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Persual on synthesis, pattern and applications of polyurethane as functional macromolecule

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ABSTRACT

Polyurethanes are one of the most versatile materials in the world today. Their many uses range from flexible foam in upholstered furniture, to rigid foam as insulation in walls, roofs and appliances to thermoplastic polyurethane used in medical devices and footwear, to coatings, adhesives, sealants and elastomers used on floors and automotive interiors. For the manufacturing of polyurethane polymers, two groups of at least bifunctional substances are needed as reactants; compounds with isocyanate groups, and compounds with active hydrogen atoms. Polyurethane can be made in a variety of densities and hardnesses by varying the type of monomer(s) used and adding other substances to modify their characteristics, notably density, or enhance their performance. The physical and chemical character, structure, and molecular size of these compounds influence the polymerization reaction, as well as ease of processing and final physical properties of the finished polyurethane. In addition, additive such as catalysts, surfactants, blowing agents, cross linkers, flame retardants, light stabilizers, and fillers are used to control and modify the reaction process and performance characteristics of the polymer.
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INTRODUCTION

Polyurethanes are one of the most versatile materials in the world today. Their many uses range from flexible foam in upholstered furniture, to rigid foam as insulation in walls, roofs and appliances to thermoplastic polyurethane used in medical devices and footwear, to coatings, adhesives, sealants and elastomers used on floors and automotive interiors[1,2]. Polyurethanes have increasingly been used during the past thirty years in a variety of applications due to their comfort, cost ben-

efits, energy savings and potential environmental soundness.

A polyurethane, commonly abbreviated PU, is any polymer consisting of a chain of organic units joined by urethane links. Polyurethanes (PU) are the polymers containing significant number of urethane groups (-NH-CO-O-) in the molecular chain. Polyurethane polymers are formed by reacting a monomer containing at least two isocyanate functional groups with another monomer containing at least two alcohol groups in the presence of a catalyst as shown in figure 1.
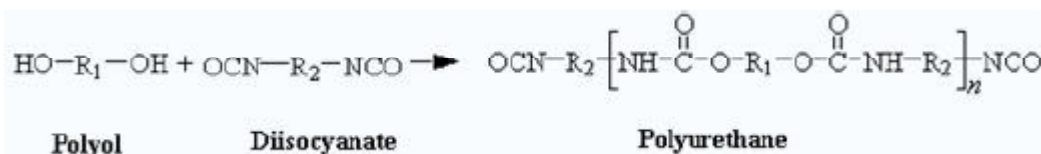

Figure 1: Schematic of polyurethane synthesis

The most common method of preparing polyurethane is condensation reaction of a diisocyanate and a polyol. Unlike conventional polycondensation, this polymerisation reaction does not eliminate any by-product.
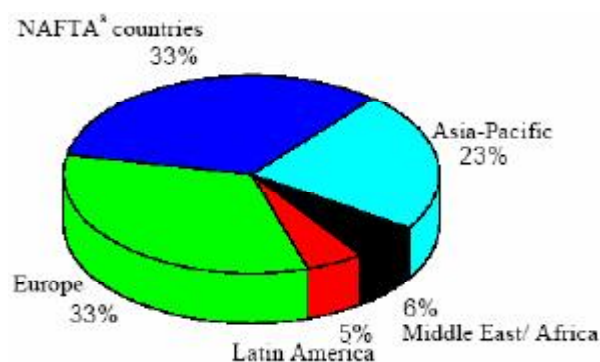
Ever since their discovery by Otto Bayer and co-workers in 1937[3,10], polyurethanes have developed as a unique class of materials and have found use in a wide variety of applications. The name polyurethane was derived from ethyl carbamate, also known as urethane. Besides incorporating the urethane linkage, these materials also sometimes contain several other types of linkages such as amide, urea, ether, and ester[7,8]. The urethane linkage is formed by the reaction of an isocyanate group of one reactant with the alcohol group of

Figure 2:Worldwide consumption of polyurethanes[6]

another component. By controlling variables such as the functionality, chemical composition, and the molecular weight of the different reactants, a wide class of materials with significantly varying properties can be obtained. This flexibility has led polyurethanes to find use as synthetic polymers in foams, elastomers, coatings, sealants, and adhesive based products. Some of the applications of polyurethanes lie in the automotive, furniture, construction, thermal insulation, and footwear industries. The 2000 urethanes market was estimated to be of the order of 8.2 million metric tons worldwide as shown in figure 2[6].

Polyurethane durability contributes significantly to the long lifetimes of many products. The extensions of product life cycle and resource conservation are important environmental considerations that often favor the selection of polyurethanes[3-5].

