ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF SILICATE NANOCOMPOSITES CONTAINING POLYURETHANE/CYCLOHEXANONE FORMALDEHYDE COPOLYMERS

M.Sc. THESIS

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Department of Science and Technology

Polymer Science and Technology Programme

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

SİLİKAT NANOKOMPOSİT İÇEREN POLİÜRETAN/SİKLOHEKZANON FORMALDEHİT KOPOLİMERLERİN SENTEZİ VE KARAKTERİZASYONU

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Date of Submission : 16 December 2013
Date of Defense : 22 January 2014

To my spouse Dr.Serden MÜJDECİ and , my sunshine Nil MÜJDECİ

FOREWORD

I would like to thank my advisor Prof. Dr. Nilgün KIZILCAN for giving me valuable advice, supporting me every step and being patient, whole this hard and long experiment .
Also I would like to thank my dear spouse, Dr. Serden MÜJDECİ for his endless support and faith in me.

December 2013

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ABBREVIATIONS

PU	**:** Polyurethane
MDI	**:** Methylene Diphenyl Diisocyanate
TDI	**:** Toluene Diisocyanate
HDI	**:** Hexamethylene Diisocyanate
IPDI	**:** Isophorone diisocyanate
TEOS	**:** Tetraethyl Orthosilicate
CFR	**:** Cyclohexanone Formaldehyde Resin
NMR	**:** Nuclear Magnetic Resonance
FTIR	**:** Fourier Transform Infrared Spectroscopy
SEM	**:** Scanning Electron Microscope
XRD	**:** X-ray Diffraction
TEM	**:** Transmission Electronic Spectroscopy
TGA	: Thermogravimetric Analysis

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SYNTHESIS AND CHARACTERIZATION OF SILICATE NANOCOMPOSITES CONTAINING POLYURETHANE/CYCLOHEXANONE FORMALDEHYDE COPOLYMERS

SUMMARY

Polyurethanes (PU) are engineering materials and have excellent mechanical and chemical properties. Beginning of this century polyurethane has incredible progress in our daily lives. Polyurethanes can be found in liquid coatings and paints, tough elastomers such as roller blade wheels, rigid insulation, soft flexible foam, elastic fiber or as an integral skin. The origin of polyurethane dates back to the beginning of World War II, when it was first developed as a replacement for rubber. The versatility of this new organic polymer and its ability to substitute for scarce materials spurred numerous applications. During World War II, polyurethane coatings were used for the impregnation of paper and the manufacture of mustard gas resistant garments, high-gloss airplane finishes and chemical and corrosion-resistant coatings to protect metal, wood and masonry. The end of the war, polyurethane coatings were being manufactured and used on an industrial scale and could be custom formulated for specific applications. By the mid-50's, polyurethanes could be found in coatings and adhesives, elastomers and rigid foams. It was not until the late-50's that comfortable cushioning flexible foams were commercially available. With the development of a low-cost polyether polyol, flexible foams opened the door to the upholstery and automotive applications we know today.

Formulations, additives and processing techniques continue to be developed, such as reinforced and structural moldings for exterior automotive parts and one-component systems. Today, polyurethanes can be found in virtually everything we touch—desks, chairs, cars, clothes, footwear, appliances, beds as well as the insulation in our walls and roof and moldings on our homes.

Polyurethane chemistry is complex, but the basics are relatively easy to understand. Polyurethanes are formed by reacting a polyol (an alcohol with more than two reactive hydroxyl groups per molecule) with a diisocyanate or a polymeric isocyanate in the presence of suitable catalysts and additives. Because a variety of diisocyanates and a wide range of polyols can be used to produce polyurethane, a broad spectrum of materials can be produced to meet the needs for specific applications.
Polyurethanes exist in a variety of forms, including flexible foams, rigid foams, chemical-resistant coatings, specialty adhesives and sealants, and elastomers.

However, there are many application areas of the polyurethanes, they are also very limited because of being weak in abrasion, flame retardancy and weatherability.

While science focused on improving the properties of polymers a new subject was born; Nano science. Particle size is transferred from micro scale to nano scale with

adding incredible values to the materials. Nano sized products generally used as reinforcing and filling materials during the production of composite materials. The sizes, surface area, structure, if there is coating, coating chemical are affecting the end properties of polymers. Silica is a well-known material and can be described as nanoproduct. There are many ways to produce silica sol. The sol-gel process is a synthesis way consisting in the preparation of a sol and a gel structure after removal of solvent. Stöber method is the most known one. Silicon alkoxides generally react slowly with water, but the reaction process, hydrolysis and condensation, can be sped up by the use of acid and base catalysts. In brief, pH, solvents, reactants and water are the main parameters affecting the silica structure. Presence of Si–O–Si bond in silica-sol can provide resistant and stable polymers like polyurethanes.

Silika can improve the pronounced thixotropic performance, the viscosity is precisely tailored to requirements, the yield point can be varied to ensure good anti-slump properties, the coating does not show sagging after application, The formulation can be stored for a long time and is easy to process

In polyurethane synthesis isocyanates (hard segment) are the key factors affecting the specifications of the products. Aromatic based isocyanates have superior properties but on the other hand they have weak weatherability and flame retardancy. Monomeric methylene diphenyl diisocyanate (MDI) is in the bifunctional structure. 4,4'-MDI is the most used one with high flexibility at low temperature, heat resistance, high tensile strength and elasticity, high abrasion resistance. Modified MDI is a polycarbodiimide-modified diphenylmethane diisocyanate. The carbodiimide linkage aids the stabilization of the polymer against hydrolytic degradation. Also using chain extenders in polyurethanes can provide branched structure, which helps to increase the hard segment. Polyols can be described as soft segments in polyurethanes. Polyether–urethanes are less thermally stable due to CH bond of the methylene group than polyester–urethanes because of the oxidative cleavage of the polyether structure at high temperatures.

Industrial resins are generally low molecular weight solid materials and they can be processed easily. They are used in order to improve hardness, gloss, weatherability and adhesion properties of coatings. Cyclohexanone formaldehyde resin (CFR) is the condensation polymer of cyclohexanone and formaldehyde, which contains carbonyl and hydroxyl . It can also be called polyaldehyde ketone resin, ketone aldehyde resin, ketonic resin and poly ketone aldehyde resin. It shows excellent compatibility with many coating/printing raw materials. It is soluble in almost organic solvents and exhibits good wetting and dispersion to the filling and pigment. It can also improve adhesion, gloss and hardness of coatings. It is a kind of excellent multifunctional additive for coating.

Combining CFR with polyurethane resin can improve the weak properties of polyurethanes.

In this study, many trials were done to monitor property changes of silicate containing polyurethane-CFR copolymers. During this characterization spectrograph,TGA, SEM and many other new methods are used.

During the trials all the steps was monitored by FT-IR. After the reaction completed; samples layered on glass plates and cured in room condition. Total curing of the samples took 7 days . Then the characterization of the polymers realized. In conclusion, it was observed that with CFR and silicate, the physical properties of polyurethanes are improved.

SİLİKAT NANOKOMPOZİT İÇEREN POLİÜRETAN/SİKLOHEKZANON FORMALDEHİT KOPOLİMERLERİN SENTEZİ

ÖZET

Poliüretanlar mühendislik malzemeleri olup, iyi mekanik ve kimyasal özelliklere sahiptir. Poliüretanlar günlük yaşantımızda birçok alanda karşımıza çıkmaktadır. Kullanım alanlarının ve çeşitliliğin yaygın olmasına rağmen yanma ve dış ortam koşullarına karşı dayanıksız olmaları bu alanları zamanla sınırlandırmıştır.

Poliüretanlar , sıvı kaplamalar ve boyalar , örneğin paten tekerlekleri , katı yalıtım, yumuşak, esnek bir köpük , esnek elyaf veya tamamlayıcı deri gibi sert elastomerler olarak kullanım alanı bulabilir. Poliüretanlar ilk olarak kauçuğa karşı alternatif olarak geliştirilmiştir. Bu süreç, ikinci Dünya Savaşı'nın başlangıcına kadar uzanır. Dünya Savaşı sırasında , poliüretan kaplamalar kağıt emprenye ve hardal gazına dayanıklı giysiler , metal , ahşap yüzeyleri korumak için kimyasal ve korozyona dayanıklı kaplamaların üretimi için kullanılmıştır . Savaşın sonunda, poliüretan kaplamaların üretimi standart hale getirilmiş ve endüstriyel ölçekte, özel uygulamalar için formüle edilebilir hale gelmiştir. 1950'lerin ortalarında, poliüretanlar; kaplamalar ve yapışkanlar, elastomer ve sert köpüklerin üretiminde yaygın şekilde kullanılmaktaydı. 1950lerin sonlarına kadar ise rahat bir sünger yatak, yaygın değildi. Düşük maliyetli polieter poliolün gelişmesiyle birlikte, esnek köpükler bugün bildiğimiz döşemelik, mobilya ve otomotiv uygulamaları için alternatif oluşturmaya başladı.

Poliüretanların formülasyonları, katkı ve işleme teknikleri geliştirilmeye devam etmektedir. Bugün, poliüretanlar hemen hemen her şeyde bulunabilir; dokunmatik masa, sandalye, araba, giysi, ayakkabı, beyaz eşya, yatak gibi… Bunun yanı sıra evlerimizde duvar izolasyonunda ve çatı kalıplamalarında da kullanılmaktadır.

Poliüretan kimyası karmaşık, ancak temelleri anlamak nispeten kolaydır. Poliüretanlar, uygun katalizörler ve katkı maddeleri varlığında bir diizosiyanat veya bir polimerik izosiyanat ile bir poliolün (molekül başına ikiden fazla reaktif hidroksil grubu içeren bir alkol) tepkimeye sokularak elde edilmiştir. Diizosiyanatların bir çeşitliliği ve poliollerin geniş bir yelpazede olması sebebi ile çok özel uygulamalar için özel poliüretanlar üretmek mümkündür. Poliüretanlar bir çok formda bulunabilir; esnek köpükler, sert köpükler, kimyasal-dirençli kaplamalar, özel yapıştırıcı ve mastikler ve elastomerler örnek olarak verilebilir.

Poliüretanlarda izosiyanatlar, sert-bölüm (hard-segment) olarak tanımlanır ve yapıyı etkiler. Aromatik bazlı poliüretanlar birçok iyi özelliğe sahipken dış ortama ve yangına dayanımları zayıftır. Monomerik bazlı MDI, bifonksyonel özelliğe sahiptir. İzosiyanatlar içerisinde yanma dayanımı ve düşük ısıda iyi fiziksel özellikleri ile diğer izosiyanatlardan ayrılmaktadır. Modifiye MDI ise polikarbodimid-difenilmetan diizosiyanat olarak geçmektedir. Karbodimid bağı ürünlere hidrolitik direnç kazandırmaktadır. Poliüretanlarda diğer bir sert-segmet ise bağ arttırıcı olarak tanımlanan ürünlerdir. Poliüretanlarda polyoller yumuşak segment olarak tanımlanır. Polyester polyollere gore polieter polyoller çok daha iyi sıcaklık dayanımı sağlamaktadır.

Bilim, polimerlerin özelliklerini iyileştirmeye yoğunlaştığında, yeni bir konuda önem kazanmaya başlamıştır; Nano. Parçacık boyutu micro dan nano boyuta geçmiştir. Nano boyuttaki dolguların özellikle kompozit malzemelerde kullanım alanları bulunmaktadır. Boyut, yüzey alanı ve yapı, polimerlerin özelliklerini değiştirebilmektedir. Silika da nano ürün olarak tanımlanmaktadır. Silika üretmek için birçok metod bulunurken sol-jel en yaygın olanı olarak tanımlanabilir. Sol-jel proseste; sol ve jel hazırlanır sonrasında ise içerisindeki solvent uçurulur. Bu metodta silikon alkoksit yavaş olarak su ile reaksiyona girer. Bu reaksiyon asit veya baz katalizörler ile hızlandırılabilir. Genel olarak sistemde pH, kullanılan çözücü, reaktanlar ve su, oluşan silikanın tanecik yapısını etkileyen başlıca parametrelerdir. Si–O–Si bağı polimerlere stabilite kazandırmaktadır.

