Polyurethane

Edited by Fahmina Zafar
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Preface

Polyurethane [PU] is a class of polymers built up of carabamate linkages, which provide special characteristics to the material. It is the outcome of pioneering research work of Otto Bayer and his coworkers in 1937 at I.G. Farben laboratories, in Leverkusen, Germany. Initial PU consisted of foams and fibres, while today, innovations and researches in the past decades have brought colossal changes in the world of PU. Attention is focussed on green PU such as from non-isocyanate technologies, from biobased polyols and isocyanates, PU hybrids, PU composites and so on. PU find versatile applications as foams, adhesive, surface coatings, and sealants, to name a few. The enchanting and worthy world of PU beckoned us to bring forth the book titled "Polyurethane". The book is divided into three sections: structures, properties and characterization of PU, applications of PU and a separate section on Biobased PU, covering the research and development in these areas. Each contributed chapter handles new and interesting topics introducing the reader to the wider known and unknown applications of PU such as PU for medical, urological stenting practice, carriers of antituberculosis drugs, orthopaedic, fuel binder, extraction of metals, grouting technologies, crashworthiness, isolation for covered conductor, treatment of industry wastewater, cast elastomers, alkanolamide PU coatings and foams, and others. The book aims to cater a larger audience comprising of readers from polymer chemistry, materials chemistry, and industrial chemistry.

It is an immense pleasure to see the book "Polyurethane" in its final shape; the credit goes together to the authors, contributors, and the technical staff of InTech Open Access Publisher, particularly, to Mrs. Marija Radja and Mr. Vedran Greblo, Editor Relations Consultants, the funding agency Council of Scientific and Industrial Research, New Delhi, India for Senior Research Associateship (Under Scientists' Pool Scheme, CSIR). Without their help and dedication, it would be impossible to have this book published so efficiently. Time has come to thank them all.

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Bio-Based Polyurethanes

Seed Oil Based Polyurethanes: An Insight

Eram Sharmin, Fahmina Zafar and Sharif Ahmad

Additional information is available at the end of the chapter

1. Introduction

Seed oils [SO] are cost-effective, eco-friendly and biodegradable in nature. They bear functional groups such as carboxyls, esters, double bonds, active methylenes, hydroxyls, oxirane rings and others, amenable to several derivatization reactions. Their abundant availability, non-toxicity and rich chemistry has established SO as focal point of polymer production, e.g., production of polyesters, alkyds, epoxies, polyols, polyethers, polyesteramides, polyurethanes and others. The escalating prices of petro-based chemicals, environmental and health concerns have further beckoned the enhanced utilization of SO as polymer precursors. SO have attracted enormous attention as potential source of platform chemicals, at both laboratory and industrial scale. Today, oil-seed bearing crop plants are being raised and modified for uses in areas covering biodiesel, lubricants, folk medicines, cosmetics, plastics, coatings and paints.

SO based polyurethanes [PU] occupy an important position due to their simple preparation methods, outstanding properties and versatile applications in foams, coatings, adhesives, sealants, elastomers and others [1-4]. In general, PU are prepared by chemical reaction of a diol, polyol or any oligomer or polymer containing hydroxyl groups, with an aliphatic, cycloaliphatic or aromatic isocyanate. SO serve as green precursors to diols, polyols and other –OH containing polymers offering greener raw materials in PU synthesis, replacing their petro-based counterparts. The choice of SO polyol or isocyanate is governed by the end-use application of SO PU ranging from soft and flexible to rigid PU foams, thermoplastic to thermosetting PU, flexible films to tough, scratch-resistant, impact resistant coatings and paints. It is well known that the structure of a triglyceride is very complex. Every SO has a characteristic fatty acid profile. Amongst the same species, the composition of triglycerides in a particular SO varies by weather conditions of crops and soil. Triglycerides vary by their fatty acid chain lengths, presence as well as the position of double bonds and degree of unsaturation of the constituent fatty acids. The structures of

natural SO and their derivatives, i.e., epoxies, diols, polyols, polyesters and alkyds are complex. Thus, the properties of PU obtained from SO derivatives depend on a number of factors such as (i) the type, composition and distribution of fatty acid residues in the constituent triglycerides, (ii) the number, distribution, site of hydroxyls (in the middle or closer to the end of the triglyceride chain) and level of unsaturation in the fatty triester chains of the parent diol or polyol, (iii) the type, position and structure of isocyanates used and (iv) the urethane content of the final PU [5-8].