Polyurethanes (PUs) represent an important class of thermoplastic and thermoset polymers as their mechanical, thermal, and chemical properties can be tailored by the reaction of various polyols and polyiso cyanates.

One of the major sectors of the polyurethane industry is flexible foam, which are manufactured by the controlled expansion of a gas during the polymerization process[7]. Flexible polyurethane foams are designed to be open-celled, i.e., at the completion of foam expansion, the cells open and form a structure composed
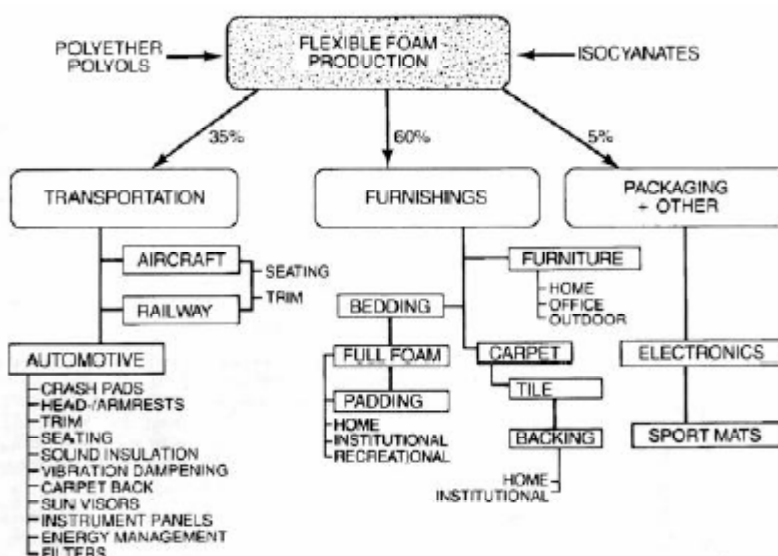

Figure 3: Applications for flexible polyurethane Foams[7]

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of interconnected polymer struts, which allow the free movement of a gas within the foam cells. The properties of flexible polyurethane foams depend on both, the elastomeric character of the polymer comprising the foams, as well as the geometry of the cells. Over the years, polyurethane foams have intrigued a broad spectrum of scientists who have tried to provide better solutions to the consumer by investigating the chemistry, physics, engineering, and economic aspects of these materials. As shown in figure 3, flexible polyurethane foams are used in applications such as seating, cushioning, carpet underlayment, fabric backing, insulation, and packaging.

The first commercial production of flexible polyurethane foams, based on the reaction between an aromatic isocyanate and a polyester polyol, was carried out in 1954[7]. However, these foams were unable to withstand the severe humidity and temperature conditions in which they were used, and thus foams based on polyether polyols were developed. These second generation foams provided better durability as well as comfort. A major advancement in polyurethane technology was the introduction of the 'one-shot' system using new catalysts and silicone-based surfactants. In the one-shot process; the isocyanate, polyol, water, and other ingredients are rapidly and intensively mixed and immediately poured to carry out the foaming. Since then, advances in flexible polyurethane foam technology have been numerous, all targeted to provide the customer with enhanced performance properties, while trying to improve process ability, increase production rates, and lower costs. The more than five-decade-old technology of polyurethane foams might have been expected to reach a mature growth by now. However, formulations based on newer and more sophisticated applications continue to develop, thus demanding a better understanding of the structure-property correlations. Also, the evaluation of foam morphology using techniques such as atomic force microscopy[8] and x-ray microscopy[9] has opened avenues to improve the understanding of these materials.

Commercial production of flexible polyurethane foam began in 1954, based on toluene diisocyanate (TDI) and polyester polyols. The invention of these foams (initially called imitation swiss cheese by the inventors[11]) was thanks to water accidentally introduced in the reaction mix. These materials were also used to produce rigid foams, gum rubber, and elastomers. Linear fibres were produced from hexamethylene diisocyanate (HDI) and 1,4-butanediol (BDO).

Another early pioneer in PU's was the Mobay corporation[11]. In 1960 more than 45,000 tons of flexible polyurethane foams were produced.

Starting in the early 1980s, water-blown micro cellular flexible foam was used to mold gaskets for panel and radial seal air filters in the automotive industry. Since then, increasing energy prices and the desire to eliminate PVC plastisol from automotive applications have greatly increased market share. Costlier raw materials are offset by a significant decrease in part weight and in some cases, the elimination of metal end caps and filter housings. Highly filled polyurethane elastomers, and more recently unfilled polyurethane foams are now used in high-temperature oil filter applications[12-18].

