

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

SYNTHESIS OF POMACE COMPOSITE RESIN

M.Sc. THESIS

Duygu ERTÜRK

Department of Polymer Science and Technology

Polymer Science and Technology Programme

JANUARY 2015

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

PİRİNA KOMPOZİT REÇİNE SENTEZİ

YÜKSEK LİSANS TEZİ

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OCAK 2015

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Date of Submission : 15 December 2014

Date of Defense : 21 January 2015

To my mother,

FOREWORD

I would firstly like to express my deep appreciation and thanks for my supervisor Prof. Dr. Nilgün KIZILCAN for her support, humanity, encouragement throughout the whole study and for providing me a peaceful environment to work at Istanbul Technical University.

Secondly, I know it is not enough to express my gratitude to her, but I am grateful to my mother Sevgi ERTÜRK for her endless support, sacrifice, love and patience for my whole life.

I am also thankful to my colleagues Esin ATEŞ GÜVEL, Nilay TANRIVER, Görkem ÜLKÜ, Burcu ALKAN, Derya ÖNEN and Sezin TARIMSAL for their invaluable support, friendship and helps.

Finally, I would like to thank my old but gold friends for all their emotional assists and motivation not just during this difficult accomplishment, for all the good and bad days in my life for years.

This work is supported by ITU Institute of Science and Technology.

January 2015

Duygu ERTÜRK
Chemical Engineer

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ABBREVIATIONS

MF	: Melamine-Formaldehyde Resin
UF	: Urea-Formaldehyde Resin
MUF	: Melamine-Urea-Formaldehyde Resin
DCM	: Dichloromethane
DMF	: Dimethylformamide
THF	: Tetrahydrofuran
N, N DMAA	: N, N Dimethylacetamide
FT-IR	: Fourier Transform Infrared Spectroscopy
F	: Formaldehyde
P	: Olive Pomace
M	: Melamine
U	: Urea

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SYNTHESIS OF POMACE COMPOSITE RESIN

SUMMARY

In this study melamine-formaldehyde, urea-formaldehyde and melamine-urea-formaldehyde resins which are thermoset amino resins are modified with olive pomace which is a natural product. Olive pomace, which is taken from Edremit region of Balıkesir/Turkey, which has been a waste of olive industry and has been used as fuel or fertilizer by local farmers. The aim of this study is to utilize olive pomace in industry by modifying the amino resins which are synthesized at basic environment with olive pomace. Therefore, resin will be more lightweight, cheaper and will have a wood-like appearance. This study consists of two parts. First part is the synthesis of melamine-formaldehyde and urea-formaldehyde resins which are classified as thermosetting amino resins and their pomace composites. The desired Formaldehyde/Melamine and Formaldehyde/Urea molar ratios are 2 and the synthesis reactions takes place at basic environment. To make a wood-like resin-pomace composite, resins are in situ modified with olive pomace while they are synthesized. The weight of pomace is determined as 10%, 20% and 50% of the weight of melamine and urea in melamine-formaldehyde and urea-formaldehyde resins respectively. In the second part a combination of melamine and urea is used. Melamine-urea-formaldehyde resin is synthesized with a pomace amount of 20% of the total weight of melamine and urea. Resins are characterized using Fourier Transform Infrared Spectroscopy. Water absorption percentage, solubility in water and solubility of in organic solvents are determined. They are resistant to solvents, they either insoluble or slightly soluble. They have wood-like appearance as intended. Moreover, they have different characteristics based upon olive pomace ratio. In low olive pomace weight ratios colour of the composites are light and it gets darker as olive pomace ratio increases. Also, in low olive pomace weight ratios composites are hard and rigid while in higher olive pomace ratios they become softer and sticky. They all have homogeneous appearance which makes them suitable for direct use in many applications.

PİRİNA KOMPOZİT REÇİNE SENTEZİ

ÖZET

Bu tezde; termoset reçinelerin aminoplast reçine grubundan olan melamin formaldehit, üre formaldehit ve melemin-üre-formaldehit reçinelerinin doğal bir ürün olan zeytin küspesi pirina ile modifikasyonu çalışılmıştır.

Pirina, zeytinyağı üretimi sırasında zeytinin kırılıp parçalanması sonucu elde edilir. Yağdan tamamen ya da büyük ölçüde ayrılmış olan pirina, zeytinin çekirdek parçaları, kabuğu ve posasından oluşur. Zeytin ağacı kendine has bir toprak çeşidi ve arazi yapısı isteyen bir ağaç cinsidir. Akdeniz ülkeleri, iklim ve coğrafik yapıları sayesinde zeytinin en çok miktarda ve en iyi kalitede üretilebildiği yerlerdir. Türkiye’de zeytin ağacının yetişmesi için uygun iklime ve toprak yapısına Marmara ve Ege bölgelerinde rastlanır. Bursa, İzmir, Manisa, Çanakkale, Balıkesir gibi birçok ilde zeytin yetiştiriciliği yapılmaktadır., Bu çalışmada kullanılan pirina da Balıkesir’in Edremit Körfezi bölgesinden alınmıştır. Zeytin yetiştiriciliğinin yapıldığı bölgelerde pirina atık kabul edilmekte ve ısınma amacıyla yakıt olarak ya da gübre olarak kullanılmaktadır. Bu çalışmada pirinanın endüstriyel anlamda işlevsellik kazandırılması hedeflenmiştir.

Kuru pirinanın, lignin, selüloz, fenoller içeren yapısının amino reçineler ile uyumlu olabileceği düşünülmüştür. Bu çalışmada kullanılan pirina yağdan tamamen ayrılmış kuru toz ve iri tanecikli yapıdadır.

Bu çalışma iki bölümden oluşmaktadır. Birinci bölüm, termoset amino reçineler olarak sınıflandırılan melamin-formaldehit ve üre-formaldehit reçineleri ve bunların pirina kompozit reçinelerinin sentezidir. Formaldehit/Melamin ve Formaldehit/Üre oranları 2 alınarak reaksiyonlar bazik ortamda gerçekleştirilmiştir. Ahşap görümlü pirina kompozit reçinesi oluşturmak için reçinelerin üretim ortamına, pirina baştan ilave edilmiştir. Pirina ağırlığı melamin ve ürenin sırasıyla melamin-formaldehit ve üre-formaldehit içindeki ağırlıklarının %10, %20 ve %50si olarak belirlenmiştir. Deneyler çeker ocak altında, sıcak su banyosu içinde 3 boyunlu balon ve mekamin karıştırıcı kullanılarak bazik ortamda yapılmıştır.

İkinci bölümde, melamin ve üre kombinasyonu birlikte kullanılmıştır. Melamin-üre-formaldehit kompozit reçinesinin üretiminde, melamin ve ürenin toplam ağırlığının %20si kadar pirina ilave edilmiştir.

Sentezlenen sıvı haldeki reçineler ve kompozit reçineler önce önce atmosfer basıncındaki etüvde 70°C’de 2 saat, sonrasında vakum etüvünde 70°C’de 2 saat bekletilerek katı hale getirilmiştir.