Silika kullanıldığı malzemede; reolojiyi iyileştirmekte, viskoziteyi uygun, çalışabilir aralıklara getirmekte, akma noktasını iyileştirmekte, özellikle kaplamalarda uygulamadan sonra akmayı engellemektedir.

Endüstriyel reçineler katıldığı ürünlerin fiziksel özelliklerini iyileştirmede kullanılır. Siklohekzanon formaldehit reçineleri, siklohekzanon ve formaldehitin kondenzasyon polimerizasyonu sonucunda oluşmuş ve karbonil, hidroksil bağı içeren polimerlerdir. Siklohekzanon formaldehit ve poliüretanlardan kopolimer sentezleyerek, poliüretanların birçok zayıf özelliği iyileştirilebilir. Neredeyse bütün organik çözücüler içinde çözünür. Dolgu ve pigment içerisinde çok iyi ıslatma ve dağılım sergiler. Ayrıca katıldığı malzeme içerisinde yapışmayı, parlaklığı vekaplamanın sertliğini arttırabilir. Kaplama için çok işlevli bir katkı malzemesidir.

Bu çalışmada öncelikle sol-jel prosesi ile silika sentezlenmiş ve ardından silika in-situ olarak poliüretan – siklohekzanon formaldehit reçineleri ile hazırlanmış kompozite eklenerek, nanokompozit bir malzeme elde edilmiştir. Bu ürüne karakterizayon tayini için birçok test uygulanmıştır.

Denemeler sırasında, tüm adımlar FT-IR ile izlenmiştir. Reaksiyon tamamlandıktan sonra, örnekler cam plakalar üzerine yerleştirilmiş ve oda koşullarında kürleşmesi sağlanmıştır. Numunelerin toplam kürleşme süresi 7 gündür. Daha sonra polimer

karakterizasyon gerçekleştirilmiştir. Karakterizasyon sırasında TGA, SEM, kullanılmıştır.
Örneklerin fiziksel özellikleri de incelenmiştir. Sonuç olarak, CFR ve silikat ile sentezlenen poliüretanların özelliklerinin iyileştiği gözlenmiştir.

1. INTRODUCTION

The aim of this work is to synthesis silicate nano-composites containing polyurethane/cyclohexanone formaldehyde copolymers via in situ method. Silica sol must be prepared according to Stöber method using Tetraethyl orthosilicate (TEOS) as the precursor and later mixed polyester polyol by in situ. Then this mixture (Polyester / Silica Sol) introduced in to methylene diisocyanate (MDI) and modified methylene diisocyante (MMDI) to synthesis polyurethane and cyclohexanone formaldehyde resin (CFR) polyurethane composites. The aim of using TEOS, CFR and polyester based polyol is to increase the flame retardancy, dynamic mechanical properties of materials.

During and after trials, physical, mechanical, thermal, spectroscopic and microscopic properties of samples are monitored.

2. THEORY OF STUDY

2.1 Nano Science and Nanocomposite Materials

The term "nanocomposites" is a relatively new in material science and is used to refer to a combination of two or more phases, where at least one dimension is in the nanometer size range.Nanocomposites are multiphase materials where one of the structural units, either organic or inorganic, is in a defined size range 1-100 nm. These types of materials are expected to exhibit new and improved catalytic, electronic, magnetic, and optical properties relative to both the parent phases and their corresponding micro or macrocomposites [1-2]

The proper nanoparticle surface engineering can give:

- Good dispersion with high filler content
- Provide good rheology
- Materials with improved mechanical properties (fatigue strength, toughness, scratch resistance…) and flame retardancy and coatings with barrier properties

2.1.1. Nanocomposite structures and characterization methodes

Depending on the nature of the components used (layered silicate, organic cation and polymer matrix) and the method of preparation, three main types of composites may be obtained when a layered clay is associated with a polymer. When the polymer is unable to intercalate between the silicate sheets, a phase separated composite is obtained, whose properties stay in the same range as traditional micro composites. Beyond this classical family of composites, two types of nano composites can be recovered. Intercalated structure in which a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained [3-5].

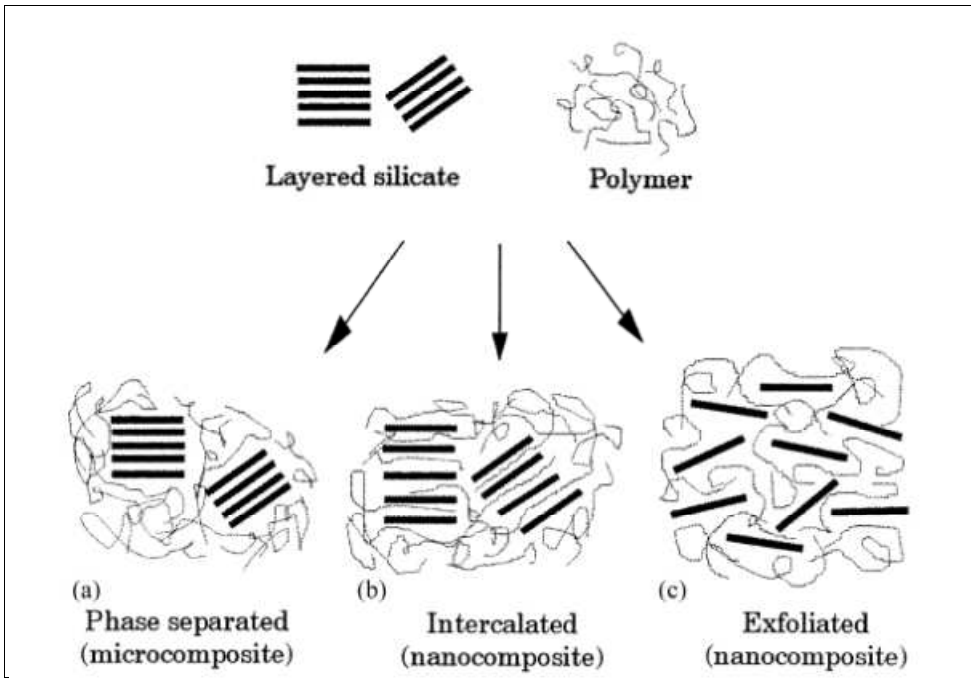

Figure 2.1: Schematic representation of the different types of composites generated based on the interactions of the layered silicate with polymer matrices. (a) Phase separated microcomposite, (b) intercalated nanocomposite and (c) exfoliated nanocomposite

Two complementary techniques are used in order to characterize those structures. XRD is used to identify intercalated structures. In such nanocomposites, the repetitive multilayer structure is well preserved, allowing the interlayer spacing to be determined.

As far as exfoliated structure is concerned, no more diffraction peaks are visible in the XRD diffractograms either because of a much too large spacing between the layers (i.e. exceeding 8 nm in the case of ordered exfoliated structure) or because the nanocomposite does not present ordering.

In the latter case, transmission electronic spectroscopy (TEM) is used to characterize the nanocomposite morphology. Besides these two well defined structures, other intermediate organizations can exist presenting both intercalation and exfoliation. In this case, a broadening of the diffraction peak is often observed and one must rely on TEM observation to define the overall structure [3-5].

2.1.2. Nanocomposite preparation

There are four main routes for the synthesis of nanocomposites. (a) template synthesis, (b) intercalation of polymer or prepolymer from solution, (c) *in-situ* intercalative polymerization and (d) melt intercalation.

Template Synthesis

Template synthesis is not a very common method. In principle, it is totally opposite in nature than the other usual techniques. General used nanocomposite synthesis technique; polymer materials are synthesized in the presence of the silicate filler. However, in this technique, the inorganic material is synthesized in the presence of the polymer matrix. Double layer hydroxide based nanocomposites have been synthesized by using this route *in-situ* in an aqueous solution containing the polymer and the silicate building blocks. The polymer aids the nucleation and growth of the inorganic host crystals and gets trapped within the layers as they grow. Though this technique presents high potential route for the dispersion of the layered silicate in the polymer matrices at nanometer scale, however it suffers from some disadvantages. The synthesis process generally requires the use of high temperatures, which is detrimental for the polymer materials. The silicate materials generated by the self-assembly process have also the tendency to aggregate [3-5].

Intercalation of Polymer or Prepolymer from Solution

In this mode of nanocomposite synthesis, the organically modified silicate is dispersed in a solvent in which the polymer is also soluble. It is well known that such layered silicates, owing to the weak forces that stack the layers together can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated (or the mixture precipitated), the sheets reassemble, sandwiching the polymer to form, in the best case, an ordered multilayer structure. Under this heading we also include the nanocomposites obtained through emulsion polymerization where the layered silicate is dispersed in the aqueous phase. The use of solvent though leads to the generation of intercalated nanocomposites, however, this approach is not environmentally friendly owing to the use of large amounts of solvent. The polymer chains lose entropy owing to diffusion inside the silicate interlayers, however, such a process is still thermodynamically viable, owing

to the gain in the entropy by the solvent molecules due to desorption from the silicate interlayers . The technique is mostly used for the intercalation of the water soluble polymers like poly(vinyl alcohol), poly(ethylene oxide), poly(acrylic acid), poly(vinlypyrrolidone) [3-5].

In-Situ Intercalative Polymerization

The *in-situ* intercalation mode of polymerization was the method reported by Toyota researchers, which led to the exponential growth in nanocomposites research. In this mode of polymerization, the layered silicate mineral is swollen in monomer. The monomer, being of low molecular weight can also diffuse easily into the interlayers thereby swelling the interlayers. On initiation of the reaction, the monomer present in and out of the interlayers polymerizes to generate nanocomposites in which the layered silicate platelets are delaminated to the nanometer level. However, a control of the polymerization in and out of the layers is required in order to achieve high extents of filler exfoliation [3-5].

Melt Intercalation

Melt intercalation has developed into one of the most attractive methods for the commercial generation of polymer nanocomposites. In this approach, the polymer is first melted at high temperature and the filler is then blended with the polymer melt at high temperature under shear.

This technique has an advantage that no solvent is required for the nanocomposite synthesis. The polymer can intercalate between the interlayers if the silicate surface is modified in a way that the electrostatic forces holding the platelets together are very weak. The use of high temperature required to achieve a homogenous mix can however lead to occasional degradation of the surface modification and polymer thus requiring care during the compounding process. As this method is environmentally friendly and does not require the usage of large amounts of solvents, and owing to its simplicity and economic viability, the melt intercalation method has been widely used for the synthesis of polymer nanocomposites with a large number of polymer materials [3-5].

2.2 Synthesis of Silica and Sol-Gel Method

Silicon is present in environment in different forms. It is generally found combination with oxygen. Additionally it is also found in dissolved form like silicic acid. Layered silicate-based polymer nanocomposites have demonstrated a significant potential to become the basis for development of the next generation of enhanced performance polymer compounds. Incorporation of only a small loading (4 to 5%) of properly treated, well dispersed/exfoliated organoclay into the base polymer results in a compound with a substantial improvement in thermal, mechanical, as well as other physical properties over those of the base polymer. Most publications still concentrate on the importance of the chemistry used to modify the surface of the silicate. They provide a description of resultant product properties but do not include the role of processing or give details of the compounding setup. Therefore, the key challenge facing many new entrants into the field is to determine how to maximize the clay exfoliation. Of course, using clay modified specifically for compatibility with the polymer matrix is extremely important; however, proper design and operation of the compounding system is equally critical

Recently numerous synthesis methods were explored and they successfully used to produce nanoparticles.

The Sol-Gel method is an outstanding route to the synthesis of hybrid nanocomposites. The sol-gel process is a synthesis route consisting in the preparation of a sol and successive gelation and solvent removal. It gives inorganic high purity materials at mild synthesis conditions (temperature and pH).