Building on existing polyurethane spray coating technology and polyetheramine chemistry, extensive development of two-component polyurea spray elastomers took place in the 1990s. Their fast reactivity and relative insensitivity to moisture make them useful coatings for large surface area projects, such as secondary containment, manhole and tunnel coatings, and tank liners. Excellent adhesion to concrete and steel is obtained with the proper primer and surface treatment. During the same period, new two-component polyurethane and hybrid polyurethane-polyurea elastomer technology was used to enter the marketplace of spray-in-place load bed liners[18-23]. This technique for coating pickup truck beds and other cargo bays creates a durable, abrasion resistant composite with the metal substrate, and eliminates corrosion and brittleness associated with drop-in thermoplastic bed liners.

The chemistry of PU

In polyurethane synthesis, tuning the ratio and composition of the isocyanate and alcohol components results in a segmented block copolymer consisting of alternating hard and soft blocks. The reaction of an isocyanate group with a chain extender and subsequent phase separation of the hard segments formed from this reaction, results in the formation of hard blocks; which are referred to as 'hard', since they are below their softening temperature at ambient conditions. These hard

blocks are covalently bound through urethane linkages to 'soft' polyether or polyester segments which are above their softening temperature, Tg, at ambient conditions. The phase separation generally leads to good elastomeric properties wherein the hard blocks serve as filler particles and also act as physical cross-linking points.

1. Isocyanate

The first essential component of a polyurethane polymer is the isocyanate. Molecules that contain two isocyanate groups are called diisocyanates. These molecules are also referred to as monomers or monomer units, since they themselves are used to produce polymeric isocyanates that contain three or more isocyanate functional groups. Isocyanates can be classed as aromatic, such as diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI); or aliphatic, such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI). An example of a polymeric isocyanate is polymeric diphenylmethane diisocyanate, which is a blend of molecules with two-, three-, and four- or more isocyanate groups, with an average functionality of 2.7. Isocyanates can be further modified by partially reacting them with a polyol to form a prepolymer. A quasi-prepolymer is formed when the stoichiometric ratio of isocyanate to hydroxyl groups is greater than 2:1. A true prepolymer is formed when the stoichiometric ratio is equal to 2:1. Important characteristics of isocyanates are their molecular backbone, % NCO content, functionality, and viscosity.

2. Polyol

The second essential component of a polyurethane polymer is the polyol. Molecules that contain two hydroxyl groups are called diols, those with three hydroxyl groups are called triols, et cetera. In practice, polyols are distinguished from short chain or low-molecular weight glycol chain extenders and cross linkers such as ethylene glycol (EG), 1,4-butanediol (BDO), diethylene glycol (DEG), glycerine, and trimethylol propane (TMP). Polyols are polymers in their own right. They are formed by base-catalyzed addition of propylene oxide (PO), ethylene oxide (EO) onto a hydroxyl or amine containing initiator, or by polyesterification of a di-acid, such as adipic acid, with glycols, such as ethyl-

ene glycol or dipropylene glycol (DPG). Polyols extended with PO or EO are polyether polyols. Polyols formed by polyesterification are polyester polyols. The choice of initiator, extender, and molecular weight of the polyol greatly affect its physical state, and the physical properties of the polyurethane polymer. Important characteristics of polyols are their molecular backbone, initiator, molecular weight, % primary hydroxyl groups, functionality, and viscosity.

3. Surfactants

Surfactants are used to modify the characteristics of the polymer during the foaming process[23-34]. They are used to emulsify the liquid components, regulate cell size, and stabilize the cell structure to prevent collapse and surface defects. Rigid foam surfactants are designed to produce very fine cells and a very high closed cell content. Flexible foam surfactants are designed to stabilize the reaction mass while at the same time maximizing open cell content to prevent the foam from shrinking. The need for surfactant can be affected by choice of isocyanate, polyol, component compatibility, system reactivity, process conditions and equipment, tooling, part shape, and shot weight.

4. Chain extenders and cross linkers

The choice of chain extender determines flexural, heat, and chemical resistance properties of polymer[34-36].

Chain extenders (f=2) and cross linkers (f=3 or greater) are low molecular weight hydroxyl and amine terminated compounds that play an important role in the polymer morphology of polyurethane fibers, elastomers, adhesives, and certain integral skin and microcellular foams.

