups. Realistically, abundance and low cost, broad-band sound absorption foam bio-polymer with relatively simple processing provides a good solution to the society since undesirable and potentially hazardous noise that became more complex and give serious problems nowadays.

1.3 Scope of Study

Vegetable oils were obtained from SMI's and fatty acid was chemically manipulated at the laboratory scale using less than 1L vegetable oils. The monomer preparations begin with the catalyst preparation to generate the epoxies from the unsaturated fatty compound, and second reaction is the acid-catalyst ring opening of the epoxies to form polyols or monomer. These polyol or monomer components were named based on the starting vegetable oils such as virgin oil monomer (VOM), 'popia' oil monomer (POM), and mixed oil monomer (MOM). The Fourier Transform Infrared (FTIR) is used to determine the formation of OH group and the Hydroxyl Index (HI) is calculated. The lowest OH formation from selected oil and waste oil will be used and utilized for sound absorbent application by impedance tube test. The effect of fillers for the mechanical properties of all solid polymers will be determined, particularly for organic fillers such as waste trye rubber particle and wood dust fillers. Realistically, abundance and low cost, broad-band sound absorption with relatively simple processing provides a good solution to the society with undesirable and potentially hazardous noise that became more complex and gives serious problems nowadays.

1.4 Objectives of this work

i   To synthesize bio-monomer from waste vegetable oils such as mixed oil monomer (MOM), 'popia' oil monomer (POM), and virgin oil monomer (VOM).

ii   Identification of hydroxylated (OH) monomer by means of Infrared Spectroscopy to determine the Hydroxyl Index (HI) and mechanical property for bio-polymer.

iii   Determination of sound absorption coefficient (α) for bio-polymer foam by impedance tube test via different fabrication technique classifieds as opened (OMM) and closed mould method (CMM) to achieve three main criteria; that were α approximately to 1.0 at different frequency level (Hz), high α at medium frequency level (Hz), and high α at above 4000 Hz.

CHAPTER TWO

LITERATURE REVIEW AND THEORY

2.1   Introduction

This chapter discusses and reviews previous studies from other researchers on bio-monomer, bio-polymer and also bio-polymer composite as sound absorption application. It helps to provide more information and explanation especially in bio-monomer and bio-polymer composite properties. The theory of bio-polymer composite as sound absorption materials will be applied in this study to achieve the research objectives.

2.2   Polymers based on renewable materials

In recent years, eco-friendly biodegradable polymers and plastics have gained increasing attention because of growing recognition worldwide of the need to reduce global environmental pollution (Kim, 2006). Today's plastics are designed with little consideration for their ultimate disposability or the effect of the resources (feedstocks) used in making them. This has resulted in mounting worldwide concerns over the environmental consequences of such materials when they enter the

mainstream after their intended uses. This led to the concept of designing and engineering new biodegradable materials; materials that have the performance characteristics of today's materials but that undergo biodegradation along with other organic waste to soil humic materials. Hence, the production of biodegradable materials from annually renewable agricultural feedstocks has attracted attention in recent years. Agricultural materials such as starches and proteins are biodegradable and environmentally friendly.

As the world approaching the twenty-first century, the polymer industry continues to evolve from its rapidly expanding petroleum-based infancy in the middle to- late twentieth century into a complicated economic, regulatory, and ecological industry. With the increase in environmental consciousness among consumers and governments, the industry is now faced not only with manufacturing and marketing concerns but with ecological and legislative issues as well. The trend is environmental conservation and regulation is toward a "cradle-to-grave" approach, in which the manufacturer is increasingly responsible for the handling of raw materials used in production and the finished products, eventual disposal (Swain *et al.*, 2004). Polymers from renewable resources have attracted an increasing amount of attention over the last two decades, predominantly due to two major reasons: firstly environmental concerns, and secondly the realization that our petroleum resources are finite (Yu, Dean & Li, 2006).

2.3 Sources and importance

According to the Andjelkovic *et al.* (2005), vegetable oils are one of the cheapest and most abundant, annually renewable natural resources available in large quantities from various oilseeds. In general, the bulk of vegetable oils produced each year is used for human food or animal feed, whereas the remainder finds non-food uses, such as the production of soaps, lubricants, coatings and paints. While, according to Demirbas (2008), vegetable oil is one of the renewable fuels and become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources. Vegetable oils have the potential to

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replace a fraction of the petroleum distillates and petroleum-based petrochemicals in the near future.

According to Marvey (2008), crop-based feedstocks have the advantage over petroleum-based; the resources are renewable, the products are biodegradable and their processes result in reduced emissions of greenhouse and harmful gases.

Vegetable oils are excellent renewable source of raw materials for the manufacture of polyurethane components such as polyols. The transformations of the double bonds of triglycerides of oils to hydroxyls and their application in polyurethanes have been the subject of many studies (Sharma & Kundu, 2008).

The word "oil" is used for triglycerides that are liquid at ordinary temperatures. They are water- insoluble products of plants. A triglyceride is an ester product obtained from one molecule of glycerol and three molecules of fatty acids as shown in Figure 2.1. They can also be artificially produced from the reaction of glycerol and fatty acids (Guner, Yagci & Erciyes, 2006). Vegetable oils and animal fats are triglyceride molecules in which three fatty acid groups are esters attached to one glycerol molecule (Demirbas, 2008).