An outstanding variation is the so-called Stöber method allowing colloidal particles (with well-defined size and shape and with narrow size distribution) be produced through hydrolysis and polycondensation of silicon alcoxides in water /alcohol /ammonia mixtures. The sol gel method allows, also, easy functionalization of silica nanoparticles with specific organic groups. Many of the hybrid nanoparticles synthesis methods take advantage of all this. The sol gel method finds, however, applications in many other research fields. The aim of this paper is to give also, shortly, a contribution to the knowledge of the basic principles of the method, with particular reference to the synthesis of functionalized silica nanoparticles through the Stöber method[2].

Stöber method (Stöber 1968) allowing preparing monodisperse silica spheres from less than 0.05 nm to 2 nm [2].

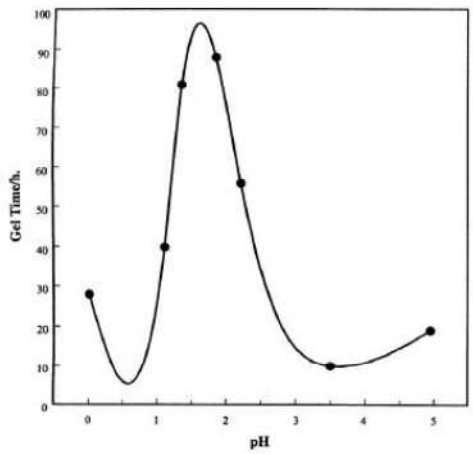

Figure 2.2: Rate of H+ catalyzed TEOS hydrolysis (gel time) as a function of pH.

The method is based on the hydrolysis and polycondensation of alkyl silicates in basic (ammonia) alcoholic solutions. The particles size strongly depended on the water and ammonia concentration but also on the nature of the alcohol used as a solvent. When using alcohols of higher molecular weigh the reaction was slowed down and both median particle size than the spread of the size distribution increased simultaneously.

The work was extended and a correlation was found allowing to predict quite well the final particles size, d, over concentrations of 0.1-0.5M TEOS, 0.5-17.0M H_2O, 0.5-3M NH_3; [2,9-10].

$$d = A[H_2O]^2 \exp\left(-B[H_2O]^{1/2}\right)$$

Where

$$A = [TEOS]^{1/2}\left(82 - 151\,[NH_3] + 1200\,[NH_3]^2 - 366\,[NH_3]^3\right)$$

$$B = 1.05 + 0.523\,[NH_3] - 0.128\,[NH_3]^2$$

2.3 Polyurethanes

Polyurethanes (PUR) were first produced in 1937 by Otto Bayer and his co-workers in Germany and represent a family of polymers rather than a single polymer. Urethane polymers can be produced with a wide variety of properties, ranging from

soft flexible foams and fibres through to hard solids so that they can be used in a diverse range of applications.

Polyurethanes represent only 5% of the worldwide polymer consumption shows around 10.6 million metric tonnes in 2004), but the dynamics of their growth is constantly high.

There are five main areas of use for polyurethanes:

1. The furniture and mattress sector, which uses almost exclusively flexible foams,
2. The automotive industry which provides a market for flexible foams, filling foams, rigid and flexible integral skin foams as well as elastomers for engineering components,
3. The consumer sector, which is diversified in a manner similar to the automotive industry,
4. The building industry, which is by far the largest consumer of rigid foams as insulation materials, and
5. Refrigeration engineering, which represents the second largest area for use of rigid polyurethane foams as insulation materials.

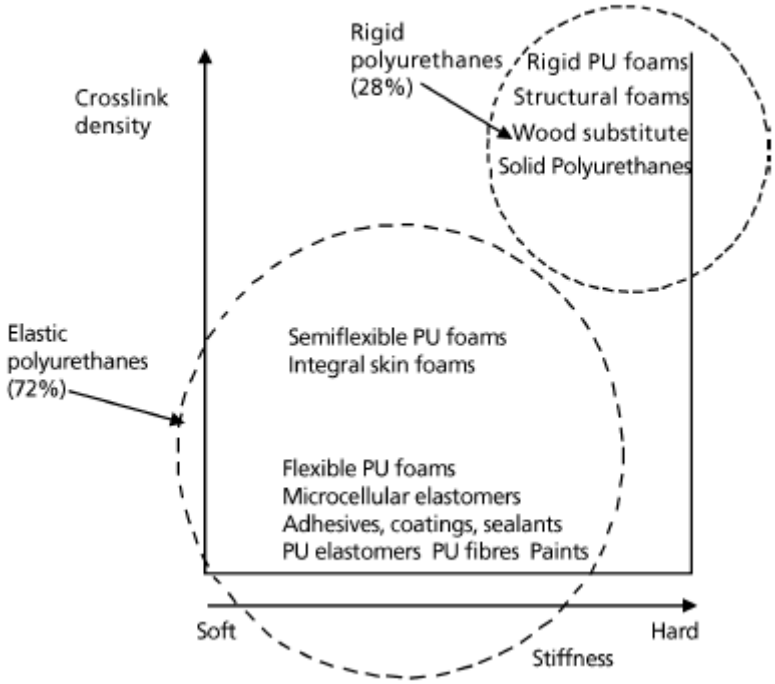

Figure 2.3: Classification of polyurethanes as function of crosslink density and stiffness

Despite these differing properties, the polymers have one common characteristic in that they all incorporate the urethane group (-NH-CO-O-) into their structure. However, the polymers differ from simple thermoplastic polymers, such as the polyolefins, in that they are not sold as ready-made polymers but as precursors that are mixed at the conversion stage. These precursors are commonly polyols (compounds containing multiple -OH groups) and diisocyanates (compounds containing -NCO groups). The primary reaction during the production of polyurethanes is of the form:

$$-NCO + HO- \rightarrow -NH-CO-O-$$

The reaction between isocyanates and alcohols, the most important reaction involved in polyurethane synthesis, is an exothermic reaction[15-17].

2.3.1 Isocyanates

Limited types of isocyanates are used. The most important isocyanates, covering the majority of polyurethane applications are aromatic isocyanates: toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). Aliphatic isocyanates such as hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) or 4,4´ dicyclohexyl diisocyanate (HMDI) are used to a much lesser extent, and only for special applications. TDI is commercialised using a mixture of the 2,4 and 2,6 isomers (TDI 80/20 having 80% 2,4 TDI and 20% 2,6 TDI and TDI 65/35 having 65% 2,4 TDI and 35% 2,6 toluene diisocyanate) or 2,4 TDI as pure isomer. The most important application of TDI is in flexible polyurethane foam manufacture. The structures of commercial TDI are presented in. The second most important aromatic isocyanate is MDI, commercialised in various forms and functionalities, the most important being: pure MDI, 'crude' MDI and polymeric MDI (PAPI).Pure MDI, having two -NCO groups/mol, is commercialised mainly as 4,4´ isomers, but it is possible to use 2,4 and 2,2 isomers. The main applications of pure MDI (especially the 4,4´ isomer) are: polyurethane elastomers, microcellular elastomers and some flexible foams. The structures of pure MDI isomers are presented [16].

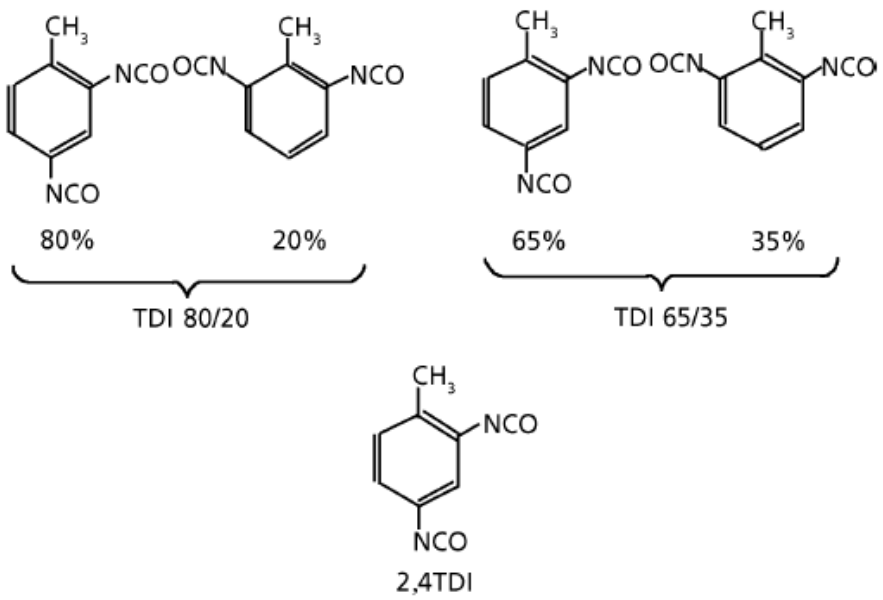

Figure 2.4: The structures of pure TDI isomers

Crude' MDI is a mixture of 4,4´ MDI isomer (around 48-50%) and high molecular weight (MW) isomers having 3, 4, 5 and higher numbers of aromatic rings, with functionalities in the range of 2-3 -NCO groups/mol [16]

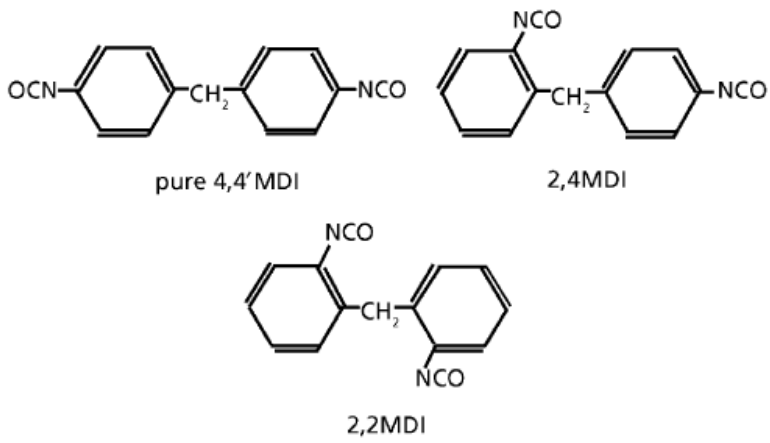

Figure 2.5: The structures of pure MDI isomers

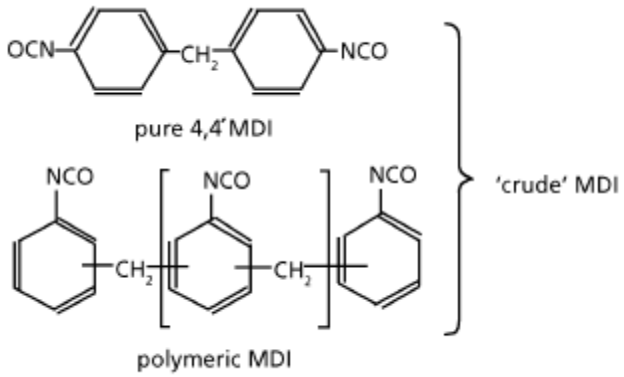

Figure 2.6: The chemical structure of 'crude' MDI

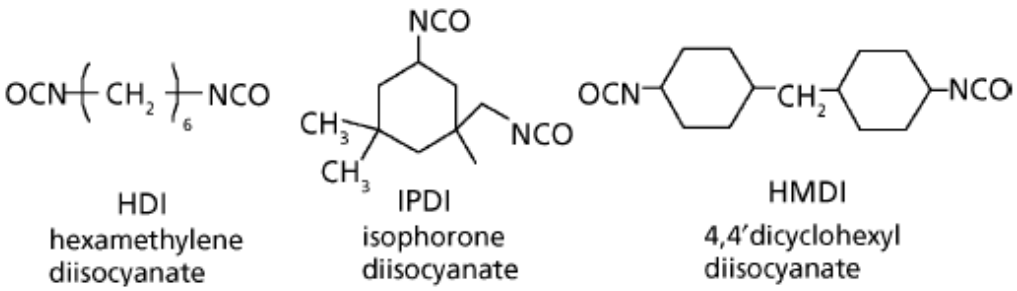

Figure 2.7: The chemical structures of some aliphatic diisocyanates

Modified MDI is a polycarbodiimide-modified diphenylmethane diisocyanate. Liquid at room temperature, this product has a low viscosity and good storage stability down to 75°F (24°C). The polycarbodiimide adduct offers extra flexibility because adduct formation is reversible (dissociation generates an additional isocyanate function). The carbodiimide linkage aids the stabilization of the polymer against hydrolytic degradation. Because this product can be used alone or in mixtures with prepolymers, its higher functionality offers faster demold times than is ordinarily possible with linear prepolymers. A unique combination of high modified MDI content, available carbodiimide, and liquid state allows ease of handling, ease of processing, and maintenance of high physical properties under strenuous wear and environmental conditions.