The ingredients for the preparation of SO based PU generally comprise of a diol or polyol (containing active hydrogens) derived from SO and an isocyanate, aliphatic and aromatic such as 1,6-hexamethylene diisocyanate [HMDI], isophorone diisocyanate [IPDI], cyclohexyl diisocyanate [CHDI], L-Lysine Diisocyanate [LDI], toluylene 2,4-diisocyanate or toluylene 2,6-diisocyanate [TDI], 4,4'- methylenediphenyl diisocyanate [MDI], naphthylene 1,5-diisocyanate [ND]. PU are prepared by polyaddition reaction between the two components, often in presence of a chain extender, cross-linker or a catalyst. Today, several environment friendly routes for the production of PU have cropped up. Research has been focussed on the preparation of PU from non-isocyanate routes, and also on the use of fatty acid based isocyanates for PU production, considering the persisting challenges of polymer industry and immediate attention sought towards environmentally benign chemicals and chemical routes for the same [9-18].

SO based PU are generally flexible in nature. Generally, these PU show low Tg due to the presence of long aliphatic chains and also poor mechanical properties (owing to the presence of dangling chains). The thermal stability of SO based PU is also lower since the decomposition of urethane bonds starts at 150-200°C. Javni et al have studied the decomposition of PU from Olive, Peanut, Canola, Corn, Soybean, Sunflower, Safflower and Castor oils [7]. The decomposition involves the dissociation of urethane bonds to isocyanate, alcohol, amine, olefin and carbon dioxide. The properties of PU depend upon their crosslinking density as well as chemical composition. In an execellent review, Petrovic has highlighted the different properties of PU prepared from polyols obtained by different methods. As the properties of polyols depend upon the methods of preparation, so also the properties of PU derived therefrom. He has presented a brief outline of the effect of polyols prepared by epoxidation, hydroformylation, ozonolysis, effect of crosslinking density, and type of isocyanate on the properties of PU. He described the effect of the structure of polyols prepared by epoxidation followed by ring opening with methanol, HCl, HBr, and by hydrogenation of epoxidized Soybean oil, and showed that PU obtained from these polyols showed relatively higher glass transition temperatures and improved mechanical properties. Halogenated polyols obtained via ring opening by HCl and HBr gave PU that were less stable than ones without halogens, and had higher Tg (70°C –80°C) than the latter. Polyols obtained via hydroformylation crystallize below room temperature while those derived through hydrogenation reveal crystallization at temperature higher than room temperature. PU from non-halogenated polyols had higher thermal stability than brominated (100°C) or chlorinated polyols (160°C). Polyols with primary hydroxyls give

more stable PU than their counterparts with secondary hydroxyls. PU with high crosslink density show higher thermal stability. Hydrolytic stability of PU also depends on the degree of crosslinking, temperature, and physical state of PU. In SO based PU, although SO have ester groups susceptible to hydrolysis, long hydrophobic fatty acid chains cause shielding effect. Under highly humid conditions, urethane bonds undergo hydrolysis producing amine and carbon dioxide [1, 19].