The elastomeric properties of these materials are derived from the phase separation of the hard and soft copolymer segments of the polymer, such that the urethane hard segment domains serve as cross-links between the amorphous polyether (or polyester) soft segment domains. This phase separation occurs because the mainly non-polar, low melting soft segments are incompatible with the polar, high melting hard segments. The soft segments, which are formed from high molecular weight polyols, are mobile and are normally present in coiled formation, while the hard segments,

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which are formed from the isocyanate and chain extenders, are stiff and immobile. Because the hard segments are covalently coupled to the soft segments, they inhibit plastic flow of the polymer chains, thus creating elastomeric resiliency.

The most important chain extenders are shown in TABLE.

TABLE 1: The famous chain extenders and cross linkers[39]

hydroxyl compounds - difunctional molecules				
	MW	s.g.	f.p. °C	b.p. °C
Ethylene glycol	62.1	1.110	-13.4	197.4
Diethylene glycol	106.1	1.111	-8.7	245.5
Triethylene glycol	150.2	1.120	-7.2	287.8
Tetraethylene glycol	194.2	1.123	-9.4	325.6
Propylene glycol	76.1	1.032	supercools	187.4
Dipropylene glycol	134.2	1.022	supercools	232.2
Tripropylene glycol	192.3	1.110	supercools	265.1
1,3-propanediol	76.1	1.060	-28	210
1,3-butanediol	92.1	1.005	-	207.5
1,4-butanediol	92.1	1.017	20.1	235
Neopentyl glycol	104.2	-	130	206
1,6-hexanediol	118.2	1.017	43	250
1,4-cyclohexanedimethanol	-	-	-	-
Hqee	-	-	-	-
Ethanolamine	61.1	1.018	10.3	170
Diethanolamine	105.1	1.097	28	271
Methyldiethanolamine	119.1	1.043	-21	242
Phenyldiethanolamine	181.2	-	58	228
Hydroxyl compounds - trifunctional molecules				
	MW	s.g.	f.p. °C	b.p. °C
Glycerol	92.1	1.261	18.0	290
Trimethylolpropane	-	-	-	-
1,2,6-hexanetriol	-	-	-	-
Triethanolamine	149.2	1.124	21	-
Hydroxyl compounds - tetrafunctional molecules				
	MW	s.g.	f.p. °C	b.p. °C
Pentaerythritol	136.2	-	260.5	-
N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine	-	-	-	-
Amine compounds - difunctional molecules				
	MW	s.g.	f.p. °C	b.p. °C
Diethyltoluenediamine	178.3	1.022	-	308
dimethylthiotoluenediamine	214.0	1.208	-	-

5. Catalysts

Catalysts are added to allow the polymerization reaction to take place at a rapid rate, and at lower temperatures. For the reaction of an isocyanate with an
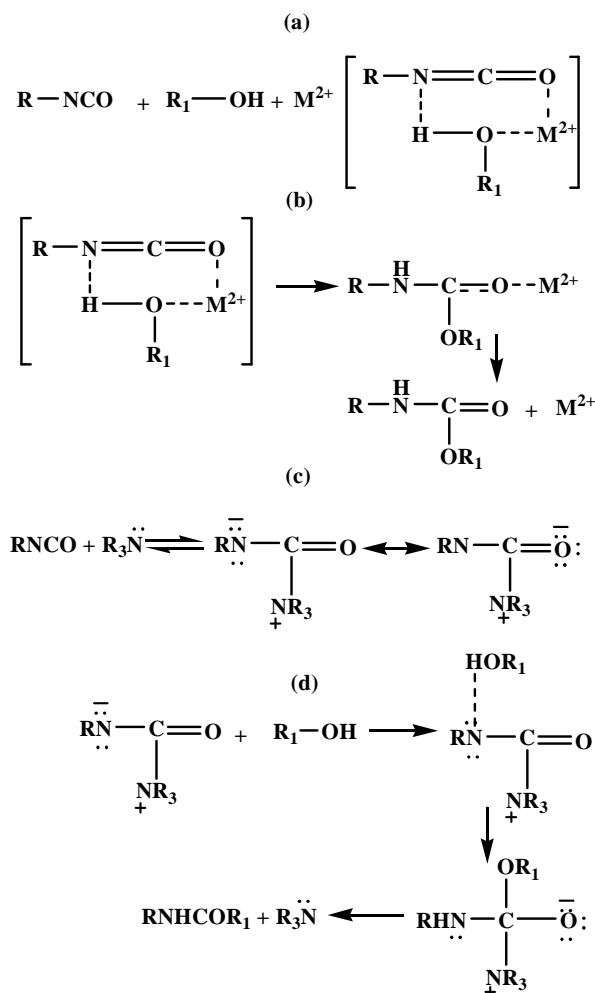
Figure 4: Reaction mechanism for the NCO/OH reaction due to: (a) and (b) organometallic