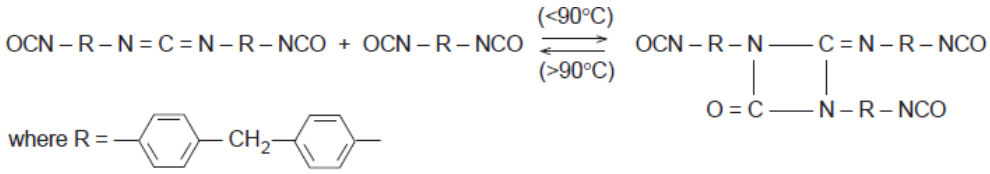

Figure 2.8: The chemical structure of Modified MDI

2.3.2 Polyols

The polyols used in polyurethane production are predominantly hydroxy-polyethers, rather than hydroxy-polyesters. But on the other hand Polyester polyols were the first polyols used in the beginning of PU development, and are produced by polycondensation of a diacid with excess diol.

Polyether polyols are produced by alkoxylation. Depending on the degree of cross-linking required, the starting alcohols used for hydroxy-polyethers may be divalent glycols (ethylene, propylene and other glycols) or multivalent alcohols (e.g. glycerol, sucrose).

The MW of the oligo-polyols used in polyurethane synthesis varies between 300-10000 daltons, in the region of low MW polymers (oligomers), the number of hydroxyl groups/molecule of oligo-polyol (the oligo-polyol functionality) being generally in the range of 2-8 OH groups/mol.

A polyol of low functionality, having around 2-3 hydroxyl groups/mol and with a high MW of 2000-10000 daltons, leads to an elastic polyurethane and on the contrary, a low MW oligo-polyol of 300-1000 daltons, with a high functionality of around 3-8 hydroxyl groups/mol leads to a rigid crosslinked polyurethane [15-16].

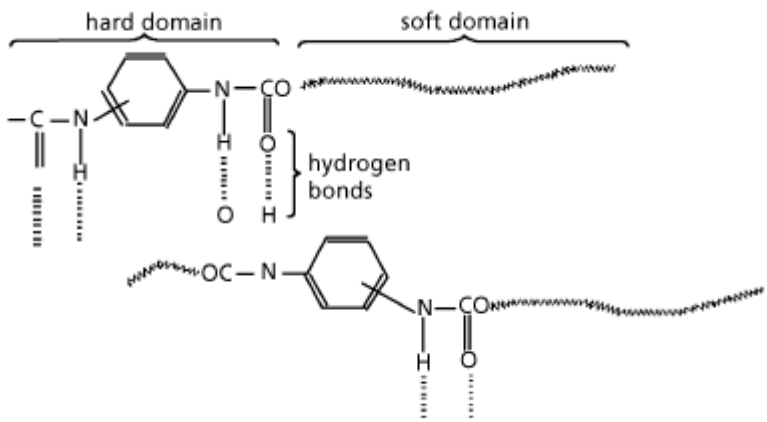

Figure 2.9: The ‘hard domains’ and ‘soft domains’ of polyurethane elastomers

With so many potential compositions, it is important to have adequate criteria for characterizing a polyol. Some of the more commonly used criteria will be discussed below.

Functionality - arises from the choice of initiator or blend of initiators. Defined simply as the average number of isocyanate reactive sites per molecule. For example, a four-functional initiator, such as pentaerythritol would give a nominal four-functional or tetrol polyol. In calculating functionality, two important variables must be considered: level of monol and level of diol.

Hydroxyl Number - a measure of the amount of reactive hydroxyl groups available for reaction. This value is determined in a wet analytical method and is reported as the number of milligrams of potassium hydroxide equivalent to the hydroxyl groups found in one gram of the sample [21-23].

Equivalent Weight - classically defined as the molecular weight of a polyol divided by its functionality. Functionality of a polyol is complex because of the presence of monols from propylene oxide isomerization and diols (derived from water). In practice, the equivalent weight is calculated from the analyzed hydroxyl (OH) number

The equivalent weight is necessary for isocyanate requirement calculations and is derived from the following expression:

$$\text{Equivalent Weight} = 56{,}1 * 1000 / \text{OH Number} \qquad (2.1)$$

Primary Hydroxyl Content - The distribution of primary and secondary hydroxyl groups directly affects the reactivity of a polyol with isocyanates. In general, polyol reactivity increases as primary hydroxyl content increases (see example data in the figure below). The earliest measurements of primary and secondary hydroxyl contents were based on differences in solution based reaction rates. Nuclear magnetic resonance (NMR) is now the preferred analytical method. With NMR, the primary and secondary hydroxyl end groups can be distinguished from one another and from the ethylene oxide and propylene oxide units in the polyol chain [24-35]..

Cloud Point - The cloud point of a polyol is defined as the temperature in degrees centigrade, at which a solution of the polyol in a water or water-alcohol mixture becomes turbid upon heating. Cloud point decreases with increasing polyol molecular weight and increases with the addition of ethylene oxide to the polyol. This analysis is taken to be a measure of the water solubility, surfactant properties and reactivity of a polyol. Since polyols have inverse solubility in water, higher cloud points indicate increases in these important performance attributes [36-38].

CPR - the CPR (controlled polymerization rate) value defines quantitatively the weakly basic materials present in a polyol. These materials are not defined qualitatively but are determined as the total weak acid salts of the strong bases. These salts may act as catalysts for the reaction of polyols with isocyanates. The reported

number is ten times the number of milliliters of 0.01 N HCl necessary to neutralize 30 grams of polyol sample [39].

Reactivity - a measure of the rate at which a polyol undergoes reaction to make a polyurethane polymer. A test measuring viscosity build in a model reaction with isocyanate has been in use since 1960. In recent years a refined Brookfield Viscosity Test (BVT) has proven useful for reactivity quantification of ethylene-oxide-capped polyols. Example data in the figure below show how polyol reactivity varies with increasing primary hydroxyl content (at a constant unsat)[40-47].

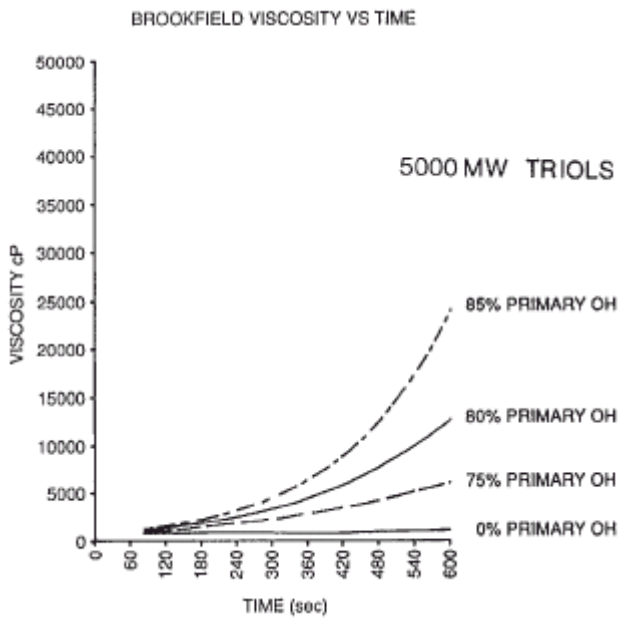

Figure 2.10: Reactivity variation with increasing primary hydroxyl content

The BVT has also been found useful for detecting polyol contamination. Other viscosity-based reactivity tests have been described. Appearent polyol reactivity in this type of model reaction can also be strongly influenced by the polymer-chain-terminating effects of monol (unsat).

In polyester polyols production process, the diol, triol, etc is first heated to a temperature of 60-90°C. Then the dicarboxilic acid is added and removal of the reaction water begins. For obtaining the targeted molecular weight, the excess diol is calculated by means of Flory Equation. Diol can be lost during removal of the water form the condensation reaction and through side reactions (formation of ethers and aldehydes). The amount of diol lost is dependent upon the processing conditions and upon type of diol. The amount of diol lost must be empirically determined. Usually

the reaction is completed at temperatures up to 200°C. Nitrogen, carbon dioxide, or vacuum is used to remove the water and to reach the wanted conversion of 99.9%, and the resulting polyester should have an acid number less than two. This conversion is necessary to minimize the presence of residual carboxylic end groups that can reduce the reactivity. The polyesters are composed of all possible oligomers raging from the monomers to high molecular weight species: the molecular weight distribution follows a Frory probability. The properties of the PU based polyester elastomers are governed mainly by the overall molecular weight of the polyester and only to a minor degree by the molecular weight distribution.

Acids, bases and compounds of the transition metals can catalyze the esterification reaction. The dicarboxylic acids also exert a limited catalytic effect. In practice catalysts are used reluctantly because they cannot be removed and can have an undesirable effect on the following PU reaction, since inorganic substances even in the smallest quantities favor or retard de PU processing reaction. The p-toluenesulphonic acid can be used as an accelerator and left in the polyester. In cases where small amounts of catalysts do not later cause problems, compounds of tin, antimony, titanium, lead and other metals, have proved especially effective. The amounts added lie in the ppm range. Solid impurities are removed by hot filtration of the finished polyester [20].

There are two main groups of polyester polyols:

- Aliphatic polyester polyols
- Aromatic polyester polyols

Table 2.1: Typical Properties of Polyester Polyols

Application	Flexible foam	Semi-rigid foam	Rigid foam	Shoe soles	Elastomers	Coatings	
						soft	hard
Structure	adipic acid,diethylene glycol,trimethylol propane	adipic acid phthalic acid, 1,2-propylene glycol, glycerine	adipic acid, phthalic acid, oleic acid, trimethylol propane	adipic acid,ethylene glycol,diethylene glycol	adipic acid,ethylene glycol, 1,4-butane diol	adipic acid,diethylene glycol	phthalic acid,maleic acid, trimethylol propane
*Average MW	2400	1000	930	2000	2000	2750	2450
OH number (mgKOH/g)	57 - 63	205 - 221	350 - 390	58-62	52 - 58	38 - 45	250 - 270
OH content (meq/g)	1.1	3.8	6.6	1.1	1.0	0.7	4.6
Average functionality	2.7	3.8	6.2	2.1	2.0	2.0	11.3
Viscosity at 75°C (mPa.s)	950 - 1100	570 - 750	1300 - 1550	500 – 700	500 - 600	700 - 800	17000 -150°C
Pour point (°C)	-12	-12	7	17 to 56	49 to 52	-9	90 to 100
Acid number	1.2	2.8	1.0	0.4	1.0	1.0	4.0
Density, 75°C (g/cm)	1.15	1.15	1.1	1.15	1.17	1.12	1.24