According to Demirbas (2008), fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdoms that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides. Chemically, fats and oils are carboxylic esters derived from the single alcohol glycerine and are known as triglycerides. Triglycerides derive from many different carboxylic acids. Triglyceride molecules differ in the nature of the alkyl chain bound to glycerol. The proportions of the various acids vary from fat to fat; each fat has its characteristic composition. Triglyceride vegetable oils and fats include not only edible but also inedible vegetable oils and fats such as linseed oil, castor oil, and tung oil, used in lubricants, paints, cosmetics, pharmaceuticals, and other industrial purposes.
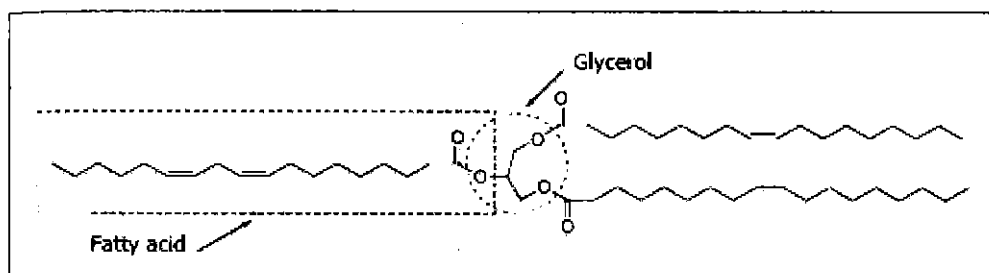
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Figure 2.1: Triglyceride molecule, the major component of vegetable oils

According to another researcher (Carlsson, 2009), the compositions of most seed oils, including oils from all our annual oil crops, are made up of a wide range of fatty acids with six dominating fatty acids: palmitic, stearic, oleic, linoleic and linolenic acids, having chain lengths of 16 and 18 carbons and lauric acids having 12 carbon chains and found in the seed kernels of coconut and oil palm. Alongside these are a great number of unusual fatty acids produced by wild plant species. Such fatty acids include those with chain lengths between 8 and 24 carbons, containing varying numbers of double bonds, conjugated systems or functional groups such as acetylenic bond (triple bond), epoxy group (oxygen containing) and hydroxyl group.

The fatty acids contribute from 94–96% of the total weight of one molecule triglyceride oil. Saturated fatty acids have no double bonds. On the other hand, unsaturated fatty acids have one or more than one double bond. If the double bonds in the carbon chain are separated by at least 2 carbon atoms, double bonds are called isolated. If single and double bonds alternate between certain carbon atoms, double bonds are called conjugated (Guner, Yagci & Erciyes, 2006).

Indeed, plant oils represent excellent renewable resources for oleo chemical production for industrial usage since they are structurally similar to the long-chained hydrocarbons derived from petroleum. The main differences that do exist such as the plant oils are generally more oxidized and unsaturated and have a weak spot in its central β-CH group on the oil molecule (triacylglycerol), give them a limited thermal, oxidation and hydrolytic stability. However, these differences also provide excellent starting points for chemical modifications to provide new types of feedstocks.

Natural oils are considered to be the most important class of renewable sources. They can be obtained from naturally occurring plants, such as sunflower, cotton, linseed. They consist predominantly of triglycerides. Among the triglyceride

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oils, linseed, sunflower, castor, soybean, oiticica, palm, tall and rapseed oils are commonly used for synthesis of oil-modified polymers. Although fatty acid pattern varies between crops, growth conditions, seasons, and purification methods, each of triglyceride oils has special fatty acid distribution (Guner *et al.*, 2006).

As shows in Table 2.1, palmitic (16:0) and stearic (18:0) are the two most common saturated fatty acids, with every vegetable oil containing at least a small amount of each one. Similarly, oleic (18:1) and linoleic (18:2) were the most common unsaturated fatty acids. Many of the oils also contained some linolenic acid (18:3) (Demirbas, 2008).

Table 2.2 lists their distribution in commercially significant vegetable oils. It should be noted that there are also exotic oils composed of fatty acids with other types of functionalities, such as hydroxyl, epoxy, and furanoid groups.

Table 2.1: Fatty acid compositions of vegetable oils and fats (Demirbas, 2008)

Sample	16:0	16:1	18:0	18:1	18:2	18:3	others
Cottonseed	28.7	0.0	0.9	13.0	57.4	0.0	0
Poppyseed	12.6	0.1	4.0	22.3	60.2	0.5	0
Rapeseed	3.8	0.0	2.0	62.2	22.0	9.0	0
Safflowerseed	7.3	0.0	1.9	13.6	77.2	0.0	0
Sunflowerseed	6.4	0.1	2.9	17.7	72.9	0.0	0
Sesameseed	13.1	0.0	3.9	52.8	30.2	0.0	0
Linseed	5.1	0.3	2.5	18.9	18.1	55.1	0
Wheat grain	20.6	1.0	1.1	16.6	56.0	2.9	1.8
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Corn marrow	11.8	0.0	2.0	24.8	61.3	0.0	0.3
Castor	1.1	0.0	3.1	4.9	1.3	0.0	89.6
Tallow	23.3	0.1	19.3	42.4	2.9	0.9	2.9
Soybean	11.9	0.3	4.1	23.2	54.2	6.3	0
Bay laurel leaf	25.9	0.3	3.1	10.8	11.3	17.6	31
Peanut kernel	11.4	0.0	2.4	48.3	32.0	0.9	4
Hazelnut kernel	4.9	0.2	2.6	83.6	8.5	0.2	0
Walnut kernel	7.2	0.2	1.9	18.5	56.0	16.2	0
Almond kernel	6.5	0.5	1.4	70.7	20.0	0.0	0.9
Oilve kernel	5.0	0.3	1.6	74.7	17.6	0.0	0.8
Coconut	7.8	0.1	3.0	4.4	0.8	0.0	65.7