alcohol, many effective urethane catalysts are available. Most often used catalysts are tertiary amines[41,42], especially 1,4-diazabicyclo[2.2.2] octane (DABCO), triethyl amine (TEA), and organo tin compounds[43], especially dibutyltin dilaurate (DBTDL), stannous octoate and THORCAT. Tetravalent tin compounds of the type RnSnX(4_n) with R being a hydrocarbon group (alkyl, aryl, cycloalkyl, etc.) and X being a halogen atom or a carboxylate group (acetate, laurate, etc.) have shown catalytic effect in urethane reaction[44]. The catalytic effect of organometallic compounds is due to their complex forming ability with both isocyanate and hydroxyl groups[45,46]. The mechanism proposed by Britain and Gemeinhardt[47] is shown in figure 4. The interation of metal cation with isocyanate, alcohol molecule results an intermediate complex (Figure 4a), which may then readily rearrange to yield the urethane product (Figure

4b). Lenz[48] suggested that the catalysis mechanism of tertiary amines (NR3) for urethane reaction involve complexation of the amine and isocyanate groups (Figure 4c) followed by reaction of the complex with alcohol to form urethane product (Figure 4d)[49]. The mercury catalyst THORCAT, however, is less efficient than either catalyst, perhaps due to a higher stability constant for the latter compound. Furthermore, mercury salt catalysts are thought to possess delayed action properties[50], which may also account for their reduced performance compared with other metal compounds[51].

PU production technique

As mentioned before, the properties of the polyurethane are determined mainly by the choice of polyol, the diisocyanate exerts some influence, and must be suited to the application. The cure rate is influenced by the functional group reactivity and the number of functional isocyanate groups. The mechanical properties are influenced by the functionality and the molecular shape. The choice of diisocyanate also affects the stability of the polyurethane upon exposure to light. Polyurethanes made with aromatic diisocyanates yellow with exposure to light, whereas those made with aliphatic diisocyanates are stable[52].

Softer, elastic, and more flexible polyurethanes result when linear difunctional polyethylene glycol segments, commonly called polyether polyols, are used to create the urethane links. This strategy is used to make spandex elastomeric fibers and soft rubber parts, as well as foam rubber. More rigid products result if polyfunctional polyols are used, as these create a three-dimensional cross-linked structure which, again, can be in the form of low-density foam.

PU coating and nanotechnology

Polyurethanes have been used in the coating industry for approximately 45 years[53].

Polyurethane-based coatings have an established place in the coatings industry. In some applications they dominate the market. There are two main reasons for this. The first is that polyurethane coatings yield a very high level of quality. They combine outstanding resistance to solvents and chemicals with good weather stability. It is possible to formulate both clearcoats and because of their good pigment wetting properties-pig-

mented topcoats which yield high-gloss, high-bodied films with excellent flow properties. The films have outstanding mechanical properties and provide the ideal balance of hardness and flexibility, even at low temperatures. Good scratch resistance is also a feature of polyurethane coatings. This high level of quality results from the primary and secondary structures of the polyurethane chains[54]. The polymer chains are protected against solvents, acids, bases and other chemicals by the urethane groups which are resistant to chemicals, especially to hydrolysis and by the high density of hydrogen bridge bonds which form a stable physical network. The hydrogen bridge bonds and the block-like structure of the polyurethane chains in hard and soft segments, which can combine and arrange themselves in microdomains, ensure the outstanding mechanical properties of the paint film[54]. The second reason is the high variability of the property profile of polyurethane coatings. The coating system can be tailored for a specific application by varying, e.g. the chemical structure of the soft segments (e.g. polyether, polyester or polycarbonate), the distribution and length of the hard segments (i.e. the density of the physical network yielded by the hydrogen bridge bonds and other interactions) or the molecular weight and degree of branching of the chains. The hard segments govern, e.g. the hardness, strength and toughness of the paint film. The soft segments determine the flexibility, low-temperature flexibility and glass transition temperature Tg. Polyurethane chemistry also permits the incorporation of additional building blocks and functional groups which can be used to tailor properties such as the feel of the film, dispersibility in water or cross-linking. Polyurethane coatings may dry physically, by oxidation or with the aid of a cross-linking agent.