Elde edilen reçineler ve kompozit reçineler Fourier Transform Infrared

Spektroskopisi kullanılarak karakterize edilmiştir. Reçinelerin ve kompozit reçinelerin su absorpsiyon özellikleri, suda çözünürlükleri ve çeşitli organik çözücülerdeki çözünürlükleri tespit edilmiştir.

Fourier Transform Infrared Spektroskopisi sonucunda kompozitlerin başarılı şekilde sentezlendiği tespit edilmiştir.

Reçineler ve kompozit reçinelerden küçük parçalar alınarak 24 saat oda sıcaklığındaki suda bekletilip kurutulmuş ve her aşamada yapılan tartımlarla su absorpsiyonu yüzdesi ve sudaki çözünürlük değerlerine ulaşılmıştır.

Reçineler ve kompozit reçinelerin oda sıcaklığında çeşitli organik çözücülerdeki çözünürlükleri gözlenmiştir. Çözücülere karşı dayanıklı oldukları, ya çözünmüyor ya da çok az oranda çözüldükleri tespit edilmiştir.

Fiziksel özelliklerine gelindiğinde, hedeflenen ahşap görünümlü kompozitlere ulaşılmıştır. İçlerine eklenen pirina miktarına bağlı olarak her kompozit farklı özelliklere sahiptir. Düşük pirina oranlarında açık kahve renkli ve sert kompozitler üretilirken, yüksek pirina oranlarında daha koyu renkli ve daha yumuşak ya da yapışkan kompozitler elde edilmiştir.

%10 pirina içeren melamin-formaldehit kompozit reçinesi açık kahve renkli, katı ve sert bir yapıya ve parlak, homojen bir görünüme sahiptir.

%20 pirina içeren melamin-formaldehit kompozit reçinesi daha koyu kahve renkli, katı ama %10luk melamin-formaldehit kompozit reçinesine göre daha kırılğan bir yapıya sahiptir. Görüntüsü homojen ve daha parlaktır.

%50 pirina içeren melamin-formaldehit kompozit reçinesi %20lik melamin-formaldehit kompozit reçinesinden daha koyu renkli, daha parlak ve daha kırılğandır. Homojen görüntüsünü ve katılığını korumaktadır.

%10 pirina içeren üre-formaldehit kompozit reçinesi, %10 pirina içeren melamin-formaldehit reçinesinden daha açık renkli ve daha mat bir görünüme sahiptir ancak pürüzsüz bir yüzey oluşturmuştur.

%20 pirina içeren üre-formaldehit kompozit reçinesi %10luktan daha koyu renklidir. Yumuşak, mat ve az da olsa yapışkan bir katı malzeme haline gelmiştir. Dokunuşu rahattır.

%50 pirina içeren üre-formaldehit kompozit reçinesi %20likten daha koyu renkli, daha yapışkan, mat ve dokunması daha rahat katı bir malzeme olmuştur.

%20 pirina içeren melamin-üre-formaldehit kompozit reçinesi oldukça koyu kahve renkli parlak ve macun kıvamında akışkan bir malzemedir. Tutkal olabilecek derecede yapışkandır.

Bu çalışma sonucunda pirininin atık olmaktan çıkıp sanayide değerlendirilebileceği kanıtlanmıştır. Pirininin zeytinyağı işletmelerine çıkardığı en büyük sorun olan kapladığı alandan ve depolama maliyetinden tasarruf edilecektir.

Pirinanın reçine içinde kullanılmasıyla daha hafif, daha ucuz bir reçine elde edilebilmektedir. Ahşap görünümüne sahip bu reçinenin kullanımı sayesinde ahşap ürünlerin kullanımı azaltılarak doğaya verilen zarar azaltılabilir. Ayrıca reçine miktarındaki azalma sayesinde hem üretim hem de kullanım sırasında oluşacak melamin, üre ve formaldehit salınımları azalarak insan sağlığına daha az zararlı ve çevreyi daha az kirleten bir ürün elde edilmiş olmaktadır.

1. INTRODUCTION

As a result of increasing environmental concerns, the demand to green products is highly increased in last decades. Green products are safe and biodegradable products which are generally from natural resources. This biomass can be specially produced to be used as a raw material, but consuming the natural waste of another industry is more convenient. Especially food, drink and oil industries generate natural waste, which is can be evaluated in many different manufacturing processes. Olive pomace is such a natural waste which originates from olive oil industry. Olive oil is produced by milling the olive drupes to extract the oil. After the oil is extracted olive peels and broken seeds stay as the waste. These are called olive pomace and it is known that olive pomace is burnt for heating in winter by farmers. However, olive pomace can be utilized when it is used in polymer based materials. It is predicted that olive pomace can give a wood-like appearance to polymers considering previous studies [1-5]. This resin-olive pomace composites will also be cheaper and more lightweight than the pure resin which are favourable features in industry. In this study, amino resins are chosen to be the polymeric compound of the composite structure.

2. THEORETICAL PART

2.1 Polymer Definition and Classification

Polymers are macromolecules which are constructed by the combining large numbers of much smaller molecules. These small molecules are called monomers which link with each other to form polymer molecules and these combining reactions are termed polymerizations. There may be hundreds, thousands, tens of thousands, or more monomer molecules bonded together in a polymer molecule. Polymers are materials whose molecular weights may reach into the hundreds of thousands or millions [6].

Thousands of polymers have been found in nature, artificially produced and more are likely to be synthesized in the future. Fortunately, all polymers can be assigned to one two groups based upon type of polymerization mechanism or their processing characteristics. Such groupings are beneficial to discuss the properties of polymers [7].

2.1.1 Classification based upon type of polymerization mechanism

1929 W. H. Carothers suggested a classification of polymers into two groups, condensation and addition polymer referring to the type of products. On the other hand Carother's original distinction between addition and condensation polymers was amended in 1953 by Flory, who emphasised the mechanisms by which the two types of polymer are formed. He distinguished the polymerization systems as chain-growth and step-growth polymerization [8].

2.1.1.1 Chain-growth polymerization

Chain-growth polymerization means the addition of monomers to a growing chain, which is initiated by some reactive groups. Such addition reactions may involve either multiple bonds or rings. The initiator reactive groups must be capable of opening one of the bonds in the monomer. They may be either a radical, an electrophile, a nucleophile, or an organometallic species. Furthermore, these

polymerizations may occur in many possible mechanisms, depending on the electronic nature of the chain-carrying groups, which are free radical, cationic and anionic groups. [9].

2.1.1.2 Step-growth polymerization

In a step-growth polymer the repeating unit lacks certain atoms which were present in the monomer(s) which will construct the polymer or to which it can be degraded by chemical means. These types of polymers are formed from bi- or poly-functional monomers by a certain reaction mechanism where some smaller molecules eliminate [10].