* Dalton type molecular weight

2.4 Cyclohexanone Formaldehyde Resin

Cyclohexanone can be reacted with aldehydes, especially formaldehyde, to give methylol compounds or resinous products. In this case it is the molar ratio and the reaction conditions which determine the properties of the end products. A high formaldehyde excess promotes the formation of methylol compounds, whereas basic catalysis leads to resin formation [48]. Higher aldehydes can likewise be used to produce resins, but have not found any industrial significance. On the other hand, methylcyclohexanone or mixtures with aliphatic ketones and, more recently, trimethylcy-clohexanone have been employed. The modification of the resins with phenols, epoxides, polyesters and sulphonamides is known. Small beads are obtained by addition of dispersants. The continuous preparation process has been described . Hydrogenation and treatment with reducing agents are ways in which the light stability can be increased.Cyclohexanone-formaldehyde resins do not have the broad

compatibility and solubility of the pure cyclohexanone resins. However, they are less expensive while being of adequate light stability. Although they can no longer be combined with oils, combination with a range of important paint binders is possible. The use of methylcyclo-hexanone as a raw material usually leads to enhanced solubility and compatibility. By using trimethylcyclohexanone, resins can be obtained whose compatibility and solubility are virtually universal.A reaction which has become important for the industrial production of the resin is the condensation of cyclohexanone with formaldehyde in the presence of alkalis.In many cases, the resins are used in order to improve drying, hardness, fullness, gloss and solids content. In coatings they are used in every case only as an accompaniment it other binders, for example in alkyd/acrylic coating materials, cement paints. Epoxy resin systems and marine paints. In addition to conventional printing ink., UV-curing printing inks also play an increasing role. A further principal area of application is represented by adhesives and sealing compound. Another application which has been described is in optical recording media. The broad compatibility of resins based on trimethylcyclohexanone makes them ideally used to use in pigment pastes capable of universal application. Some examples of commmercial resins are Kunstharz AFS (Bayer), Kunstharz CA (Hills), Kunstharz EP (Hiils),Krumbhaar-Types (Lawter) and MR85 (A.O. Polymers) .All the resins mentioned can be modified with many molecules for different purposes. Cyclohexanone-formaldehyde resins was in situ modified with using methyl isobutyl ketone, methyl ethyl ketone, methyl cyclohexanone, acetaldehyde, propion-aldehyde, cinnamaldehyde, dicynadiamide, arninotriazine and phenol [49]. Also siloxane-containing block copolymers were investigated and reported. Many types of cyclohexanone-formaldehyde block copolymers with poly-siloxanes and their unique properties were reported [50].

3. EXPERIMENTAL DETAILS OF STUDY

In this study, silica sol was synthesized (Stöber method) and added in-situ to the polyurethane polymer, which is prepared from polyester polyol and aromatic isocyanates and lastly composite of polyurethane with cyclohexanone formaldehyde was synthesized.

3.1 Materials

TEOS is supplied by Merck. Acetic acid and ethanol which were used in silica sol, received from J.T. Baker, For the synthesis of polyurethane, Polyester Polyol was provided by COIM, Monomeric MDI (33,6% NCO content) was supplied by Bayer Material Science and modified MDI (31,5% NCO content) was taken from Yantai-Borsodchem.Cyclohexanone and formaldehyde solution (37%) were supplied by Riedel-de Haen and Lab-Scan.

3.2 Synthesis of Silica sol

The silica sol was prepared according to the Stöber method. TEOS, absolute ethanol and acetic acid aqueous solution were mixed at molar ratios of H_2O/TEOS=1/2 and 4, respectively using the same molar ratio of TEOS/EtOH/CH_3COOH = 1/12/0.015, and reacted at 50 $^{\circ}$C; for 5 h. The resulting homogeneous solutions were transferred to a closed Petri dish and were allowed to stand at 60°C for 140 h. After waiting 140 h, the dried silica was prepared in powder form.

3.3 Synthesis of Polyurethane Polymer / Silica Sol

Polyurethane prepolymer was synthesized without and with silica sol. Polyester polyol, propylene glycol and silica silica sol was directly mixed (in different ratios of silica sol-%1.5-%3) at 70 ^{o}C under nitrogen blanket for 0.5 h by vigorous stirring. After reaching 70°C, MDI was added. For isocyanates two different types of

isocyanates were used (monomeric MDI and modified MDI). Reactions were monitored for 3 hours and the NCO % was checked every hour. After 3 hours tin catalyst is added for termination of polymerization. The viscosity increased after addition of catalyst so xylene was used for the adjustment of the viscosity.

Table 3.1: Contents of trials, which were done with monomeric MDI

Trial Name	Isocyanate	% Silica Sol
A –PU-1	Monomeric MDI	without
A –PU-2	Monomeric MDI	1,5
A –PU-3	Monomeric MDI	3

Table 3.2: Contents of trials that were done with modified MDI

Trial Name	Isocyanate	% Silica Sol
B –PU-1	Modified MDI	without
B –PU-2	Modified MDI	1,5
B –PU-3	Modified MDI	3

3.4 Synthesis of Polyurethane /Cyclohexanone Formaldehyde Resin Composite

98 g (1 mol) of cyclohexanone, 25 mL of cyclohexane and 30 mL of 37% formalin put into a three-necked flask equipped with a stirrer and a condenser. When the temperature of the mixture was raised to 65-70 ^{o}C, refluxing started, subsequently, 100 mL of 37% formalin was added. As a catalyst NaOH solution (20 wt%) was used. The reaction was further continued under pH values of 11-12 for 5h. After reaction time was completed, two layers were formed. The resin was separated and purified by decanting the water layer. The resin was washed several times with warm water until it was free from and it was dried at 100°C in vacuum.

For the preparation of PU-CFR composite, firstly silica containing polyurethane polymer was synthesized as it is mentioned above and before addition of catalyst, CFR solved in xylene and added to the polymer-silica mixture. The NCO % of the polymer checked and lastly tin catalyst is added for termination of polymer.

Table 3.3: Content of trials that were done with modified and monomeric MDI

Trial Name	Isocyanate	% Silica Sol	% CFR
A –PU-4	Monomeric MDI	Without	20
A –PU-5	Monomeric MDI	3	20
B –PU-4	Modified MDI	Without	20
B –PU-5	Modified MDI	3	20

4. RESULTS AND DISCUSSION

4.1 Reaction Mechanism and Characterization of Silica

As it is well-known, the sol-gel process can be viewed as a two-step network forming process, the first step being the hydrolysis of a metal alkoxide and the second consisting of a polycondensation reaction. Most of the interest in this method is concentrated on metal-organic alkoxides, especially silica, since they can form an oxide network in organic matrices. The sol-gel reactions of alkoxysilane can be described as follows:

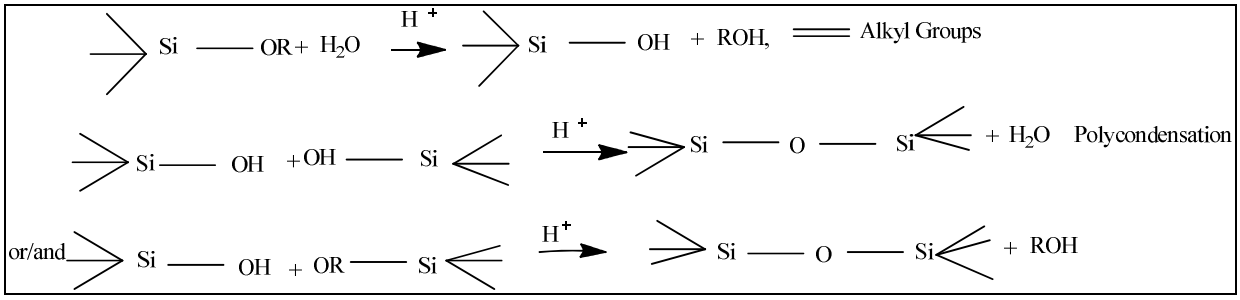

Figure 4.1: Reactions of TEOS with acid catalyst

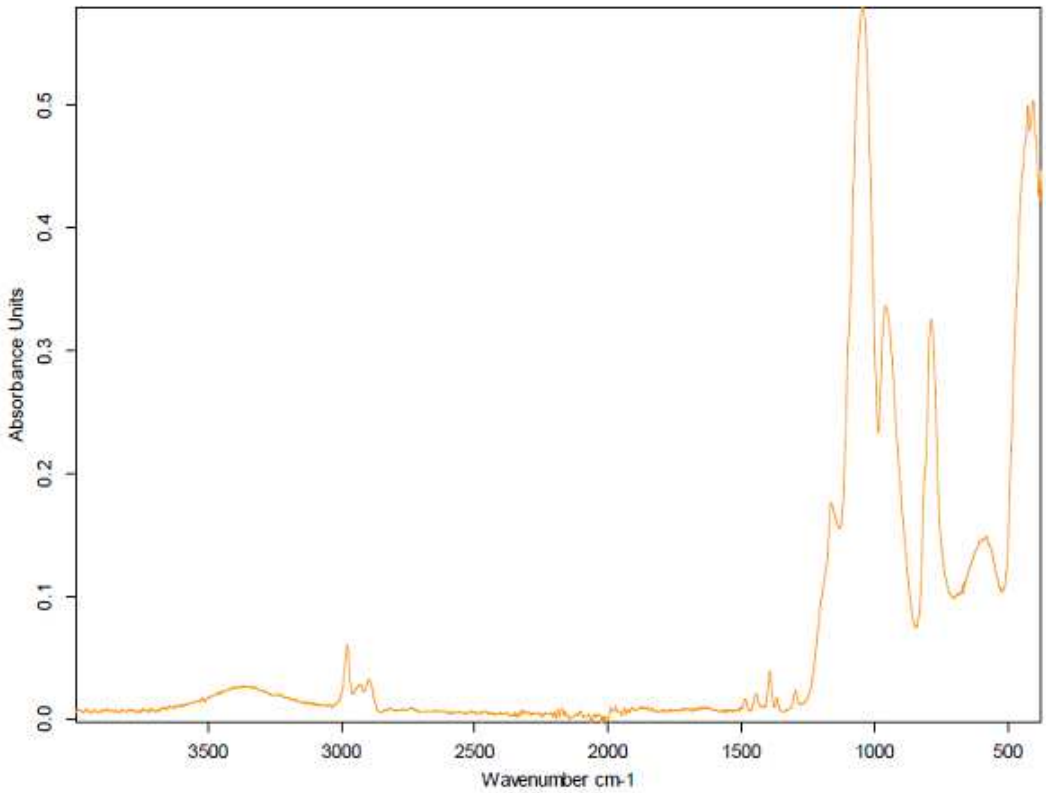

Figure 4.2: FT-IR of Silica

4.2 Reaction Mechanism and Characterization of Silica Containing Polyurethane Polymer

PU polymer was synthesized with 3% free NCO. According to literature characteristic wavelength of PU (functional group; N=C=O) must be between 2200-2300 cm^{-1}. As it can be seen from the Figure 4.3 and 4.4, polyurethane structure observed and showed that functional group is at 2259 cm^{-1}.