1. Automotive clear coat

One of the most important properties of automotive clear coats is their scratch resistance, so there is a big challenge among automobile producing companies to improve the quality of their final coating[55]. The scratch resistance of a coating is even more important in refinish coating because the cars are normally used very soon after paint application so that the coating does not have enough time to reach its ultimate hardness. Several methods have been utilized to improve the

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scratch resistance of coatings. The application of nano-fillers is one of the most widely used methods for improving the mechanical properties of polymeric coatings[56,57].

The effect of nano layered silicates on the properties of an automotive refinish clear coat based on polyurethane has been studied by B. Ahmadi and others[58]. A synthetic nano layered silicate was dispersed in polyurethane matrix in different weight percents. The XRD results showed partially increase in inter-layer distance of layered silicates which means a partially intercalated nanocomposite. Scratch and mar resistance tests, showed significant improvement in nano-filled coating's properties. The adhesion was increased for 1 and 3 wt% nano-filled samples. The gloss was not changed till 3 wt% of nano-filler. Gloss retention test showed 10% increase. Other standard properties of a clear coat like impact or bending resistance were not changed. Attention to spectral study of reflectance spectra of clear coats, 3 wt% nano layered silicate filled clear coat was preferred as the best percentage.

2. Nano composite

Two different types of nano-silica (i.e. hydrophilic and hydrophobic nano-silica) were employed as fillers in order to vary the properties of the resultant nano-composite polyurethane coatings[59].

Various morphological, mechanical, rheological and optical properties of such coatings were investigated. The results showed that coatings based on hydrophilic nano-silica gave a less transparent more UV absorbent coating. However, coatings based on hydrophobic nano-silica gave more miscible, transparent coating having improved mechanical properties especially scratch resistance. In the fluid state these coatings showed shear thinning behavior. The optimum range of adding 4-8% by weight of hydrophobic nano-silica to the chosen 2-pack acrylic polyol polyurethane clear coat gave optimal morphological, rheological, mechanical and optical properties to the final nano-composite coatings.

The polyurethane/titania (PU/TiO2) nanocomposites were prepared in ultrasonic process and characterized electron microscopy and SEM (scanning electron microscopy) by Yuming Zhou and coauthors[60].

Results indicated that the nanoparticles were dispersed homogeneously in PU matrix on nanoscale.

TGA-DSC confirmed that the heat stability of the composite was improved. Infrared emissivity study showed that the nanocomposite possessed lower emissivity value than those values of pure polymer and nanoparticles.

A sonochemical method employed here may be a simple and inexpensive route to synthesize the PU/nano-TiO2. Infrared emissivity study at wavelength of 8-14μm of nanocomposite and its components showed that the composite possessed lower emissivity value than those of pure PU and TiO2, and interfacial interactions had great effect on emissivity of nanocomposites. Thereby, the nanocomposites can be extended in application as a novel low infrared emissivity material.

Kinetics of polyurethane preparation reaction

The prepolymerization and curing reaction kinetics of polyurethane/montmorillonite have been studied with end group analysis and FTIR respectively by You Cao and coauthors[61]. Montmorillonite was modified with acidification and organic modification. Prepolymerization and curing reaction kinetics of polyurethane/montmorillonite nanocomposites were studied.

The reaction system was noted as various PUs (PU, PU-1, PU-2, PU-3, PU-4) when the Org-MMT contents were 1%, 2%, 3%, 4% respectively The reaction of PPG and TDI was a 2nd-order reaction:

$d\alpha/dt = k[OH][NCO]$

α is the NCO content which had been consumed, k is the rate constant, t is reaction time. In prepolymerization, $[OH] \neq [NCO]$. Note the initial OH content as x, initial NCO content as y. k can be calculated from:

$$\text{In}\frac{y-\alpha}{x-\alpha} - \text{In}\frac{y}{x} = k(y-\alpha)t$$

Arrhenius formula: $\text{In } k = \text{In } A - \dfrac{Ea}{RT}$

$R = 8.314 \, J \, mol^{-1} K^{-1}$

The plots of ln (y-α) /(x- α) against t at 50 8C are shown in figure 5. The plot of ln (y-α) /(x-α) against t was linear in prepolymerization system. It can be concluded that the prepolymerization was still 2nd-order after the montmorillonite was added into the reaction system as shown in figure 6. Ea of pure PU prepoly merization system was 42.7 kJ/mol, and closed to 42 kJ/mol which had been reported[62,63].