Table 2.2: Fatty acid percentage distribution in various plant oils (Puig, 2006)

Fatty Acid	C:D B[1]	Cano la	Corn	Cotto nsee d	Linse ed	Olive	Palm	Soyb ean	Sunfl ower	High Oliec [2]
Nyristic	14:0	0.1	0.1	0.7	0.0	0.0	1.0	0.1	0.0	0.0
Myristoleic	14:1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Palmatic	16:0	4.1	10.9	21.6	5.5	13.7	44.4	11.0	6.1	6.4
Palmitoleic	16:1	0.3	0.2	0.6	0.0	1.2	0.2	0.1	0.0	0.1
Margalic	17:0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Margaroleic	17:1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Strearic	18:0	1.8	2.0	2.6	3.5	2.5	4.1	4.0	3.9	3.1
Oleic	18:1	60.9	25.4	18.6	19.1	71.1	39.3	23.4	42.6	82.6
Linoleic	18:2	21.0	59.6	54.4	15.3	10.0	10.0	53.2	46.4	2.3
Linolenic	18:3	8.8	1.2	0.7	56.6	0.6	0.4	7.8	1.0	3.7
Arachidic	20:0	0.7	0.4	0.3	0.0	0.9	0.3	0.3	0.0	0.2
Gadoleic	20:1	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4
Elcosadienoi c	20:2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Behenic	22:1	0.3	0.1	0.2	0.0	0.0	0.1	0.1	0.0	0.3
Erucic	22:1	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Lignoceric	24:0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DB/triglycer ide		3.9	4.5	3.9	6.6	2.8	1.8	4.6	0.0	3.0

[1]C, number of carbon atom; DB, number of C=C double bonds

[2]Genetically engineered high oleic acid content soybean oil (DuPont)

2.4 Monomer from renewable resources

Monomer is single repeating unit of a polymer that are covalently bonded into long chains (Smith & Hashemi, 2006; Chang & Cruickshank, 2005). Meanwhile, oil-based polyols are often oligomers with a wide distribution of molecular weights and a considerable degree of branching, which affect the viscosity and processing properties of polyurethane foams produced from them. Precise characterization of the polyol composition and its properties are very important for understanding synthetic processes as well as for quality control. Polyols are a component in the production of polyurethanes used in appliances, automotive parts, adhesives, building insulation, furniture, bedding, footwear and packaging. Although, polyols are currently

produced from petroleum, vegetable oils are also used extensively for their production. The vegetable oil molecules must be chemically transformed in order to obtain hydroxyl moieties.

Vegetable oils are becoming extremely important as renewable resources for the preparation of polyols required for the polyurethane industry. Polyols from natural oils, such as soybean, castor, and palm oils are increasingly being viewed by industry as a viable alternative to hydrocarbon based feedstocks. These oils are annually renewable, and are cost-competitive as well as environment friendly. According to a market summary published by the United Soybean Board in February 2000, vegetable oil-based polyurethanes are best suited to three markets namely: polyurethane foams, polyurethane binders and agricultural films (the last may not be polyurethanes) (Sharma & Kundu, 2008).

2.5 Polymer from renewable resources

Polymer is a molecular compound distinguished by a high molar mass, ranging into thousands and millions of grams, and made up of many repeating units (Chang & Cruickshank, 2005).

Oil-based biopolymers have many advantages compared with polymers prepared from petroleum-based monomers. They are biodegradable and, in many cases, cheaper than petroleum polymers (Guner *et al.*, 2006). According to previous researcher Yu *et al.* (2006), generally, polymers from renewable resources (PFRR) can be classified into three groups: (1) natural polymers, such as starch, protein and cellulose; (2) synthetic polymers from natural monomers, such as polylactic acid (PLA); and (3) polymers from microbial fermentation, such as polyhydroxybutyrate (PHB). Three ways biopolymer plastics can be produced are through converting plant sugars into plastic, producing plastic inside microorganisms, and growing plastic in corn and other crops.

PLA is a thermoplastic and compostable polymer made from lactic acid which can totally degrade in an aerobic or anaerobic environment in six months to five years. PLA has the tensile strength, modulus, flavor and odor barrier of

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polyethylene and PET or flexible PVC; the temperature stability and processability of polystyrene; and the printability and grease-resistance of polyethylene. The glass transition temperature of PLA (Tg) ranges from 50°C to 80°C while the melting temperature (Tm) ranges from 130°C to 180°C. PLA can be processed by injection molding, sheet extrusion, blow molding, thermoforming and film forming. PLA can be recycled by chemical conversion back to lactic acid and then repolymerized. Unmodified PLA has limitations such as brittleness, a low heat distortion temperature, and slow crystallization rates.

PHAs are polyesters that accumulate in a wide variety of microorganisms. Primary research shows that PHA has a considerably low volume of the biopolymer market, somewhere around 100,000 lbs. per year. PHAs are polyesters, but they can also imitate polypropylene, polystyrene, and polyethylene. PHAs are considered to be the broadest biopolymer because they have their own class and can have many different chemical structures. These polymers have a wide range of properties ranging from stiff and brittle plastics to rubberlike materials. They also can exhibit properties similar to many synthetic polymers. There are currently 100 different monomer types of PHA that have been discovered. Like numerous other petroleum-based polymers, many properties of polymers from renewable resources can also be improved through blending and composite formation.