SO are rich in various functional groups such as double bonds, active methylenes, esters, hydroxyls and others. These undergo several chemical transformations yielding numerous derivatives with versatile applications as inks, plasticizers, lubricants, adhesives, coatings and paints. Amongst various SO derivatives, those containing hydroxyl groups are used in the production of PU. These include SO based diols, triols, polyols, polyesters, alkyd, polyesteramide, polyetheramide and others (Figure 1).
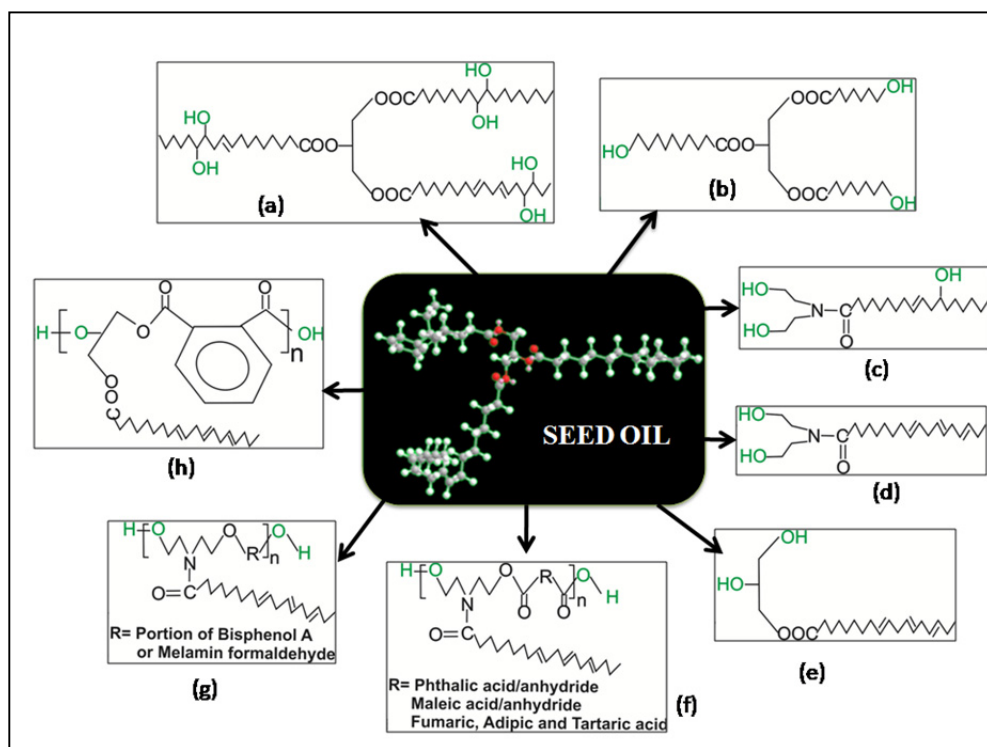
Figure 1. SO derivatives used in the production of PU (a) polyol, (b) triol, (c) fatty amide triol, (d) fatty amide diol, (e) monoglyceride, (f) polyesteramide, (g) polyetheramide, and (h) alkyd.

The chemistry of SO based PU is very vast, governed by several factors such as the type of diol or polyol, type of isocyanate, preparation method of diols or polyols, type of chain

extender, cross-linker, reaction temperature and other reaction conditions. In this chapter we have focussed on the preparation, structure and properties of PU obtained from diols, triols and polyols derived by amidation of SO termed as "SO alkanolamides". In the proceeding sections, we have also discussed the modifications of the said SO alkanolamides based PU at the forefront of PU chemistry such as SO based metal containing PU, PU hybrids, composites for applications mainly in coatings, paints and foams.