PU recycling and recovery
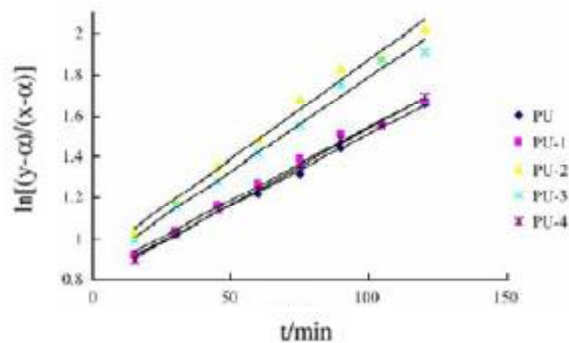
Figure 5: The plots of ln (y-α) /(x-α) against t of various sample
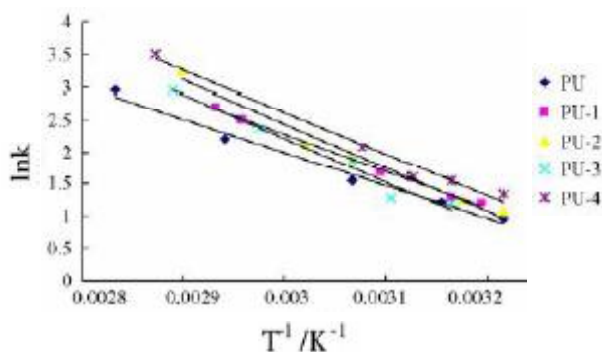
Figure 6: The plots of ln K against 1/T

Recent progress in the recycling and recovery of polyurethane and polyurethane composites is reviewed by H. N. Bhatti and coauthors[64].

The various types of polyurethane waste products, consisting of either old recycled parts or production waste, are generally reduced to a more usable form, such as flakes, powder or pellets, depending on the particular type of polyurethane that is being recycled. The various recycling technologies for material and chemical recycling of PU materials have greatly contributed to improve the overall image regarding the recyclability of polyurethanes in recent years, by far the most important being regrinding and glycolysis. These technologies open an emerging, effective and economic route for recycling polyurethane rigid foams and composite. Polyurethane foam in automotive seating has been successfully recycled using regrind technology. Glycolysis of polyurethanes can be economically acceptable, but still requires more development in order to tolerate more contamination in the post-consumer material. Current technologies can recover the inherent energy value of polyurethanes and reduce fossil fuel

consumption. Energy recovery is considered the only suitable disposal method for recovered material for which no markets exist or can be created. Increasing waste-to-energy and other thermal processing activities involving gasification, pyrolysis and two-stage combustion has contributed for the disposal of significant amounts of scrap PU without many difficulties. It is concluded that many of the plastic feedstock recycling processes appear to be technically feasible and robust enough to warrant further development in the future.

The polyurethane industry has identified workable technologies for recovering and recycling polyurethane waste materials from discarded products as well as from manufacturing processes. For example, in 2002, 850 million pounds of polyurethane were used to make carpet cushion[65], of which 830 million pounds were made from scrap polyurethane foam. Of the total scrap used, 50 million pounds came from post-consumer waste. EC Draft directive[66] for end-of-life vehicles (ELV) disposal reported that in the year 2005, 15.0% of vehicle weight is disposed (maximum) to landfill, and predicted that in the year 2015, only 5.0% of vehicle weight will be disposed (maximum) to landfill. The polyurethane industry is committed to meeting the current needs of today without compromising the needs of tomorrow. The continued development of recycling and recovery technologies[67-69], investment in infrastructure necessary to support them, the establishment of viable markets and participation by industry, government and consumers are all priorities.

Mechanical, chemical & thermo chemical recycling and energy recovery, are all ways to recycle polyurethane[69].

Degradation of PU

After years of production of PUs, manufacturers found them susceptible to degradation. Variations in the degradation patterns of different samples of PUs were attributed to the many properties of PUs such as topology and chemical composition[70].

The regularity in synthetic polymers allows the polymer chain to pack easily, resulting in the formation of crystalline regions. This limits accessibility of the polymer chains to degradative agents. Research was initiated to elucidate whether additives to the chemical structure of PUs could decrease biodegradation.

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Kanavel et al.[71] observed that sulfur-cured polyester and polyether PUs had some fungal inertness. However, they noted that even with fungicides added to the sulfur- and peroxide-cured PUs, fungal growth still occurred on the polyester PUs and most fungicides had adverse effects on the formulations. Kanavel[71] also recognized the need for physical testing of the PUs after extended exposure to the activity of fungi. Santerre et al.[72] varied the amount of degradation products released by varying the physical makeup of the polyester PUs, as coatings on glass tubes or as films. This implied that while urethane and urea groups are susceptible to hydrolysis, they are not always accessible to the enzyme and degradation may never proceed past the polymer surface. Although the polyether PUs showed no significant degradation, they consistently showed higher radiolabel products release from soft-segment-labeled, enzyme-incubated samples than controls. The authors attributed these results to the shielding of ester sites by secondary structures and hydrogen bonding within the hard segment.