According to Plackett & Vazquez (2004), biodegradation has been defined as 'an event that takes place through the action of enzymes or through chemical decomposition associated with living organisms' (e.g. bacteria, fungi). Another proposed definition is 'the gradual breakdown of material mediated by specific biological activity' (Ali et al., 1994). Abiotic reactions involving photodegradation, oxidation and hydrolysis may also occur before, during or instead of biodegradation. Biodegradable polymers are classed as biosynthetic, semi-biosynthetic or chemosynthetic depending on their manner of preparation. Steinbuchel (1995) studied the use of biosynthetic, biodegradable thermoplastics and elastomers from renewable resources and Mohanty et al. (2000) prepared a recent summary in the context of biocomposite applications.

The most widely used method to characterize material is infrared spectroscopy, particularly Fourier transform infrared (FTIR) spectroscopy. It can also

be used for the structural analysis of oils. In Table 2.3, the absorption bands and the corresponding function/groups are assigned (Guner et al., 2006).

Table 2.3: Some representative IR absorption band values for fatty acids (Guner et al., 2006)

| Absorption band (cm^{-1})	Functionality
3500	-OH functions corresponding to free gycerol and/or residual moisture
2930-2850	-CH2- groups (with an additional weak shoulder around 2960cm-1 reflecting the presence of terminal methyl groups)
1745	-COOH group
1160	C-O-C functions of the ester group
720	-(CH2)n- sequences of the aliphatic chains of the fatty acids
1650, 3010	Non-conjugated unsaturation of linoleic acid for linseed oil
990	Conjugated unsaturation of eleostearic acid chain for tung oil
970	*Trans* configuration of eleostearic acid chain for tung oil
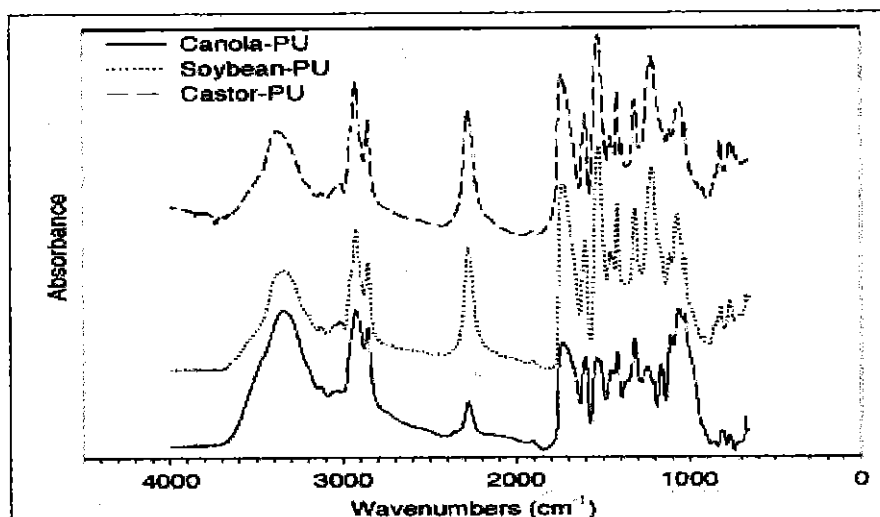
Figure 2.2: FTIR spectra of polyurethane foams. Solid line: canola oil based polyurethane (Canola PU); dotted line: soybean oil based polyurethane (Soybean-PU), and dashed line: castor oil based polyurethane (Castor-PU) (Narine *et al.*, 2007).

From another researcher, Narine *et al.*, (2007), the FTIR spectra of Canola-PU, Soybean-PU and Castor-PU foams are shown in Figure 2.2. A broad absorption band at 3,340 cm^{-1} characteristic of the N-H group and an absorbance band centered around 1,720 cm^{-1} characteristic of the C $=$ O group are present in all the FTIR spectra. However, both bands are not symmetrical. The asymmetrical shape of the band around 1,720 cm^{-1} shows that the hydrogen bonded C $=$ O group vibration region is overlapping with the free C $=$ O group vibration region. In addition, the band centered at 2,270 cm^{-1} characteristic of the –NCO group observed in all spectra indicated that the isocyanate has not completely reacted.
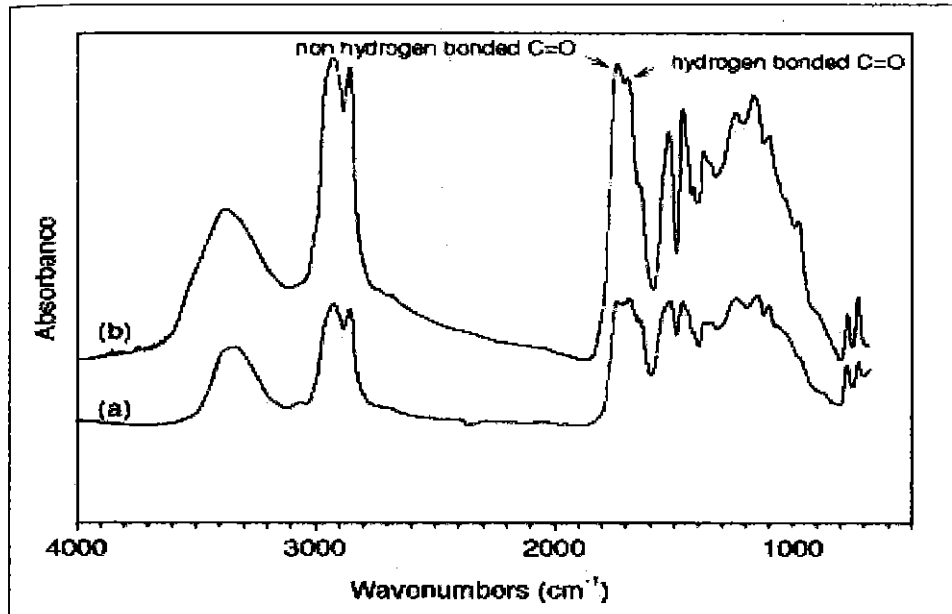
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Figure 2.3: FTIR spectra of polyurethane elastomers with OH/NCO molar ratio 1.0
(a) canola-oil-based polyurethane (COBPU), (b) soybean-oil-based polyurethane
(SOBPU) (Narine *et al.*, 2007)