In this type of polymerization, the molecular weight of the polymer chain increases slowly and polymerization takes place with only one reaction mechanism. It does not have distinct initiation, propagation, and termination steps of chain-growth polymerization. To build up a linear high molecular weight polymer, at least a di-functional monomer or equal molar amounts of two different di-functional monomers are necessary. The polymerization reaction proceeds by one by one reactions of the functional groups of monomers. Two monomers react to form a dimer which then either reacts with another dimer to produce a tetramer or reacts with more monomer to form a trimer. It takes a relatively long time until each reaction of the functional groups reaches essentially at the same reaction rate and a high molecular weight polymer is obtained [11].

Any two molecular species present can react which means random growth takes place. Molecular weight increases steadily throughout the reaction. For high molecular weight polymer long reaction time is needed.. Monomers disappear in the early stages of the polymerization. At an average degree of polymerization of 10, less than 1 weight percent of the monomer remains. A relatively broad, calculable distribution of molecular species are seen throughout the polymerization [11].

Many commonly used plastics like polyurethane, polyamine, polyester, some natural polymers like proteins and sugars and some types of resins like melamine-formaldehyde, urea-formaldehyde are step-growth polymer examples [12].

2.1.2 Classification based upon processing characteristics

There are two types of polymes based upon proessing characteristics. They are

thermoplastics and thermosets.

2.1.2.1 Thermoplastics

Generally thermoplastic polymers are linear polymers. Along the polymer backbone the bonding which occurs is covalent and the bonding between the polymer molecules is via secondary forces like ionic bonding, hydrogen bonding, dipole interaction and Van der Waals forces.. With the increasing in temperature, the bonding energy of secondary forces decreases and thermal energy of the linear polymer molecule increases. The individual polymer molecules slide past one another with a stress appliance and this effect is called melt flow. When cooled, the thermal energy of individual molecules decreases, the secondary forces increases and secondary bonds are restored. As long as the polymer temperature stays below degradation temperature, the response is reversible [13, 14]. Polymer can be reshaped and recycled. Some of common thermoplastic polymers are polyethylene, polypropylene, polyvinyl chloride, and polystyrene.

2.1.2.2 Thermosets

Thermoset polymers are synthesized by chemical reactions of one or more pre-polymers under heat or in the presence of a catalyst or a curing agent. The polymerization reaction, which is called cross-linking or curing, transforms the pre-polymers to a thermoset polymer with a network structure instead of linear construction like thermoplastics. By simultaneous polymerization and cross-linking, hard thermosets; by vulcanization with sulfur, peroxide or silane, elastomers; by radiation cross-linking, elastomers or elastic thermosets are obtained. The uncured polymer can be in solid, liquid or pasty state and the processing techniques vary upon their state. Solid ones can be moulded by compression, transfer, injection methods, while liquid or pasty ones can be moulded by casting, liquid injection moulding, reaction injection moulding, rotational moulding or foaming [15, 16].

There are a few limitations of using thermoset polymers. First, depending on the curing system and temperature used, the curing reaction may take several minutes to several hours to end up. This makes the processing time for thermoset polymers significantly longer than that for thermoplastic polymers. Another limitation is that thermoset polymers cannot be re-melted or returned to liquid state, and therefore cannot be directly reused or recycled. However, in the cured state, thermoset

polymers have higher heat and chemical resistance than most thermoplastic polymers, and they do not show as much creep deformation [16].

Some classes of thermoset polymers are elastomers like synthetic rubbers (styrene-butadiene rubber, silicone rubber, polychloroprene etc), polyurethanes, polyimides and thermosetting resins.

2.2 Thermosetting Resins

Thermosetting resins have a network structure which may be established by heating or via a chemical reaction. Thermosetting resins are a popular choice in industry. Some of common thermosetting resins are phenol formaldehyde resins (trade name Bakelite, Plenco, Durite), epoxy resins (Araldite, Epon, Epikote), polyester resins (Laminac, Aropol, Baygal), polyurethanes (Lycra, Elastan) and amino resins (Avisco, Plaskon) [17].

2.2.1 Amino resins

Amino resins are thermosetting polymers which are commonly used in coatings, laminates, moulding compounds and wood-based products, which are wood-based panels, such as particleboards, fiber boards and plywood and furniture. The three major commercially used amino resins are urea-formaldehyde (UF), melamine-formaldehyde (MF) and melamine-urea-formaldehyde (MUF) [18, 19]

While the condensation of urea and formaldehyde had been described in 1884, urea-formaldehyde (UF) resins were not patented until 1918 and condensation of formaldehyde and melamine (2, 4, 6-triamino-1, 3, 5-triazine) were not patented until 1939 [20, 21]. Today, they are commonly known resin types. A recent report emphasizes that Asia-Pacific leads the consumption of amino resins (China is the biggest consumer in the global market), followed by Europe (mainly Western Europe) and North America. The demand for amino resins has increased since 2011 and will possibly remain at moderate rates for the next decade. The total interest for amino resins, especially for wood products, depends on the degree of construction activity and comprehensive situation of regional economies [18, 22].

2.1.1.1 Melamine-formaldehyde resin

Synthesis

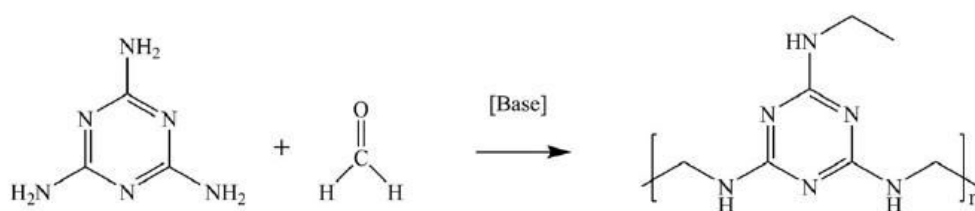


Figure 2.1 : Melamine-Formaldehyde Resin [23].

Melamine-formaldehyde (MF) is one of the hardest and stiffest polymeric materials [24]. The regular melamine-formaldehyde resin (MF) synthesis procedure starts with the methylation of melamine which can be catalyzed by base or acid where melamine react with formaldehyde to give methylol groups. Subsequently, these methylol groups condense upon further heating and/or acidifying the system, to form ethylene ether and methylene bridges [25-29]

The curing behaviour of a melamine-formaldehyde resin and its degree of crosslinking determine the product properties. If the resin is not sufficiently cured, MF glued particleboards will have lesser degree mechanical strength and surface finishes based on MF-impregnated papers will lack hardness, durability, gloss, and resistance towards hydrolysis and chemical agents [30-32].

Advantages and Disadvantages

Melamine-formaldehyde resin is advantageous as an important thermosetting resin material with distinguished transparency and the resistance to heat, abrasion, weathering acid and alkali [33].