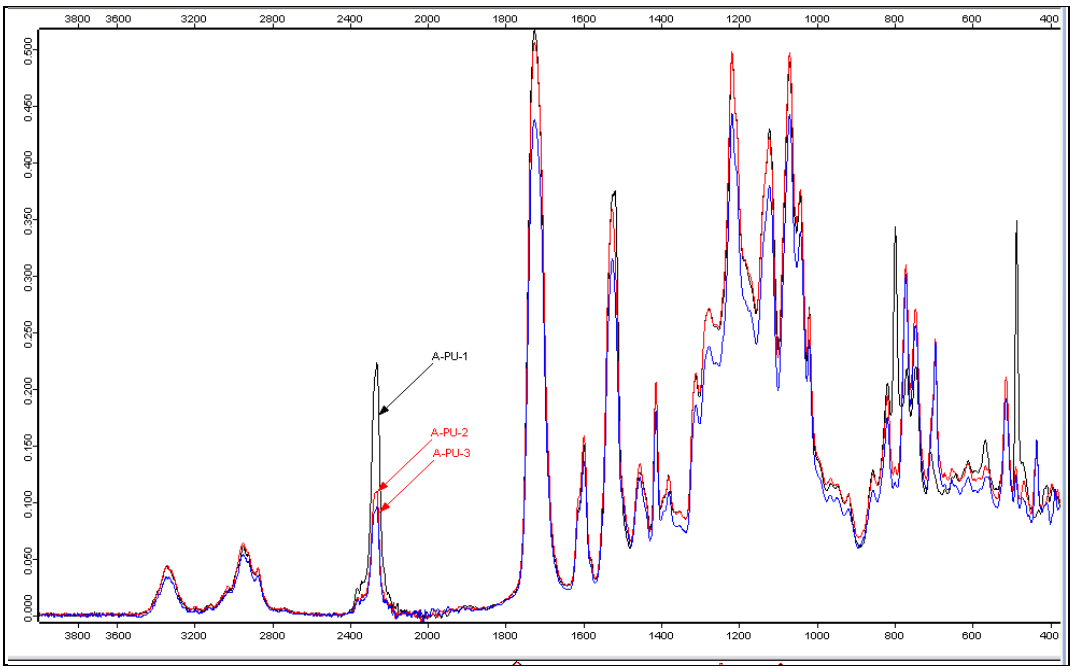

Figure 4.3: FT-IR of polyurethanes done with Monomeric MDI (A-PU-1-2-3)

The functional groups (OH) of silica also reacted with the isocyanate. The functional group polyurethane polymer (N=C=O) reached the lowest value (Figure 4.3) with 3% Silica addition,

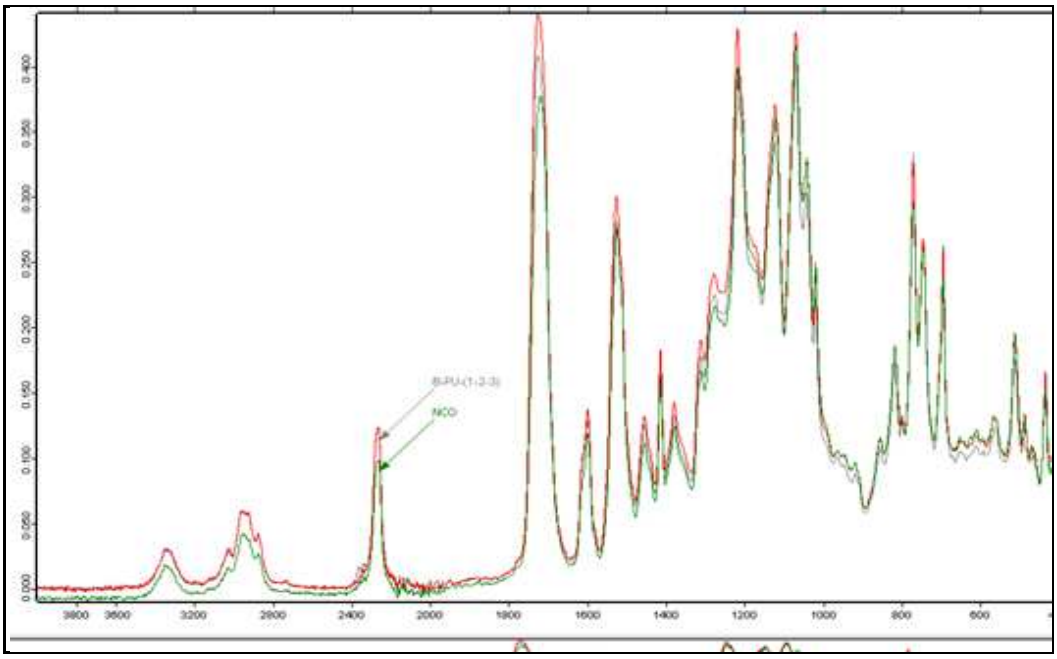

Figure 4.4: FT-IR of polyurethanes made with Modified MDI-(B-PU-1-2-3)

Reaction with monomeric MDI gave better results than modified MDI. Figure 4.4 shows that, in trials B-PU-2 and 3, silica did not have big effect on the polyurethane structure.

4.3 Reaction Mechanism of CFR

The formation of CF resin starts with an aldol-like reaction. Reaction follows a base catalyzed elimination reaction of water from methylol derivatives of cyclohexanone. Then methylol derivatives of cylohexanones are joining together and polymerizing with monomers in the reaction media. The final product, CF resin, is obtained with the polymerization between them. The figure of the reaction mechanism illustrated below (Figure 4.5).

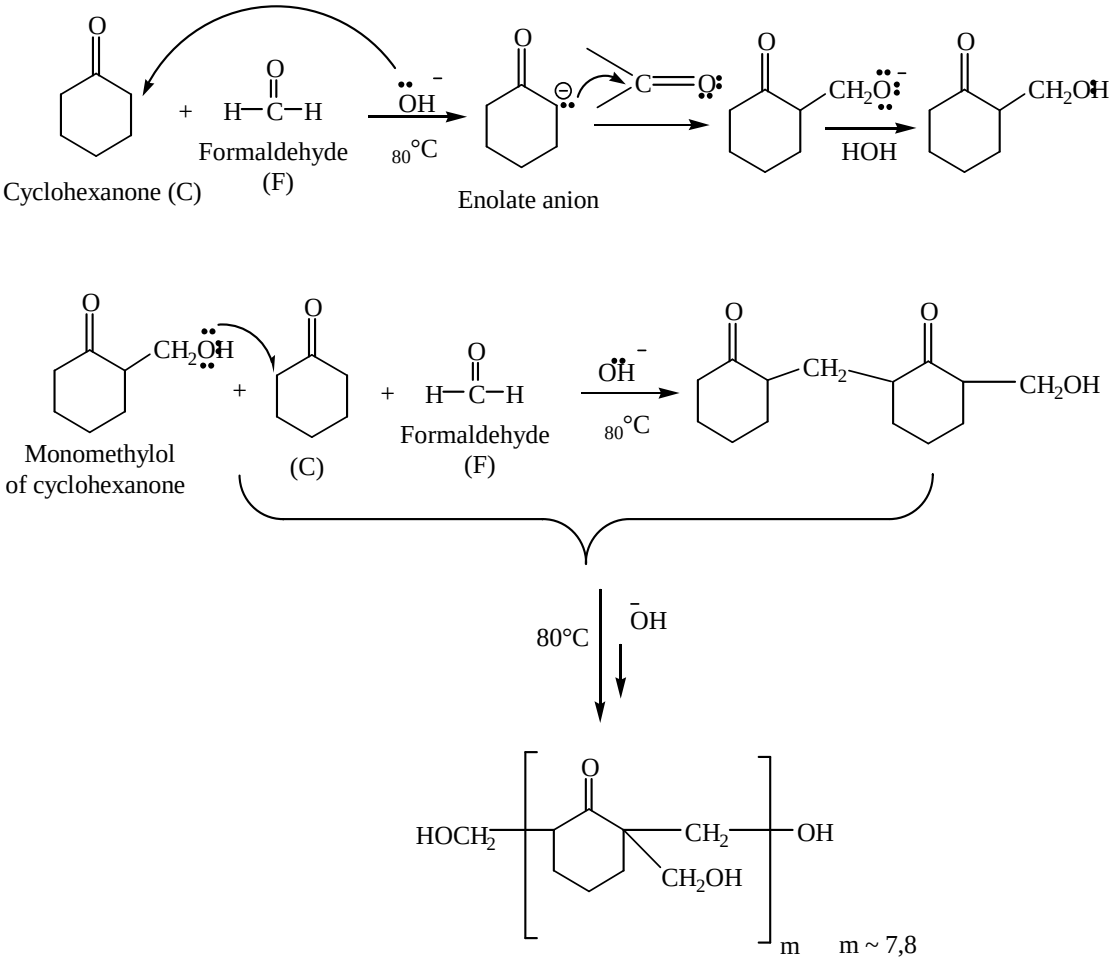

Figure 4.5: Reaction mechanism of CFR

4.4 Characterization of Silica Containing Polyurethane –CFR Composites

The ^{1}H-NMR spectra were recorded from the solvent solution which is $CDCl_2$. The peaks are appearing at about 1.1 – 2.4 ppm were due to the aliphatic -CH_2 and –CH groups, 3.2 – 4.2 ppm due to the –CH_2 methylen bridges and methyl groups, 4.5 – 4.8 ppm due to the –OH groups of the methyl groups .

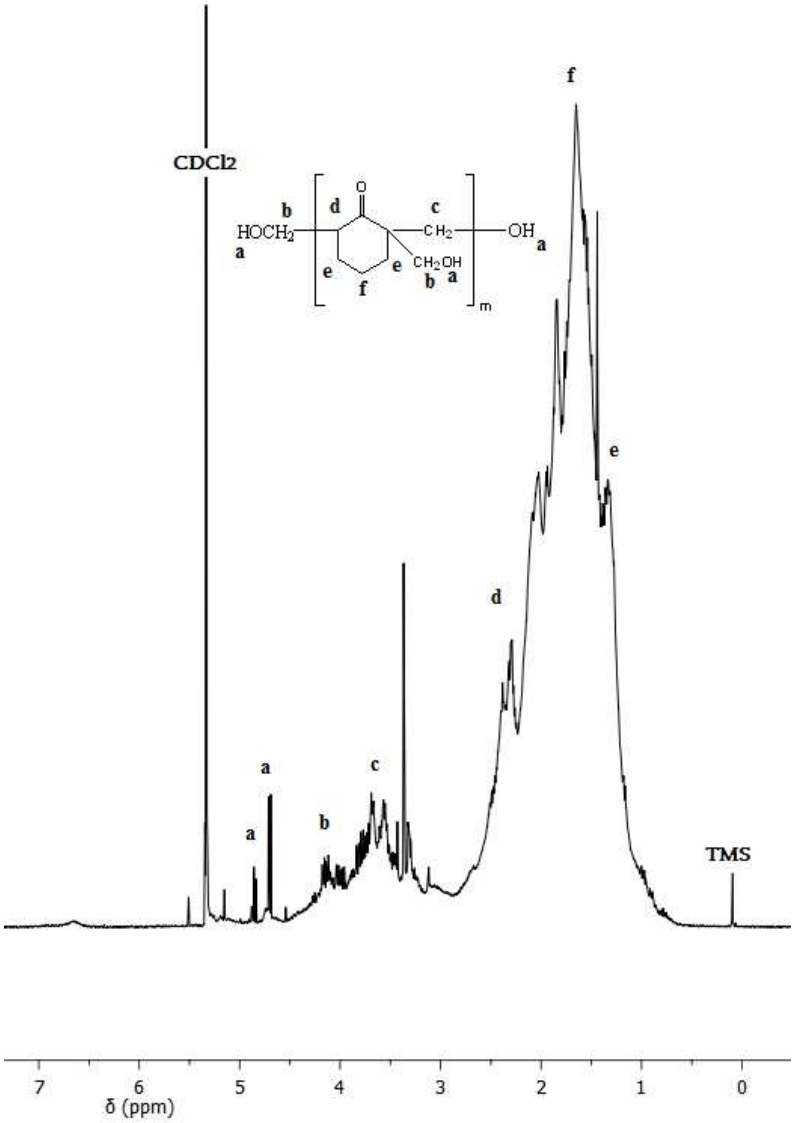

Figure 4.6: ^{1}H-NMR spectrum of CFR

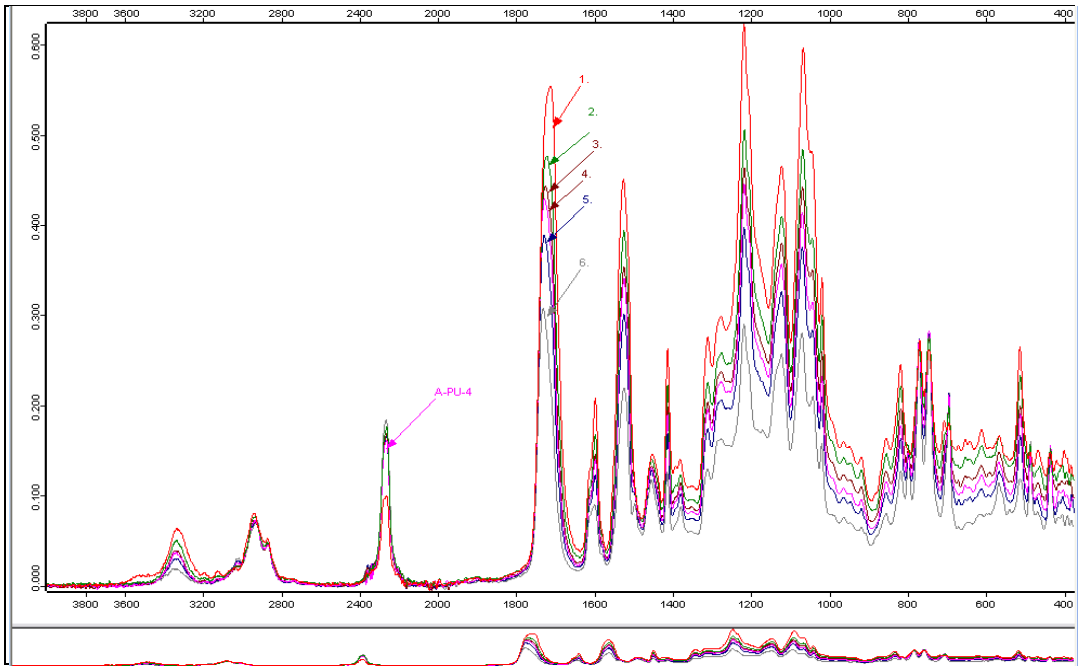

Figure 4.7: FT-IR of PU- CFR composite done with Monomeric MDI (A-PU-4)