2. SO based diols

The most excessively used SO based diol in PU production is fatty amide diol or fatty alkandiol-amide [FAD] (Figure 2). FAD is obtained by the base catalysed amidation of SO with diethanolamine. The structure of FAD is determined by the fatty acid composition of the starting SO.
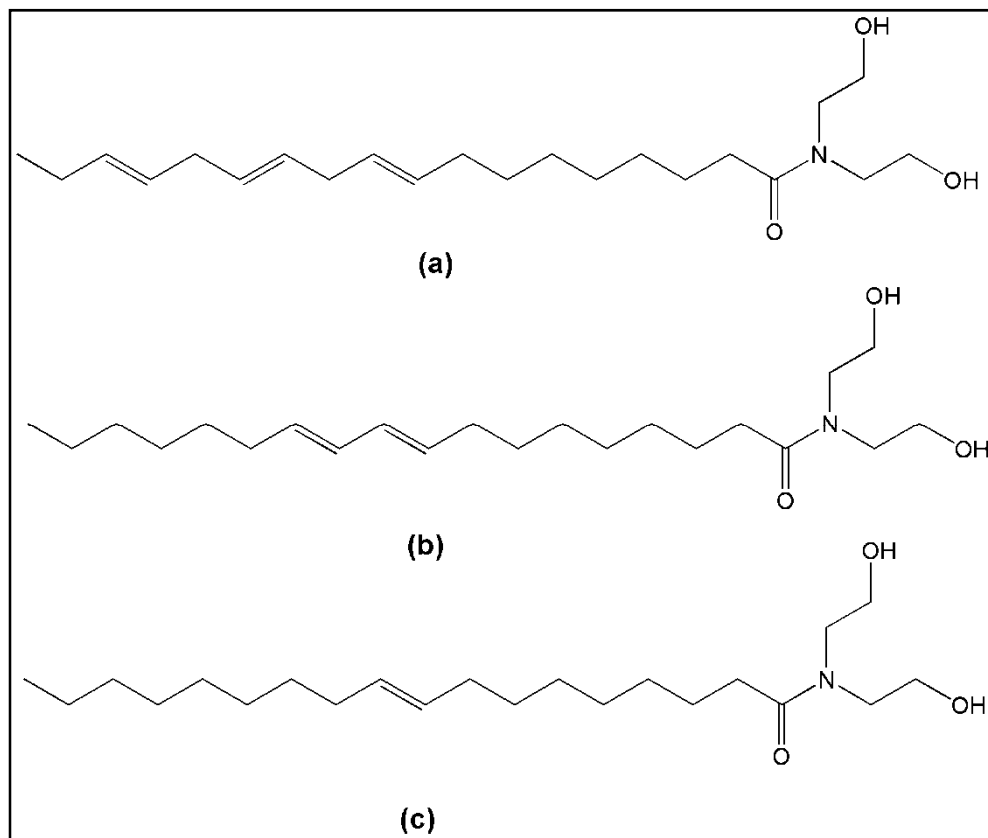
Figure 2. Figure 2. FAD from (a) Linseed (35.0-60.0 % Linolenic acid), (b) Soybean (43.0-56.0 % Linoleic acid) and (c) Karanj (44.5–71.3 % oleic acid), Nahor (55-66% oleic acid) , Jatropha (37-63 % oleic), Olive (65-80 % oleic acid)

The reaction proceeds by nucleophilic acyl substitution bimolecular (SN2) reaction mechanism. As the name suggests, FAD contains an amide group, with two hydroxyl ethyl groups directly attached to amide nitrogen along with the pendant aliphatic chain of SO. FAD is derived from different SO such as Linseed (*Linum ussitassimum*), Soybean (*Glycine max*), Karanj (*Pongamia glabra*), Nahor (*Mesua ferrea*), Jatropha (*Jatropha Curcus*), Olive (*Olea europea*), Coconut (*Cocos nucifera*) and others [20-30] (Figure 2). FAD is used as raw material for various polymers such as PU, poly (esteramide) and poly (ether amide).