On the other hand, melamine-formaldehyde belongs to the triazine family which is known for being used largely as nitrogen fertilizers and for their accumulation and persistence in the environment. Triazine residues have been detected in many soils and sediments. Melamine-formaldehyde is emitted to the environment from many industrial plants. Melamine-formaldehyde releases both melamine and formaldehyde which are hazardous to human health [34-41]

Industrial use

Favoured for its toughness, chemical resistance, and relative ease of manufacture, MF is incorporated into a wide variety of products that are still in use today. Familiar products include Formica and melamine dinnerware. Commercial applications have included fabric impregnation, adhesives, paints, electrical mouldings, glass-reinforced substrates and engineered wood products. These condensed amino-plastic products are generally stable [34, 42].

Alkyd-amino resins are used as matrix resins in the lacquer and paint industry. The short oil alkyd resins containing nearly 35–45% phthalic anhydride which contains a higher proportion of hydroxyl groups that provide compatibility and reactive sites with alkylated urea formaldehyde and melamine formaldehyde resins. This combination is widely used in industrial baking enamels for metal cabinets, appliances, window blinds and toys [43, 44].

Also, MF foams are important for their fire or flame resistance. Compared to other organic insulation materials (polyurethane, phenol-formaldehyde and polystyrene foams) the melamine-formaldehyde foams have higher nitrogen content, which provides the foams to be extremely flame-resistant. According to the EU fire classification standard for buildings (DIN 4102-1), melamine-formaldehyde foams can be rated as a construction material of “low flammability”, (i.e. Class B1) [45, 46].

The major melamine consumers are the wood-based panel and laminate manufacturers that provide high-quality surface-coated interior and exterior materials to the furniture and construction industries. Typically, particleboards are manufactured by gluing comminuted lignocellulosic material with 20–25% (w/w) of a melamine-formaldehyde resin in a hot press. Practically all of these boards are subsequently coated with sheets of decorative paper that are impregnated with melamine-formaldehyde resins to obtain wood-like or custom design surfaces [30, 47- 49].

2.2.1.2 Urea-Formaldehyde Resins

Synthesis

Urea-formaldehyde resin is synthesized as follows: in a three necked round bottom flask urea is mixed with formaldehyde. The pH of the solution is maintained

basic the mixture is stirred at 80-90°C. Resulting product dried in a vacuum oven under reduced pressure [51, 52].

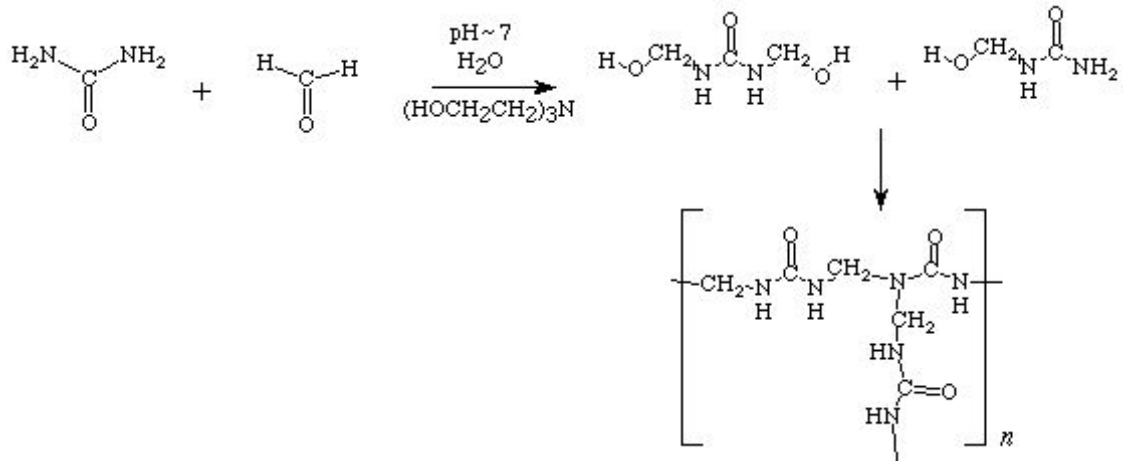


Figure 2.2 : Urea-Formaldehyde Resin [50].

It is known that low formaldehyde/urea (F/U) ratio leads to low emissions of free formaldehyde. However, lowering the ratio of F/U to a determined limit decreases not both the reactivity of UF resin and impaired the physical and mechanical properties [53].

Advantages and Disadvantages

Despite being advantageous in terms of fast curing, good performance in the panel, water solubility and lower price, UF resin adhesives also have a critical disadvantage, formaldehyde emission from the panels. Its lower resistance to water also limits the use of wood-based panels bonded with UF resin adhesives to interior applications. Moreover, the formaldehyde emission from the panels used for interior applications is known as one of the main factors, causing sick building syndrome in an indoor environment. Therefore, the formaldehyde emission issue has been one of the most important aspects of UF resin research. Free formaldehyde in UF resin and the hydrolysis of UF resin under acidic and moisture conditions are known to be the cause of the formaldehyde emission from wood-based panels. For example, the amount of free formaldehyde present in UF resin proportionately contributed to the emitted formaldehyde from particle board even after hot-pressing at high temperature. However, it was reported that hydrolysis of cured UF resin was a major factor affecting long-term formaldehyde emission of UF resin-bonded wood panels [54-65].

Industrial Use

Urea-formaldehyde resin is mainly used in the manufacture of medium density fibreboard (MDF) [66]. UF resin is a major commercial adhesive, chiefly used in the forest product industry. Approximately one million metric tons of UF resin are produced annually and more than 70% of them is used by the wood industries as an adhesive for bonding particleboard, medium density fiberboard, hardwood plywood and as a laminating adhesive for bonding [51, 67-69].

2.2.1.3 Melamine-Urea-Formaldehyde Resins

Due to high formaldehyde emission from urea-formaldehyde resin, adding melamine is considered a useful way to improve this environmental problem. Thus, MUF resin is created [18, 70, 71].

The production of MUF resin is lower than that of the UF resin, which is only 8% of the UF annual production in the U.S. and less than 5% in Brazil. The price of MUF resin is cheaper than that of MF resin, but more expensive than that of UF resin [18, 72, 73].

2.3 Composites

Composite materials are multiphase materials achieved through the artificial combination of different materials in order to accomplish properties that the individual components by themselves do not have. They are not built up naturally by reactions of different phases, phase transformations, or other phenomena. Composite materials should be recognized as different from alloys, which can comprise two more components but are formed naturally through processes such as casting. Composite materials can be tailored for different kinds of properties by favourably choosing their components and their proportions. Due to this strong tailorability, composite materials can be designed to accomplish the demands of aerospace, automobile, electronics, construction, energy, biomedical and other industries. As a result, composite materials have become most commercial engineering materials [74].

2.3.1 Nanocomposites

In many cases, the dimensions of one of the phases of a composite material are small, which is between 10nm and a few micrometers and under these conditions that

particular phase has properties rather different from those of the same material in the bulk form. When the microstructural scale falls in the range of nanometers, then the material is called a “nanocomposite” [75].

Nanocomposites are an encouraging new class of materials containing filler. Despite being ordinary composites only with the difference of having one phase in the +nanometer scale they are obtained to be the leading way for the improvement in the mechanical and thermal properties [44, 76, 77].