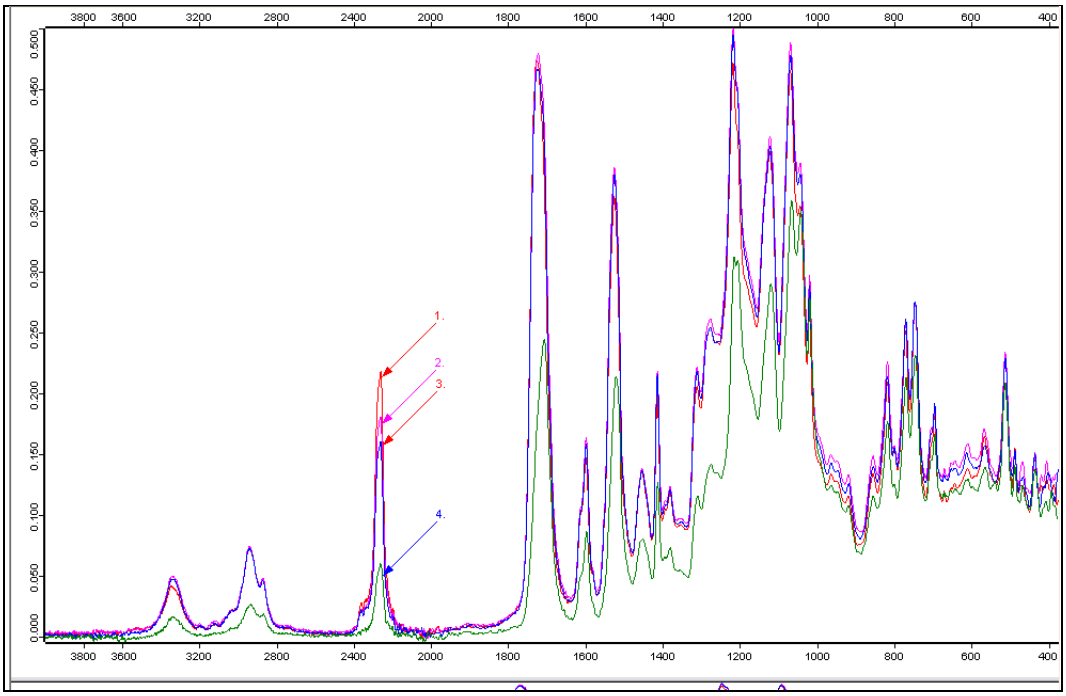

Figure 4.8: FT-IR of PU- CFR composite done with Monomeric MDI (A-PU-5)

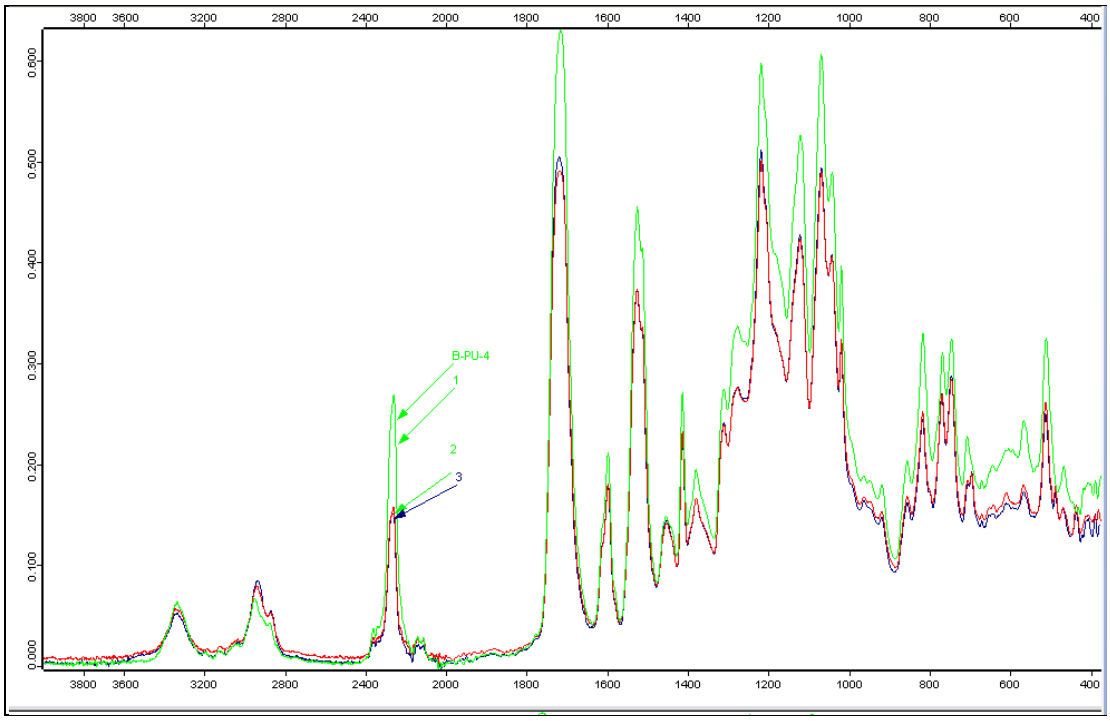

Figure 4.9: FT-IR of PU- CFR composite done with Modified MDI (B-PU-4)

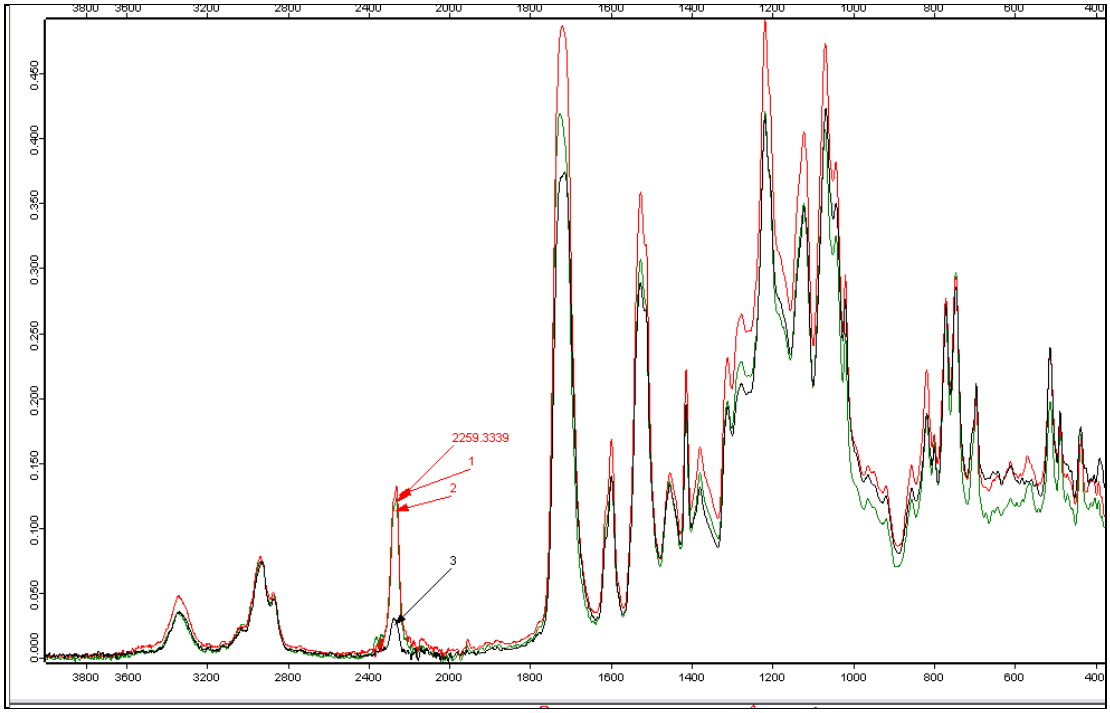

Figure 4.10: FT-IR of PU- CFR composite done with Modified MDI (B-PU-5)

CFR has functional groups (OH) that can react with isocyanate. Figure 4.7 and 4.8 show that after addition of CFR, the area of N=C=O (functional group) decreased.

According to integration method, the free isocyanate amount was calculated and found as < 1.5%. The tests were repeated with addition of silica (Figure 4.9-4.10) and it was observed that free isocyanate amounts reached the lowest values.

All the reactions were done in steps. CFR was solved in xylene and this mixture was added to polymer.

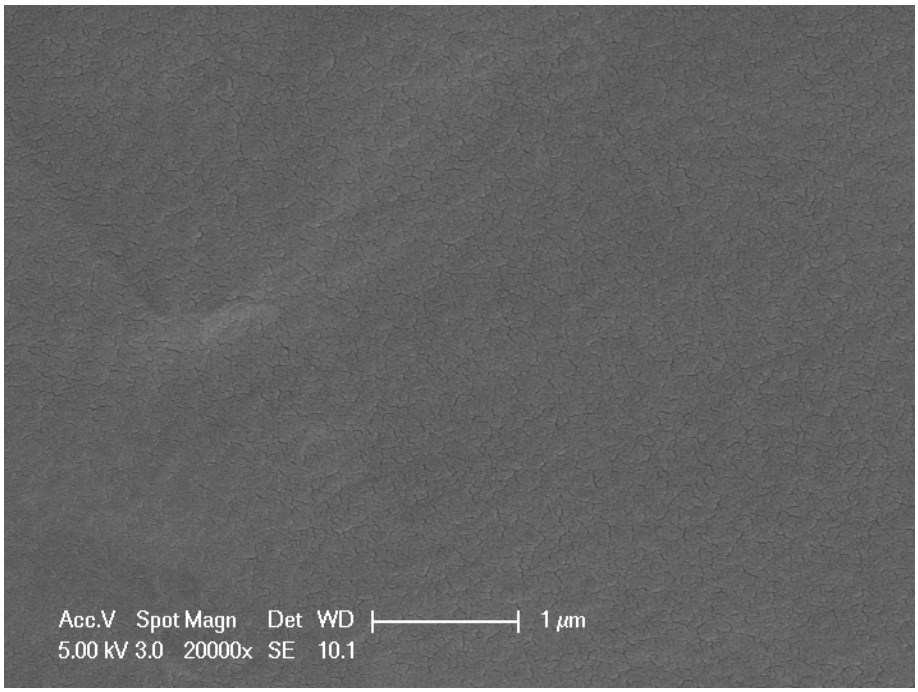

Figure 4.11: SEM of PU done with Modified MDI (B-PU-1)

Also the TGA of the samples were taken. As it can be seen from the Figure 4.12 (which the monomeric MDI and silica were tested) the trial containing silica started to broke up faster than the trial containing no silica.