3. PU from SO FAD

FAD can be treated with an isocyanate such as TDI, IPDI, HMDI, MDI, ND, CHDI and LDI forming poly (urethane fatty amide) (Figure 3) [FADU] [31].
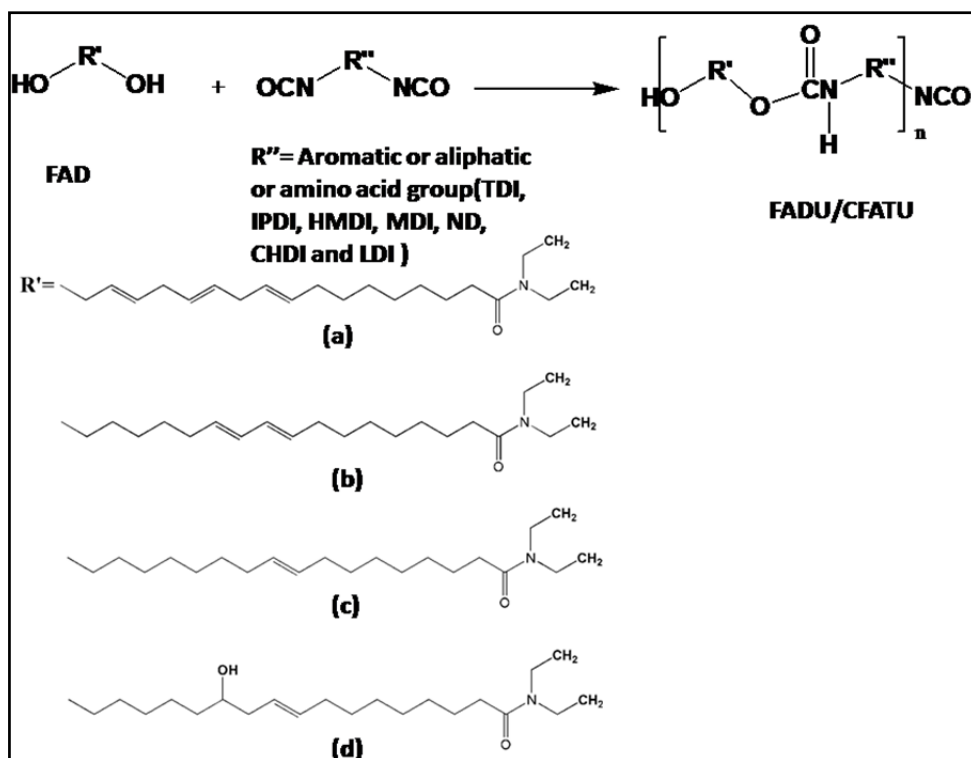
Figure 3. FADU from (a) Linseed, (b) Soybean (c) Karanj, Nahor, Jatropha, Olive and (d) Castor

For the first time, Linseed oil [LO] derived FAD [LFAD] was treated with TDI by one-shot technique to prepare PU [LFADU] as introduced by Ahmad et al [32] (Figure 4).
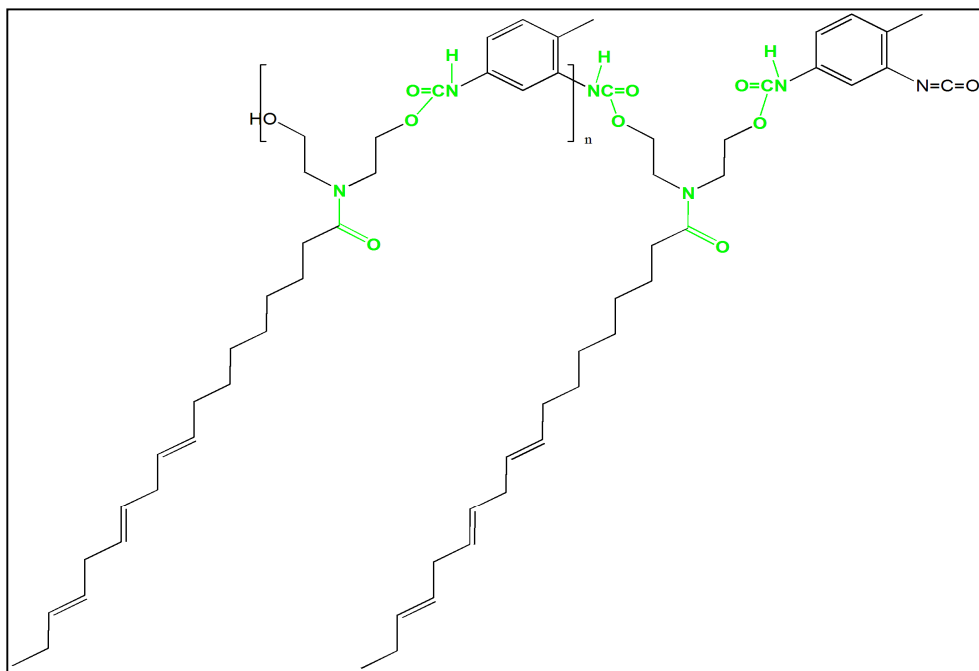
Figure 4. Chemical structure of LFADU.