2.3.2 Green Composites from Natural Resources

Rising in environmental pollution, concerns over petroleum supplies and lack of resources lead scientist to conduct more research in health and environment friendly materials. Green composites are a specialized class of composites with at least one of the components (such as the matrix or the reinforcement) from natural resources. Green composites, biocomposites, and eco-composites all attribute to the same class of materials. Many types of natural and synthetic polymers are convenient for green composites, including polyethylene, polypropylene, polystyrene, polyester, resins, starch, and polylactic acid [78-84].

Green composites can be classified as into three main groups depending on the type of reinforcement and polymer matrix:

1. Totally renewable composites, where both the matrix and reinforcement are from renewable resources
2. Partly renewable composites, where the matrix is retrieved from renewable resources and reinforced with a synthetic material
3. Partly renewable composites, where a synthetic matrix is reinforced with natural biopolymers

Even though the number of green composites has been rising, triggered by increasing criticalness of environmental problems, the processing temperature is still a limiting factor in the choice of a suitable polymer matrix for green composites. Polymer matrices are generally divided into thermosetting, thermoplastic, or biodegradable groups (Bledzki and Gassan 1999; John and Thomas 2008) [78, 85-87].

Natural biomass (agricultural residues, wood, plant fibers, etc.), which mainly include cellulose, hemicelluloses, and lignin, portrays a huge source of renewable

reinforcement for green composites and is recognized one of the most important components of green composites. Natural fiber–reinforced green composites has many advantages like low cost, light weight, eco-friendliness, nonabrasiveness, and biodegradability which place them among the high-performance composites. “Natural fiber” means a wide range of animal and vegetable fibers which often contribute to the structural performance of the plant and, when added to polymer composites, can provide good reinforcement. Natural fibers have been further separated into two categories based on their origins: animal fibers and plant fibers [78, 87, 88- 92].

Animal fibers mainly involve proteins. Typical examples are hair (from sheep, goats, rabbits, alpaca, and horses) and silk. Plant fibers mainly involve cellulose fibrils embedded in a lignin matrix along with minor amounts of additional extraneous components. Their main components are cellulose, hemicellulose, pectin, and lignin. The extraneous components involve low-molecular weight organic compounds (extractives) and inorganic matter. Natural fibers are lighter than traditional inorganic reinforcements inducing possible benefits such as fuel savings when their composites are used in transportation applications. Plant fibers can be subdivided into several classes: straw, seed, bast, leaf, and wood fibers [78, 93-95].

2.3.2.1 Olive Pomace

Among the natural fibers which are generally consist of natural by-products, plant seeds have an important place. Olive pit is a good example for this. Olive pits are obtained during the processing of fresh olives for oil [96]. Olive tree is hard to cultivate and only grows in a constricted region in world due to its needs a special soil and terrain. Mediterranean countries have these specialities and in olive industry have become an important industrial branch in these countries. As one of them, in Turkey olive cultivation is common in Marmara and Aegean regions.

In a classic olive oil manufacturing process the fresh olives in colours pink, green and black as seen in Figure 2.3, are milled to extract the oil [97, 98]. Hence, a mix of olive pit, skin and dry paste is obtained which is called olive cake or olive pomace. Olive pomace has a lignocellulosic structure with its cellulose, lignin, uronic acid, and polyphenol content [99- 101].



Figure 2.3 : Fresh olives

3. EXPERIMENTAL PART

3.1 Materials

Melamine, Urea, Formaldehyde (37% Solution), NaOH Solution (20%), Olive Pomace. All chemicals are used without further purification.

3.2 Synthesis of Melamine-Formaldehyde Resin

The desired F/M molar ratio is 2. Therefore, 18.9 g (0.15 mole) of melamine and 25 ml (0.3 mole) of formaldehyde solution are put into a three-necked round bottom flask. pH is set to 9-10 using 20% NaOH solution and temperature is set to 85-95°C. The mixture is stirred with mechanical stirrer for 2 hours and the white solution is observed. Under fume hood the formaldehyde vaporized instantly leaving solid product. This solid product is taken to a beaker. Later, it is dried in a vacuum oven for 2 hours at 70°C.

3.3 Synthesis of Melamine-Formaldehyde Resin-Pomace Composite

3 different pomace weight ratios as 10%, 20% and 50% of melamine are tested. The desired F/M molar ratio is 2. For 10% and 20% pomace ratios 18.9 g (0.15 mole) of melamine, 25 ml (0.3 mole) of formaldehyde solution and olive pomace are put into a three-necked round bottom flask. For 50% pomace ratio composite, 37.8g (0.3 mole) melamine and 50 ml (0.6 mole) formaldehyde solution is used, since increased viscosity and decreased volume of composite is observed with the increased pomace ratio of the composites. pH is set to 9-10 using 20% NaOH solution and temperature is set to 85-95°C. The mixture is stirred with mechanical stirrer for 2 hours and the brown composite resin is observed. It is taken to a beaker. Later, it is dried for 2 hours at 70°C and put under vacuum for more 2 hours again at 70°C.

3.4 Synthesis of Urea-Formaldehyde Resin

The desired F/U molar ratio is 2. Therefore, 9 g (0.15 mole) of urea and 25 ml (0.3 mole) of formaldehyde solution are put into a three-necked round bottom flask. pH is set to 9-10 using 20% NaOH solution and temperature is set to 85-95°C. The mixture is stirred with mechanical stirrer for 2 hours and the white solution is observed. It is taken to a beaker. Later, it is dried at 70°C for 2 hours and then put under vacuum for more 2 hours at 70°C.

3.5 Synthesis of Urea-Formaldehyde Resin-Pomace Composite

3 different pomace weight ratios as 10%, 20% and 50% of urea are tested. The desired F/U molar ratio is 2. For 10% and 20% pomace ratios 9g (0.15 mole) of urea, 25 ml (0.3 mole) of formaldehyde solution and olive pomace are put into a three-necked round bottom flask. For 50% pomace ratio composite, 18g (0.3 mole) melamine and 50 ml (0.6 mole) formaldehyde solution is used, since increased viscosity and decreased volume of composite is observed with the increased pomace ratio of the composites. pH is set to 9-10 using 20% NaOH solution and temperature is set to 85-95°C. The mixture is stirred with mechanical stirrer for 2 hours and the brown sample is observed. It is taken to a beaker. Later, it is dried for 2 hours at 70°C and put under vacuum for more 2 hours again at 70°C.

3.6 Synthesis of Melamine-Urea-Formaldehyde Resin-Pomace Composite

50 ml (0.6 mole) of formaldehyde is put into the three-necked round bottom flask. Then 9 g (0.15 mole) urea, 18.9 g (0.15 mole) melamine are added. The desired olive pomace ratio is 20% of the total weight of both urea and melamine and it is calculated to be 5.58g. After adding 5.58g of olive pomace, pH is set to 9-10 using 20% NaOH solution and temperature is set to 85-95°C. The mixture is stirred with mechanical stirrer for 2 hours and the brown composite is observed. It is taken to a beaker. Later, it is dried for 2 hours at 70°C and put under vacuum for more 2 hours again at 70°C.