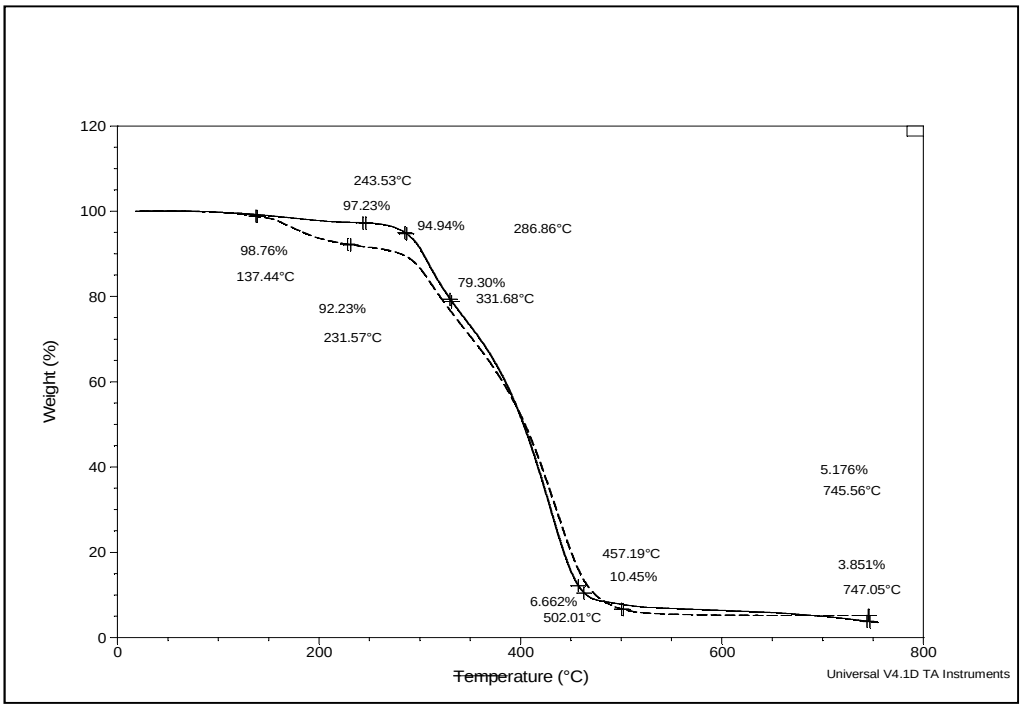

Figure 4.12: TGA of PU done with Monomeric MDI (A-PU-1-2)

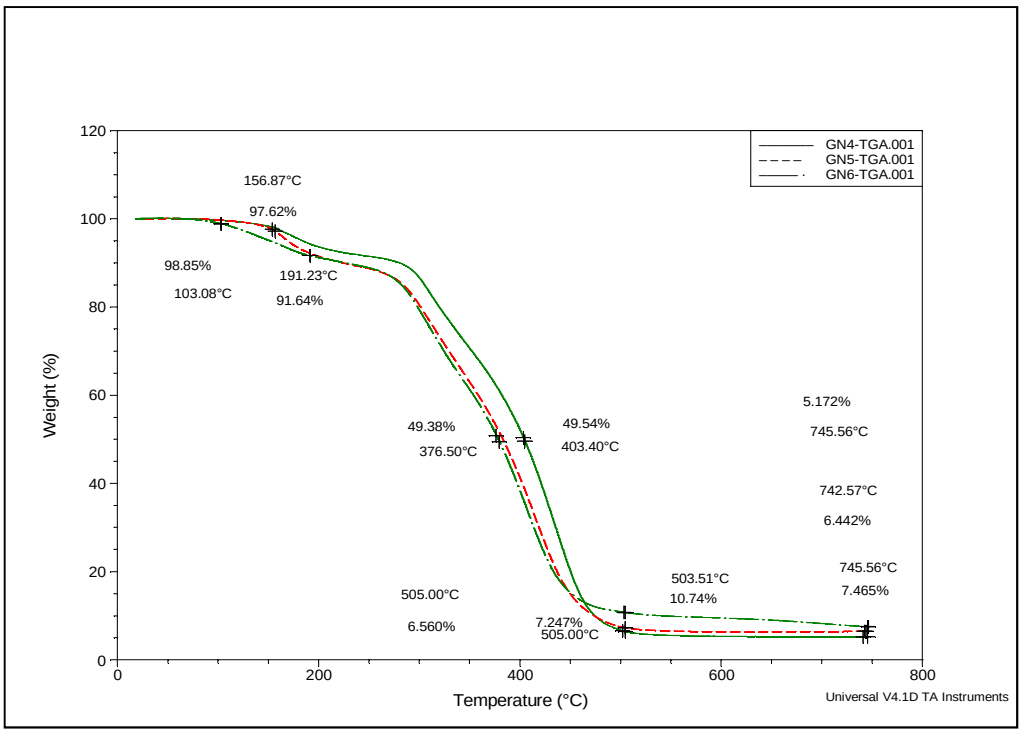

Figure 4.13: TGA of PU- CFR composite done with Modified MDI (B-PU-1-2-5)

On the other hand the residual of the A-PU- 2 has higher value than A-PU-1. The same results are obtained for the trials done with modified MDI.

4.5 Solvent Resistancy of Silica Containing Polyurethane-CFR Composite

Polymers were conditioned at 23 ^{o}C-50% Relative Humidity for 14 days. After conditioning, polymers weighted and placed in solvents and kept there 24 hours. The weight loss was measured at the end of the test.

Table 4.1: Physical Properties of Composites (with monomeric MDI)-Solubility

Sample Name	Sea Water (2%)	Acetic Acid (CH_3COOH)	Methanol (CH_3OH)	Chloroform ($CHCl_3$)	Xylene
A-PU-1	None	Low	None	Low	Low
A-PU-2	None	Low	None	Low	Low
A-PU-5	None	Low	None	Low	Low

Table 4.2: Physical Properties of Composites (with modified MDI)-Solubility

Sample Name	Sea Water (2%)	Acetic Acid (CH_3COOH)	Methanol (CH_3OH)	Chloroform ($CHCl_3$)	Xylene
B-PU-1	None	Low	None	Medium	Low
B-PU-2	None	Low	None	Medium	Low
B-PU-5	None	Low	None	Medium	Low

Table 4.1 and 4.2 show that the PU-CFR composite, prepared with modified MDI, have better solubility.

Also the shore hardness of the trials are measured.; results can be seen from the Table 4.3 and 4.4.

Table 4.3: Shore A hardness of Composites (with monomeric MDI)

Sample Name	Shore A
A-PU-1	45
A-PU-2	46
A-PU-3	46
A-PU-4	65
A-PU-5	67

Table 4.4: Shore A hardness of Composites (with modified MDI)

Sample Name	Shore A
B-PU-1	47
B-PU-2	47
B-PU-3	49
B-PU-4	76
B-PU-5	76

4.6 Weatherability of Silica Containing Polyurethane-CFR Composite

Polymers were conditioned at 23 ^{o}C-50% relative humidity for 14 days. After conditioning, weatherability test applied. Elastocon UV cabinet (Metal Halide Arc Lamp-1100 W/Im^2) was used. Samples were kept there 22 days. The cycle was 102 min dry time, 18 min wet time.

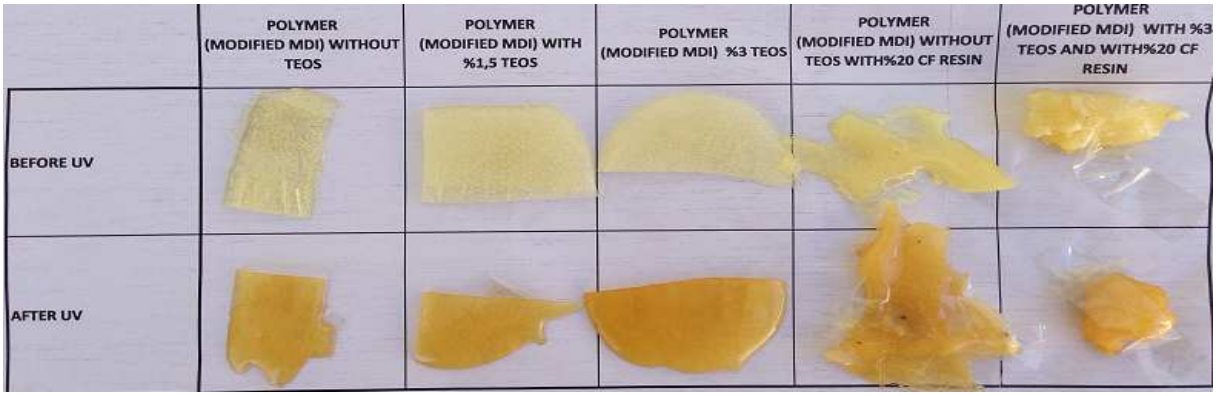

Figure 4.14: Weatherability test of polyurethane composite (with Modified MDI)

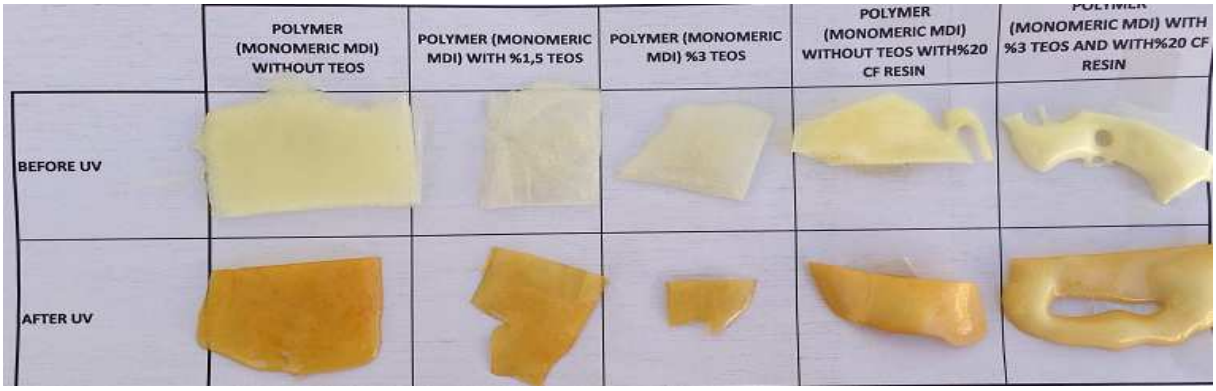

Figure 4.15: Weatherability test of polyurethane composite (with Monomeric MDI)

In this study aromatic isocyanates were used (Modified and monomeric). Aromatic isocyanates were weak in light and uv stabilization when they compared to aliphatic isocyanates. Addition of CFR and silica did not improve this property but as it can be seen from the Figure 4.15 that, A-PU-5 had low color change when compared to other trials.

5. CONCLUSION

FTIR results show that all the polyurethane polymers synthesized successfully. Also the copolymer of PU/CFR study, was completed properly. SEM of the polymer showed that; polymer have a straight structure. When the thermal properties of the trials are compared; it can be said that silica cause an early break up but there was a residual due to silica, at the end of heating procedure. Solubility of polymers done with Modified MDI is better than Monomeric MDI. Normally CFR has good solubility with different organic solvents but due its reaction with isocyanate, the PU-CFR composite material did not give good result. On the other side, the physical properties and weatherability of the trials are not well improved with CFR. Lastly, the shore hardness of the materials was tested and it is observed that CFR increased the shore hardness of the PU polymer.

For further trials instead of silica, TiO_2 can be used to improve the light/UV resistance of materials.

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PUBLICATIONS/PRESENTATIONS ON THE THESIS

Müjdeci, Ç., G., Kızılcan, N., 2013: Synthesis and Characterization of Silicate Nanaocomposites Containing Polyurethane Coating, Poster Presentation, *44th World Chemistry Congress*, 11th-16 thAugust, İstanbul TURKEY.