Santerre and Labrow[73] tested the effect of hard segment size on the stability of PUs against cleavage. Analysis was performed with polyether PUs and their susceptibility to cholesterol esterase. Three polyether PUs were synthesized with varying molar ratios of 14^0C diisocyanate to chain extender and constant polyether makeup. A ten-fold increase in enzyme concentration of cholesterol esterase previously used[72] was utilized to approach plateau values for polyether PU hydrolysis. Upon treatment with cholesterol esterase, Santerre and Labrow[73] observed that radiolabel release was significantly dependent on the amount of hard segment contained within the polymer. In the polymer with the lowest concentration of hard segment, higher numbers of carbonyl groups are exposed to the surface. With increased hard segment size, a greater number of carbonyl groups are integrated into secondary hard segment structures through hydrogen bonding. The investigators also concluded that an increase in hard segment size does lead to restrictions in polymer chain mobility. In the medical field PUs show resistance to macromolecular oxidation, hydrolysis and calcification[74]. Polyurethane elastomers are being used in place of other elastomers due to higher elasticity and toughness, and resistance to tear, oxidation and humidity

[75-77]. In addition, polyether derivatives are inexpensive to produce as prepolymers, which can lower the overall cost of polymer production.

Synthesis of polyurethane microspheres

A novel polycondensable macrodiol with a long hydrophobic acrylate ester moiety and an amphiphilic block copolymer were successfully used in the particle forming polymerization of diisocyanate and diol. The performance of the macrodiol and the block copolymer as stabilizers depends both on its molecular weight and concentration. The particle size decreases as the concentration of the stabilizer increases and nearly monodisperse polyurethane microspheres are formed in nanometer size range in the case of macrodiol stabilizer. This new class of macrodiol steric stabilizer participates in the urethane forming reaction and is enchained in the polymer. Further studies are in progress to fully elucidate the mechanism of stabilization and compare the efficiency of steric stabilization by polymerizable stabilizer with a conventional steric stabilizer which functions solely by an adsorption mechanism. Ramanathan[78] has reported for the first time, the synthesis of polyurethane microspheres by particle forming polymerization techniques using a novel polycondensable macromonomer[79] and an amphiphilic block copolymer as steric stabilizers.

Preparation of polymers in particulate form has been well studied using techniques such as suspension, emulsion and dispersion polymerization. Of these, dispersion polymerization has been found to be an efficient method for producing monodisperse polymer particles. A comparison of various techniques employed for producing nano and microspheres have been reviewed[80] Particle forming polymerization process reported so far are typically performed with vinyl monomers[81-83]. There is, however, no report on the particle forming polymerization of an isocyanate with a diol to produce polyurethane microspheres. Conventionally, polyurethane particles can be prepared by cryogenic grinding of thermoplastic polyurethanes[84] or by suspension polymerization of isocyanate terminated prepolymers in aqueous or non-aqueous medium[85]. However, in none of these prior methods the control of particle size has been demonstrated[86].

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CONCLUSION

Two groups of at least bifunctional substances are needed as reactants for the manufacturing of polyurethane polymers,; compounds with isocyanate groups, and compounds with active hydrogen atoms. Polyurethane can be made in a variety of densities and hardnesses by varying the type of monomer(s) used and adding other substances to modify their characteristics, notably density, or enhance their performance.

Polyurethane-based coatings have an established place in the coatings industry. The results showed that coatings based on hydrophilic nano-silica gave a less transparent more UV absorbent coating. However, coatings based on hydrophobic nano-silica gave more miscible, transparent coating having improved mechanical properties especially scratch resistance.

It has concluded that the prepolymerization was still 2nd-order after the montmorillonite was added into the reaction system. The activation Energy of pure PU prepolymerization system achieved 42.7 kJ/mol that is closed to 42 kJ/mol which had been reported in literature.

The various recycling technologies for material and chemical recycling of PU materials have greatly contributed to improve the overall image regarding the recyclability of polyurethanes in recent years, by far the most important being regrinding and glycolysis.

It was founded that variations in the degradation patterns of different samples of PUs were attributed to the many properties of PUs such as topology and chemical composition.

ACKNOWLEDGMENTS

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