The structure of LFADU was established by spectral analyses. FTIR, ^{1}H NMR and ^{13}C NMR spectra showed the presence of the main characteristic absorption bands of parent SO [32]. Along with these bands, additional absorption bands are observed supporting the presence of urethane groups in the backbone of LFADU such as those at 3375cm^{-1} for hydroxyl groups, 1716.11 cm^{-1} for urethane carbonyl (str), 1227.56cm^{-1} for C–N of urethane groups, 1735cm^{-1} typical for carbonyl (str) of TDI. The characteristic peaks for hydrogen bonded and non-hydrogen bonded protons of –**H**NCOO– appear at 7.99–7.82ppm and 7.1–6.9ppm, respectively. The aromatic ring protons of TDI occur at 7.5–7.22 ppm. The peaks of –**H**NCOOCH$_2$– are observed at 4.1–3.9ppm and for **CH**$_3$ of TDI appear at 2.25ppm. ^{13}C NMR spectrum also shows the presence of characteristic peaks of LFADU at 17ppm (**CH**$_3$ of TDI), 143.97ppm {–NH–(**C** O)–O–} and 137.46, 136.2, 134.4, 125.94, 125.4, 116.0 ppm (aromatic ring carbons of TDI). TGA thermogram of LFADU has shown four step degradation pattern, at 260 °C (27% weight loss), 360 °C (21% weight loss), 505 °C (40% weight loss), 640 °C (9% weight loss) corresponding to the degradation of urethane, ester, amide and hydrocarbon chains, respectively.

PU from Karanj or *Pongamia glabra* [PGO] oil [PFADU] has also been prepared by similar method. PU obtained from both FAD showed similar structure except for the difference in the structure of pendant fatty amide chains attributed to the variation in the structure of the parent SO chain [33] (Figure 5).
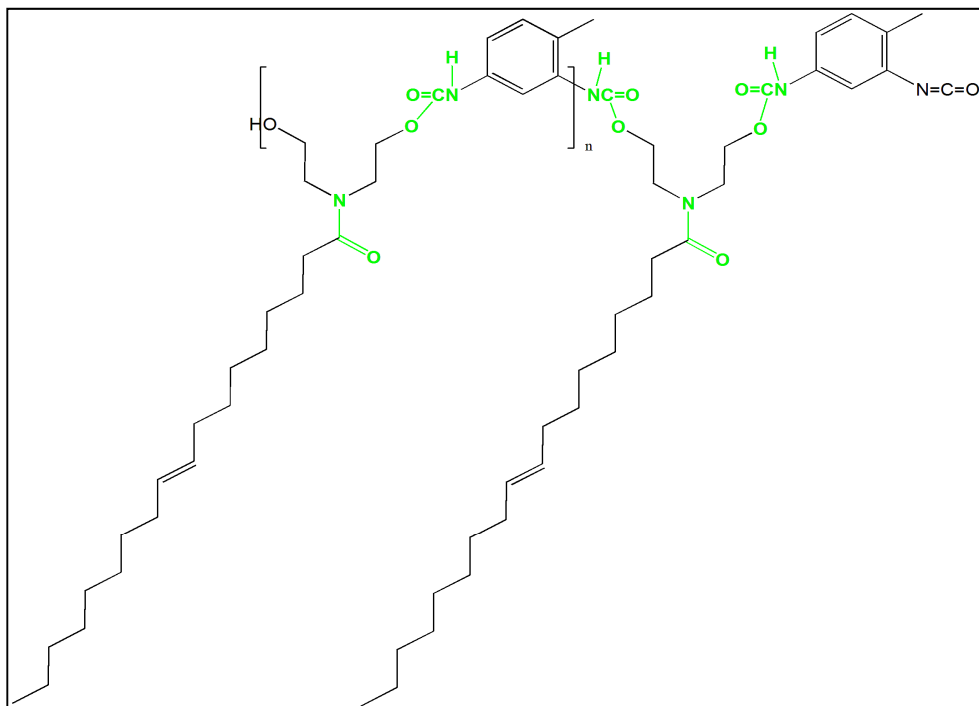
Figure 5. Chemical structure of PFADU or NFADU