From same researcher in another journal Narine *et al.*, (2007), the FTIR
spectra for the two elastomers that were canola oil- based PU (COBPU) and
soybean-oil-based PU (SOBPU) with an OH/NCO molar ratio of 1.0 are shown in
Figure 2.3. The –NCO group absorption band centered at 2,270 cm^{-1} is clearly
missing, and a strong 3,340 cm^{-1} absorption band characteristic of the N–H group
and an absorption band characteristic of the C=O group centered around 1,700 cm^{-1}
are present in all FTIR spectra. FTIR spectra confirmed that almost all of the
diisocyanate groups reacted during polymerization and formed urethane linkages and
amide groups.

2.6   Modification of polymers using fillers

According to George (2000), fillers are solid additives, different from plastic
matrices in composition and structure, which are added to polymers to increase bulk
or improve properties. According to Brydson (1999), the term filler is usually applied

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to solid additives incorporated into the polymer to identify its physical (usually mechanical) properties. Air and other gases which could be considered as fillers in cellular polymers are dealt with separately. In general, filler are defined as materials that are added to the formulation to lower the compound cost.

For effective utilization of fillers, a complete understanding of individual characteristics is essential. Each class of the fillers appears to exhibit specific characteristics which make them especially suited for the given application (Lutz & Grossman, 2000). Fillers, being much stiffer and stronger than the polymer, usually increase its modulus and strength. Thus, mechanical property modification may be considered as their primary function, although their presence may significantly affect thermal expansion, transparency, thermal stability, etc (Xanthos, 2005). A number of types of filler are generally recognized in polymer technology and these are summarized in Figure 2.4.
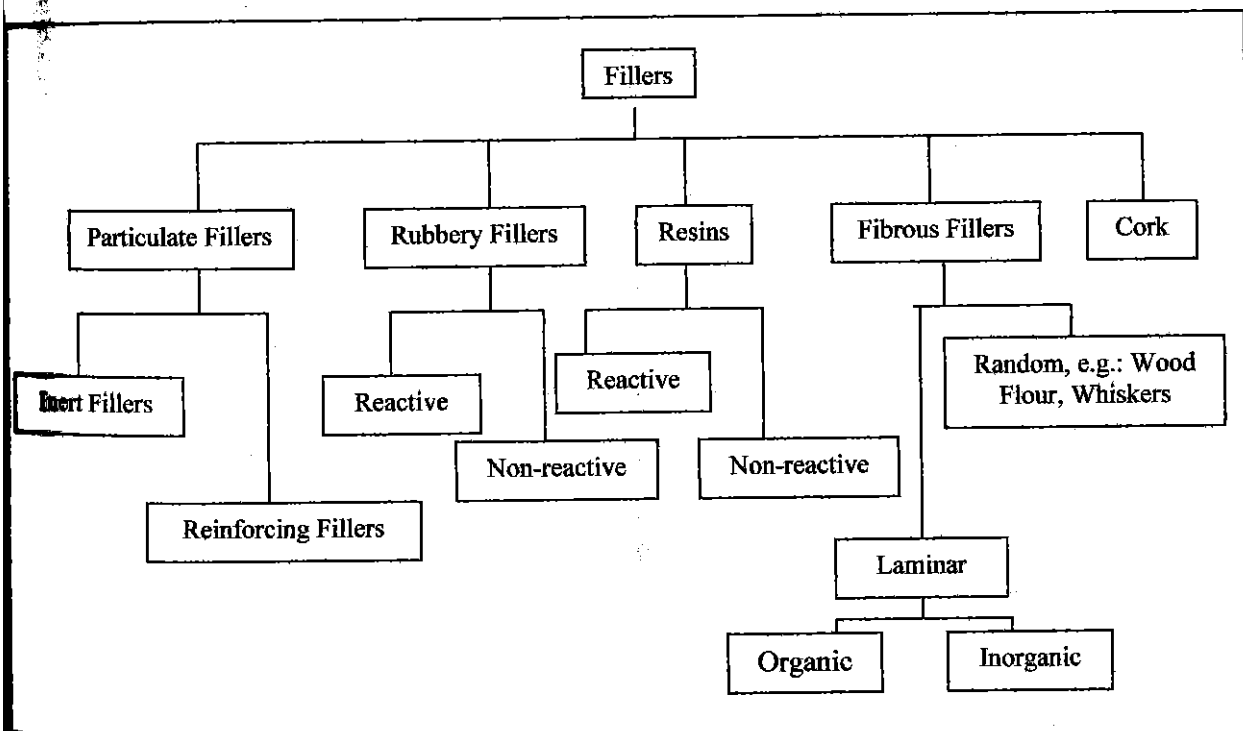

Figure 2.4: Types of fillers in polymer (Brydson, 1999)

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Particulate filler are divided into two types, 'inert' fillers and reinforcing fillers (Brydson, 1999). According to Rothon, (2001), from the earliest days, particulates fillers have played a vital role in the development of commercial uses for polymer. Originally, they were mainly such as cheap diluents. However, their ability to beneficially modify many properties soon began to be realized and they are used for many purposes today. The term functional filler is often uses to describe materials that do more than provide cost reduction. Particulate filled thermoplastic are used in large quantities in many fields of application from household appliances to automotive parts. In particulate filled polymers two type of interaction may be distinguished. Particle-particle interaction lead to aggregation, while matrix-fillers interactions determine micromechanical deformation processes as well as the macroscopic behavior and performance of the materials.