The reactor system and synthesized liquid melamine-urea-formaldehyde resin are seen in Figure 3.1.



Figure 3.1 : Reactor system and liquid resin

3.7 Characterization of Resins

Samples characterization is carried out with a Fourier Transform Infrared (FT-IR) spectroscopy.

The behaviour of the resins and composites in water is determined. Resin pieces are soaked into water in test tubes. After 24 hours pieces are removed from water and they are weighed and then they are dried in oven and weighed again to observe their water absorption capacity and water solubility.

To specify the solubility of samples in varying solvents. The solvents used are acetone, ethanol, dichloromethane, chloroform, methanol, dimethylformamide, tetrahydrofuran, toluene and N, N dimethylacetamide.

4. RESULTS AND DISCUSSION

4.1 FT-IR Analysis

As seen in Figure 4.1, FT-IR analysis olive pomace has phenolic and cellulosic hydroxyl groups at 3280 cm^{-1} , a little amount of aliphatic CH at $2925\text{--}2850\text{ cm}^{-1}$, a great amount of aromatic groups at 1640 , and carbonyl at 1740 . UF resin alone has methylol group at 3300 cm^{-1} , aliphatic CH and CH_2 at 2958 cm^{-1} , carbonyl groups of urea at $1677\text{--}1650\text{ cm}^{-1}$ and C-O at 1100 cm^{-1} which are in agreement with literature[102]. It can be interpreted that phenolic OH groups in olive pomace are bonding to formaldehyde in resin structure which is approved by the homogeneous appearance of the composites.

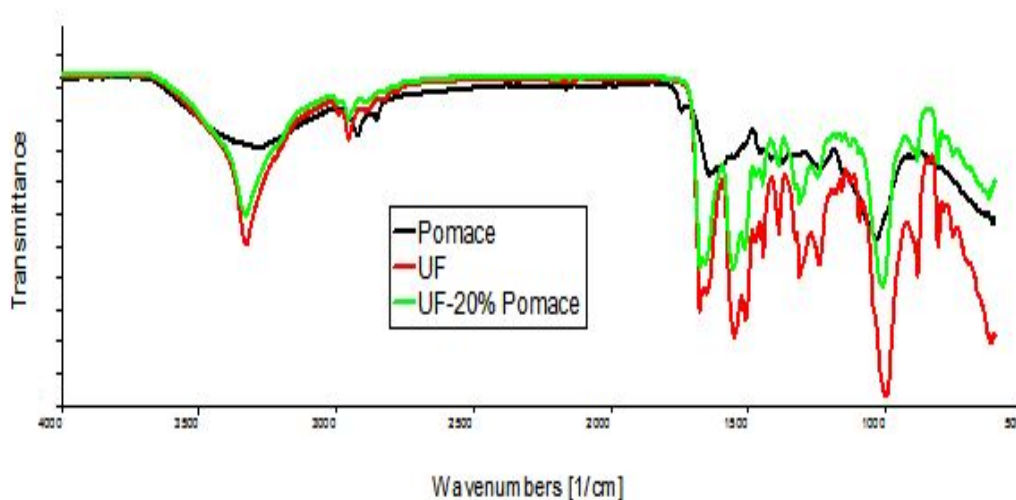


Figure 4.1 : FT-IR Analysis of Pomace, UF and UF-20% Pomace Composite

In FT-IR analysis of melamine composites as seen in Figure 4.2, no methylol peak is seen. This is because melamine has 6 active hydrogens and formaldehyde to melamine molar ratio is 2. Therefore formaldehyde melamine resin has no methylol groups but it is crosslinked with methylene bridges. However, melamine formaldehyde resin has peaks at 1585 and 1484 cm^{-1} which are attributed to C=N in

aromatic structure; 1300-1000 cm^{-1} which are attributed to C-N stretching and at 800-700 cm^{-1} which are attributed to N-H bonds. The characteristic peaks of melamine-formaldehyde are in agreement with literature [103]. On the other hand melamine formaldehyde-10% and 20% pomace composites have methylol groups at 1372 cm^{-1} . With increasing pomace ratio the hydroxyl peak increases. MF aromatic peak at 1580 cm^{-1} disappears at pomace composites and 1480 and 1580 cm^{-1} peaks merge to give a peak at 1505 cm^{-1} . Likely, double peaks at 1585 and 1493 cm^{-1} in MF merge and give the peak at 1510 cm^{-1} in pomace composites. With increasing pomace ratio aromatic proton peaks at 985 and 810 cm^{-1} increase.

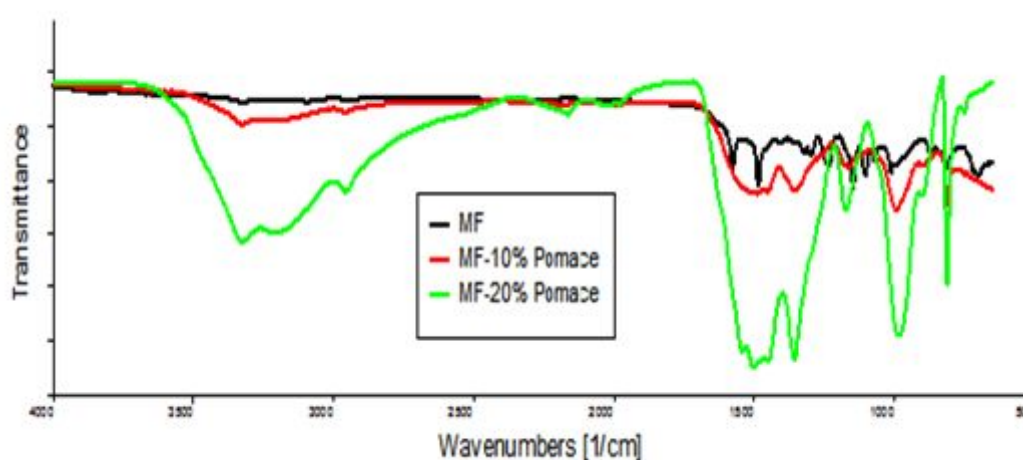


Figure 4.2 : FT-IR Analysis of MF, MF-10% Pomace Composite and MF-20% Pomace Composite

As seen in Figure 4.3, MUF resin composite has some differences from UF resin composite. Carbonyl peak at 1653 cm^{-1} is a result of urea in the resin because there is no carbonyl in melamine. The peak density at 1500 cm^{-1} is higher compared to UF composite with the NH group from melamine. While pomace does not have aliphatic peak at 1170 cm^{-1} , it appears in UF and MUF composites.

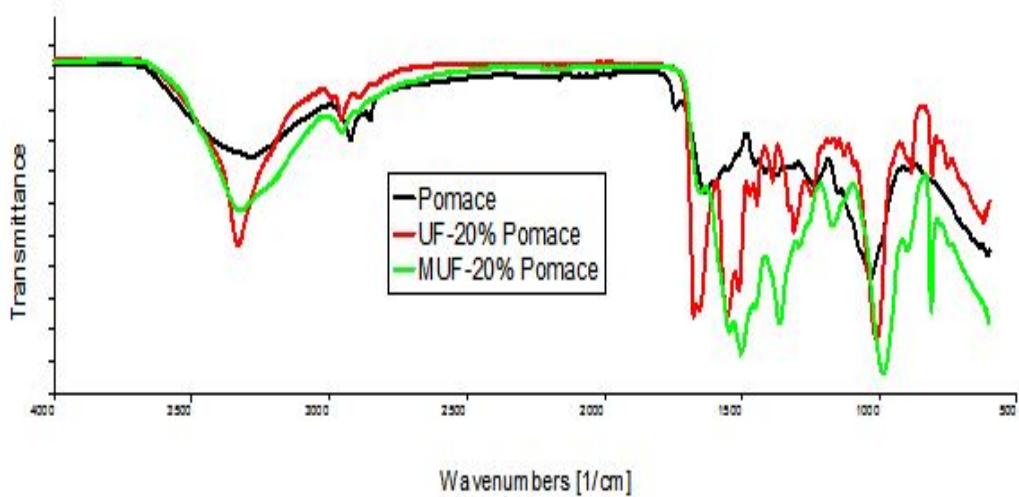


Figure 4.3 : FT-IR Analysis of Pomace, UF-20% Pomace Composite and MUF-20% Pomace Composite

4.2 Physical Appearances of Materials

Olive pomace has an appearance like soil. It is brown and a mix of dust and coarse-grained particles as seen in Figure 4.4.



Figure 4.4 : Olive Pomace.

Melamine-formaldehyde resin is a white, non-sticky hard solid as seen in Figure 4.5.



Figure 4.5 : Melamine-Formaldehyde resin

Melamine-formaldehyde resin-10% pomace composite is rigid, slightly less hard than the blank resin, homogeneous light brown and glossy as seen in the Figure 4.6.



Figure 4.6 : MF Resin-10% Olive Pomace Composite

Melamine-formaldehyde resin-20% pomace composite which is seen in Figure 4.7 has a homogeneous brown colour. It is glossy, and more fragile than 10%.



Figure 4.7 : MF Resin-20% Olive Pomace Composite

Melamine-formaldehyde resin-50% pomace composite which is seen in Figure 4.8 has homogeneous dark brown colour. It is glossy and more fragile than 20%.



Figure 4.8 : MF Resin-50% Olive Pomace Composite

Urea-formaldehyde resin seen in Figure 4.9 is a white solid, less hard than melamine formaldehyde resin.

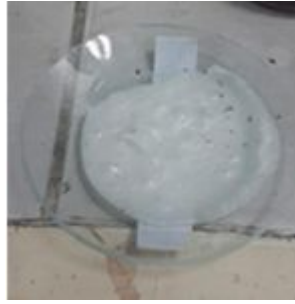


Figure 4.9 : Urea-Formaldehyde Resin

Urea-formaldehyde resin-10% pomace composite seen in Figure 4.10 has homogeneous milk-coffee colour. It is less hard than blank resin and has good haptic properties.



Figure 4.10 : UF Resin-10% Olive Pomace Composite

Urea-formaldehyde resin-20% pomace composite seen in Figure 4.11 has homogeneous brown colour, not glossy, softer than 10%, has good haptic properties and is a little sticky.

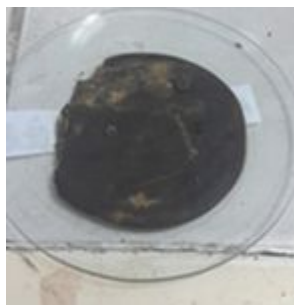


Figure 4.11 : UF Resin-20% Olive Pomace Composite

Urea-formaldehyde-50% pomace composite seen in Figure 4.12 has homogeneous dark brown colour. It is not glossy and softer than 20%. However it has good haptic properties and it is a little more sticky than 20%



Figure 4.12 : UF Resin- 50% Olive Pomace Composite

Melamine-urea-formaldehyde resin-20% pomace composite seen in Figure 4.13 has homogeneous dark brown colour. It is glossy, soft and highly sticky.



Figure 4.13 : MUF Resin-20% Olive Pomace Composite

4.3 Solubility in Solvents

The solvent resistance of the resins and composite resins are tested with 9 different solvents. The results can be seen in Table 4.1. Acetone, ethanol, dichloromethane (DCM), chloroform, methanol, dimethylformamide (DMF), tetrahydrofuran (THF), toluene, N, N, dimethylacetamide (N, N DMAA) are the chosen solvents due to their common use in industry and ease to reach. Composites are generally resistant to solvents with the exception of DMF and N, N dimethylacetamide. The composites with urea based matrices are slightly soluble in DMF and the samples with melamine based matrices are slightly soluble in N, N DMAA.

Table 4.1 : Solubility in Solvents

	Acetone	Ethanol	DCM	Chloroform	Methanol	DMF	THF	Toluene	N,N DMAA
MF	i	i	i	i	i	i	i	i	i
MF-10% Pomace	i	i	i	i	i	i	i	i	i
MF-20% Pomace	i	i	i	i	i	i	i	i	ss
MF-50% Pomace	i	i	i	i	i	i	i	i	ss
UF	i	i	i	i	i	ss	i	i	i
UF-10% Pomace	i	i	i	i	i	ss	i	i	i
UF- 20% Pomace	i	i	i	i	i	ss	i	i	i
UF-50% Pomace	i	i	i	i	i	ss	i	i	i
MUF	i	i	i	i	i	ss	i	i	ss

i=insoluble ss=slightly soluble s=soluble

4.4 Water Absorption and Solubility in Water

Composites are immersed in water in order to observe their water absorption capacity and solubility in water. The dry resins and composites weighed (m_1) and they soaked in water for 24 hours. Then they are removed from water and weight (m_2) of the resins and composites are recorded. After that, they are put in oven for anew drying. Finally, the weight of the resins and composites are measured again (m_3). It is observed that water absorption capacity of the resin-olive pomace composites increases with the increasing in resin content as seen in Figure 4.14 and Figure 4.15, as a result of lignocellulosic structure of olive pomace, which is in agreement with literature [3, 4, 104]. To calculate water absorption % (absorbed water in gram/dry sample in gram)*100 and water solubility (dissolved sample in gram/dry sample in gram) ratio of the samples, the following equations 4.1 and 4.2 are used which are derived from the calculation method in literature [105-107].