Fibrous fillers have been long used in plastics materials. Wood flour, cotton flock, macerated fabric, macerated paper and short lengths of synthetic organic fibres such as nylon can improve the impact strength and often the rigidity and toughness of moulding compositions. Inorganic fibres such as asbestos and glass fibre are also used in moulding compositions, both thermoplastic and thermosetting where heat resistance and strength respectively are required. More recently, chopped carbon fibre and whiskers (single crystal of high length-diameter ratio of very high strength) have been used for highly specialized purposes.

Fibrous fillers are often embedded in a laminar form. The fibres used have higher moduli than the resins in which they are embedded so that when the composite of resin plus fibre is strained in the plane of fibrous layer the bulk of stress is taken up by the fibre. This results in enhancement of both strength and modulus when compared with unfilled resin (Brydson, 1999).

Some of the main reason for using particulates fillers are cost reduction improved processing, density control, optical effect, such as translucency, thermal conductivity, control of thermal expansion, electrical properties like antistatic, magnetic properties, flame retardancy and improve mechanical properties like notably hardness, stiffness, abrasion and tear resistance (Rothon, 2001). Besides, electrical properties can be affected by many types of filler. For example, by adding conductive fillers, an electromagnetic shielding property can be built into plastics, which are normally poor electrical conductors.

Anti-static agents can be used to attract moisture, reducing the build-up of static charge. Coupling agents are added to improve the bonding of the plastic matrix and the reinforcing fibers. Different fillers are used to lower the cost of materials. Other additives include flame retardants to reduce the likelihood of combustion, lubricants to reduce the viscosity of the molten plastic, plasticizers to increase the flexibility of the materials, and colorants to provide colorfastness (Shoemaker, 2006).

Fillers modify the properties and molding of the compound to which they are added. If the fillers are characterized with a low aspect ratio between the longest and the shortest dimensions, the basic properties will be less changed from those of the unfilled polymer. Fillers benefit plastics parts in the following ways like shrinkage will be less, thermal resistance may be improved, strength, especially compressive strength, will be improved, impact resistance will often be lower than for the unfilled polymer, and solvent resistance will often be improved. When the aspect ratio between the longest and the shortest dimension of the filler is large, for example, greater than 25, the filler can be characterized as a fiber. Fiber reinforcements will significantly affect the properties of the compounds to which they are added (Shoemaker, 2006).

Assuming good bonding between the fiber and the polymer matrix, the strength in the fiber direction will be significantly increased. If many fibers are oriented in the same direction, large differences will be noted between the modulus in the orientation direction and in the direction perpendicular to the orientation. The latter will be very close to that for the unfilled polymer. The fibers will also have a significant effect on the shrinkage properties of the compound: shrinkage in the orientation direction will be much less than the shrinkage in the cross direction. Because the fiber orientation varies with the flow direction, in the thickness direction, and at weld line locations, it is important to be able to predict these orientations, in order to predict the properties of the molded article (Shoemaker, 2006).

Polymer composites are mixtures of polymers with inorganic or organic additives having certain geometries (fibers, flakes, spheres, particulates). Thus, they consist of two or more components and two or more phases. The additives may be continuous, e.g. long fibers or ribbons; these are embedded in the polymer in regular geometric arrangements that extend throughout the dimensions of the product.

Familiar examples are the well-known fiber-based thermoset laminates that are usually classified as high performance polymer composites. On the other hand, the additives may be discontinuous (short), as, for example, short fibers (say <3 cm in length), flakes, platelets, spheres or irregulars; these are dispersed throughout the continuous matrix. Such systems are usually based on a thermoplastic matrix and are classified as lower performance polymer composites compared to their counterparts with continuous additives. Nature uses composites for all her hard materials. These are complex structures consisting of continuous or discontinuous fibrous or particulate material embedded in an organic matrix acting as glue (Xanthos, 2004).

2.7   Bio-polymer composite

Refer to previous researcher Plackett & Vazquez (2004), polymers derived from natural sources and their use in composites reinforced with natural fibres referred to as biocomposites, a term frequently used in the literature (Mohanty *et al.*, 2000, 2002), but also now commonly extended to composites in which biopolymers include inorganic fillers (e.g. nanoclays). Naturally derived polymers are usually biodegradable, and therefore biocomposites reinforced with natural fibres should also be fully biodegradable. In addition to this characteristic, biocomposites containing natural fibres generally exhibit enhanced mechanical properties and, because of the partial replacement of the polymer matrix with less costly reinforcing material, are less expensive than the starting polymer in overall material costs. Biocomposites have been the subject of international research since at least the mid-1990s and a number of practical applications are now emerging, including interior automotive components and housings for notebook computers. Commercial interest in manufacturing these products is driven by the derivation of the polymers from renewable sources as well as by their specific properties including biodegradability.

Suarez, Countinho & Sydenstricker (2003), was studied the tensile properties and the fracture mechanisms for the composites of polypropylene (PP) or PP plus maleated polypropylene (MAPP) and sawdust coated with 22.4 wt% MAPP. The effects of MAPP content on the properties of PP mixes were also studied. Scanning

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electron microscopy (SEM) was also performed to analyze the tensile fracture surfaces and the interfacial fiber/matrix adhesion. The result shows the tensile properties of composites with up to 10% MAPP have not been improved by increasing MAPP content. This has been attributed to the poor filler/matrix adhesion. The addition of higher MAPP content to the PP composites produces better adhesion of sawdust to PP matrix and an increase in the tensile strength.

Toro *et al* (2007), was studied the different proportions of chicken eggshell (ES) as bio-filler for polypropylene (PP) composite were compared with different particle sizes and proportions of commercial talc and calcium carbonate fillers by tensile test. The results showed the Young's modulus (E) was improved with the increment of ES content, and this bio-filler was better than all types of carbonate fillers with different particle sizes used in their study. Although ES composites showed lower Young's modulus, E values than talc composites, talc filler could be replaced by up to 75% with ES while maintaining a similar stiffness and Young's modulus, E compared to the talc composites. Scanning electron microscopy showed an improved interfacial bonding on the tensile fractured surface. The improvement in the mechanical properties was attributed to a better ES/matrix interface related to the geometric ratio of the ES particles similar to talc particles.

2.8   Sound

Sound is an oscillation in atmospheric pressure (a traveling vibratory movement of molecules) within an elastic medium (material) of any phase- (gas, liquid or solid). Sound is the result of a source setting a medium into vibration. Usually, the medium is air where the receptor is the ear. Based on the sound characteristics, the sensory conclusion drawn by the brain may be noise or sound, which mean, unwanted or wanted sound (Cheremisinoff, 1996).

Vibrations in a medium result in sound. The vibration produces alternating waves of relatively dense and sparse particles-compression and rarefaction, respectively-which travel away from the source as longitudinal waves, much like ripples in water. The resultant variation to normal ambient pressure is translated by

the ear and perceived as sound. Like other waveforms, sound waves may be refracted, reflected or scattered. Under normal conditions of temperature, pressure and humidity at sea level, sound waves travel at approximately 344 meter/set (1100 ft/sec) through air, 1433 meter/set in water, 3962 meter/set in wood and 5029 meter/sec in steel. Thus, sound may be transmitted through any media initially and eventually travel through air to a receiver, the ear.

Sound may be described in terms of three variables: (1) amplitude (perceived as loudness), (2) frequency (perceived as pitch) and (3) duration (time) (Cheremisinoff., 1996). Noise is simply unwanted sound, which is a series of vibrations in the air. Human ears are sensitive to these vibrations; they sense them and pass them on to the brain to decipher. Acoustics is the branch of physics that deals with the production, transmission, and control of sound which has its own concepts and vocabulary (Sturz & Fullerton, 2002).

The human ear is sensitive to sound extending from approximately 20 to 20,000 Hz but is most sensitive to sound in the 500 Hz to 4000 Hz frequency range. Above and below this frequency range, in which the ear is most sensitive, the ear is progressively less sensitive to sound (Tocci, 2007). From other researcher, Crocker, (2007), human hearing is most sensitive at about 4000 Hz. Human can hear sound down to a frequency of about 15 or 16 Hz and up to about 15,000 to 16,000 Hz.

Normal speech is in the range of about 100 to 4000 Hz with vowels mostly in the low- to medium-frequency range and consonants mostly in the high-frequency range. Music has a larger frequency range and can be at much higher sound pressure levels than the human voice. Besides, according to Cheremisinoff, (1996), the human ear is functionally a receiver of all sound vibrations received from the environment. The ear may respond from a low of 16 Hz at birth to a high of 30,000 Hz; however, a range of 20 Hz to 20,000 Hz is considered a broad frequency response. Throughout life frequency perception declines (presbycusis) to a point at which a normal adult may have difficulty hearing sounds pitched higher than 12 000 Hz. Speech frequencies are in the range of 20 Hz to 2000 Hz.

Early researcher, Sturz & Fullerton (2002), the audible frequency range extends from about 20 to 20,000 Hz for a young person with ideal hearing, but for adults this range is frequently narrower due to aging and noise exposure effects. For engineering analysis purposes, the audible frequency range is often divided into a

series of octave bands. Just like an octave on a piano keyboard, an octave in sound analysis represents the frequency interval between a given frequency and twice that frequency. For ease of use and to develop a consistent basis for communication, standard octave bandwidths have been defined and are built into measurement instrumentation.

2.9 Reflection and absorption of sound waves

Sound waves travel outward in all directions from a sound source. When they strike an obstacle, such as wall, the direction of travel of the waved is changed; they are reflected (Harris, 1991). Figure 2.5a illustrates the reflection of waves, originating at the sound source, which strike a large flat wall. The curved solid lines represent waves spreading outward from the source while the curve dotted lines represent the waves after they have been reflected from the wall. The straight lines with arrows indicate the direction of travel of the sound waves (these are called sound rays). Note that the angle of the reflected sound is equal to the angle of the incident of sound; this is called the *law of reflection*. This law holds only for the reflection of sound from a surface that is large compared with the wavelength. The reflected sound waves travel as if they had originated from the "image" of the sound source.