$$W_{\text{sorption}\%} = (m_2 - m_3) / m_3 * 100 \quad 4.1$$

$$W_{\text{solubility}} = (m_1 - m_3) / V_{\text{water}} \quad 4.2$$

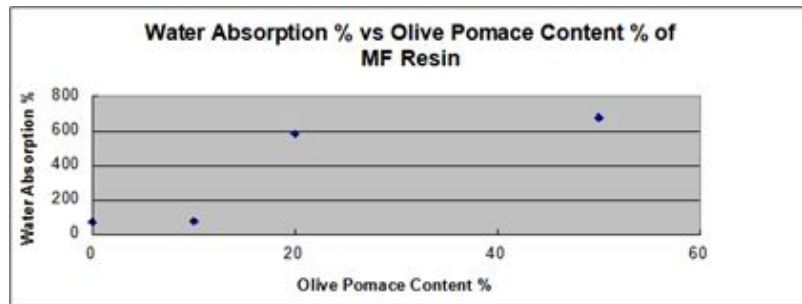


Figure 4.14 : Water Absorption % vs Olive Pomace Content weight % of MF Resin

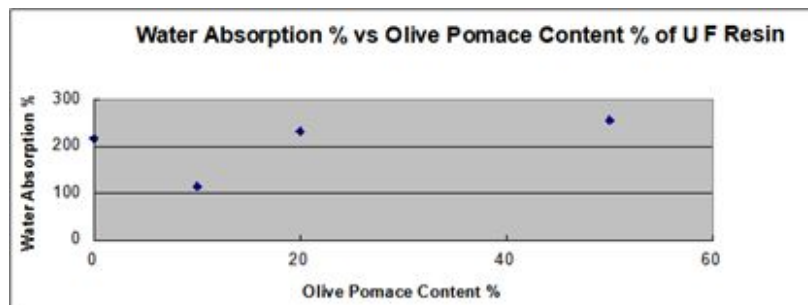


Figure 4.15 : Water Absorption % vs Olive Pomace Content weight % of U F Resin

Water absorption ratios of composites are compared in Table 4.2 where the water absorption ratio of MUF composite is between MF and UF composites.

Table 4.2 : Water Absorption of 20% Composites

Resin-20% Pomace Composite	Water Absorption
MF Composite	%583
UF Composite	%257
MUF Composite	%450

On the other hand, solubility in water shows a different characteristic which increases at the beginning and then decreases with the increasing weight ratio of olive pomace which are seen in Figure 4.16 and 4.17.

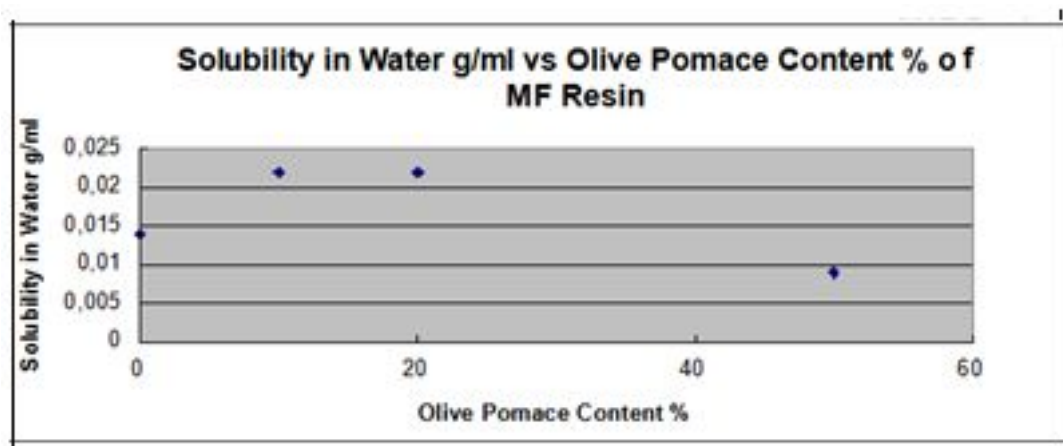


Figure 4.16 : Solubility in Water g/ml vs Olive Pomace Content weight % of MF Resin

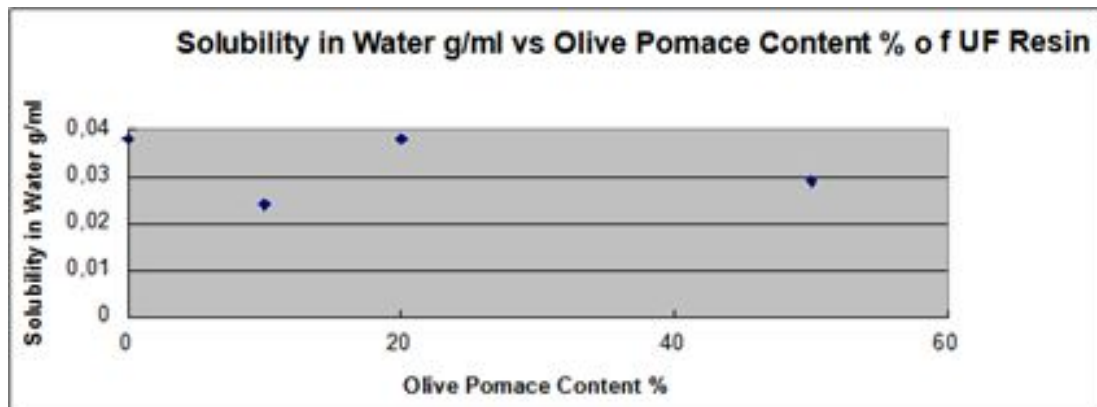


Figure 4.17 : Solubility in Water g/ml vs Olive Pomace Content weight % of UF Resin

Solubility in water of 20% pomace composites are compared in Table 4.3.

Table 4.3 : Solubility in Water of 20% Composites

Resin-20% Pomace Composite	Solubility in Water
MF Composite	0.022 g/ml
UF Composite	0.038 g/ml
MUF Composite	0.048 g/ml

MUF composite has higher solubility in water than MF and UF composites.

5. CONCLUSION

In the first part of this study blank melamine-formaldehyde and urea-formaldehyde resins and their pomace composites are synthesized. The pomace weight is determined as 10%, 20% and 50% of the weight of melamine and urea in melamine-formaldehyde and urea-formaldehyde resins respectively. In the second part of the study, melamine-urea-formaldehyde resin-20% pomace composite is synthesized. Then all the resins, composites and olive pomace itself are characterized using FT-IR spectroscopy method and tested. Their chemical structures are in agreement with literature. Water absorption ratios are determined to be increasing with increasing pomace ratio. Solubility in water is increasing to a limit but with increasing pomace ratio it decreases. The effects of olive pomace to resin are observed. Melamine-formaldehyde resin-pomace composites are hard and have a glossy appearance. Urea-formaldehyde resin-pomace composites are softer with good haptic properties. Melamine-urea-formaldehyde resin is glossy and significantly sticky. For all the composite samples all homogeneous brown wood-like appearance is successfully achieved. They all suitable for different applications. It is established that olive pomace can be utilized in industry. Amino resin-olive pomace composite is a healthier alternative to amino resins with its less melamine, urea and formaldehyde content. Also the use of wood products in industry and the hazard to environment can be reduced.

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