An image is an imaginary source located the same distance behind the wall as the real source as in front of the wall (along a perpendicular line drawn between the source and the wall). If the reflecting surface is nonporous and perfectly rigid, there is no loss of acoustic energy on reflection. Then the reflected waves produce the same sound pressure level at any given point as an image, if the wall were removed and the image had the same sound power as the source. However, no physical surface is a perfect reflector, which means some of the incident acoustic energy always is absorbed by the surface. If the reflecting surface is not large compared to the wavelength of the incident sound, the law of reflection does not hold; then the angle of incidence is not equal the angle of reflection.

As the example, Figure 2.5b shows a very large surface with splays, 0.3 m (1ft) of the centers. Sound at a frequency of 100 Hz has a wavelength of 3.4 m (11ft),

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which is large compared with dimensions of the splays. Therefore, the sound waves are reflected from the wall as through it were smooth. This is because the dimensions of the surface irregularities are very small compared with the wavelength. In contrast, sound at a frequency of 1000 Hz, which has a wavelength of 0.34 (1.1 ft) does not obey this law; the sound waves are reflected in all directions, as illustrated in Figure 2.5c. At a frequency of 10 000Hz, sound has a wavelength of 0.034 (0.11ft); the splays are large compared with the wavelength, so the law of reflection holds for reflection from the splays, as illustrated in Figure 2.5d; not the difference in the pattern of reflection from the pattern of reflection for the 100 Hz sound waves shown in Figure 2.5b.
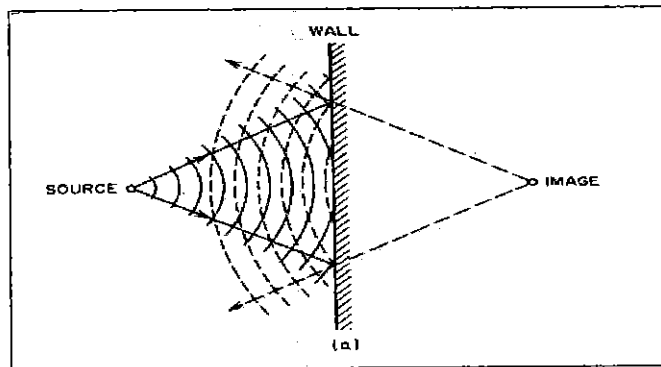

Figure 2.5: (a) Reflection of sound waves from a surface that is very large compare with the wavelength of the incident sound (Harris, 1991).
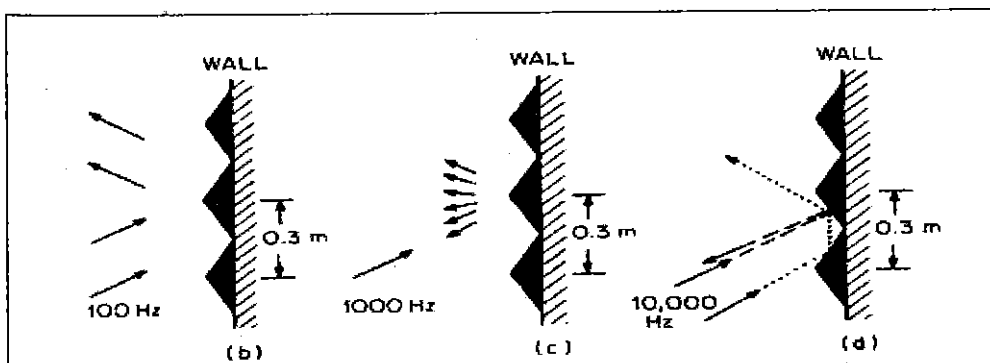

Figure 2.5: (b) Reflection of sound having a frequency of 100Hz (wavelength 3.4 m) from a plane surface having splays which are small compared with the wavelength; in this case, the source is reflected in a manner similar to (a). (c) Reflection of sound having a wavelength similar in size to that of the splays. (d) Reflection of sound whose wavelength is very small compared with the size of the splays; in this case, the law of reflection is valid to reflections from the splays (Harris, 1991). ·

2.10   Sound absorbing materials

Sound-absorbing materials absorb most of the sound energy striking them and reflect very little. Therefore, sound-absorbing materials have been found to be very useful in the control of noise. They are used in a variety of locations: close to sources of noise (e.g., close to sources in electric motors), in various paths, (e.g., above barriers), and sometimes close to a receiver (e.g., inside earmuffs). Although all materials do absorb some incident sound, the term acoustical material has been primarily applied to those materials that have been produced for the specific purpose of providing high values of sound absorption. The major uses of acoustical materials are almost invariably found to include the reduction of reverberant sound pressure levels and, consequently, the reduction of reverberation time in enclosures (rooms) (Crocker, 2007)

2.11   Sound Absorption Coefficient (α)

The fraction of the acoustic energy absorbed when strike a surface is called its sound absorption coefficient. The absorption coefficient of a material depends on the material and on the frequency of the sound which strikes the surface of the material. A coefficient of 0.00 indicates reflection (i.e., 0 percent absorption); a coefficient of 1.0 indicates perfect (100 percent) absorption (Harris, 1991). Therefore, absorption coefficients range between 0 and 1. However, absorption coefficients vary with frequency (Rossing, 2007).

When sound waves strike a boundary separating two media, some of the incident energy is reflected from the surface and the remaining energy is transmitted into the second medium. Some of this energy is eventually converted by various processes into heat energy and is said to have been absorbed by that medium. The fraction of the incident energy absorbed is termed the absorption coefficient α (f), which is a function of frequency and defined as