The thermal degradation of PFADU was observed at 177°C and 357°C, with 5% weight loss occurring at 200°C attributed to the entrapped solvent and moisture, 10wt% loss at 225 °C, attributed to the decomposition of urethane moieties, 50wt% and 80wt% losses at 390 °C and 455 °C, respectively, attributed to the degradation of the aromatic ring and aliphatic pendant fatty alkyl chains, respectively.

It was observed that in both LFADU and PFADU, beyond 1.5moles loading of TDI, formation of some lumpy aggregates occurred. Upto 1.5 moles of TDI addition, it is speculated that the isocyanate groups of TDI react with hydroxyl groups of FAD forming PU linkages. Beyond this amount, any additional isocyanate added reacts with the urethane groups of LFADU or PFADU forming allophanate groups (secondary reaction). The final PU attains very high viscosity and crosslinking, so much so that the formation of lumpy aggregates occurs and PU is deprived off its free flowing tendency.

Karak and Dutta have reported the production of PU by amidation and urethanation of methyl ester of *M. Ferrea* or Nahor oil [NO], rich mainly in triglycerides of linoleic, oleic, palmitic and stearic acids. They investigated the structure and physico-chemical aspects of FADU from NO [NFADU] [26].

3.1. PU as coatings

LFADU has free –OH, –NCO, aliphatic hydrocarbon chains (from parent LO), amide and urethane groups, which make it an excellent candidate for application in protective coatings (Figure 4). LFADU coatings undergo curing at ambient temperature (28-30ºC) by three stage curing phenomenon, (i) solvent evaporation (physical process), (ii) reaction of free –NCO groups of LFADU with atmospheric moisture, and (iii) auto-oxidation. These coatings show good scratch hardness (2.5kg), impact resistance (200lb/inch), bending ability (1/8inch) and chemical resistance to acid and alkali. PU from PGO [PFADU] has shown moderate antibacterial behavior against *Salmonella* sp. with good scratch hardness (1.9kg), impact resistance (150lb/inch), bending ability (1/8inch), and gloss (46 at 45º) [33]. LFADU coatings have shown superior coating properties than PFADU owing to the fatty acid composition of parent oils (PGO, a non-drying oil has higher content of oleic acid while LO, a drying oil, is rich in linolenic acid).

Karak and Dutta have reported the use of NFADU coatings with very good alkali resistance (Figure 5)[32].

3.2. PU as hybrids

Organic-inorganic hybrid materials have been developed with FADU as organic constituent and metal/metalloid as inorganic component to improve the performance and broaden the applications of PU (Figure 6).
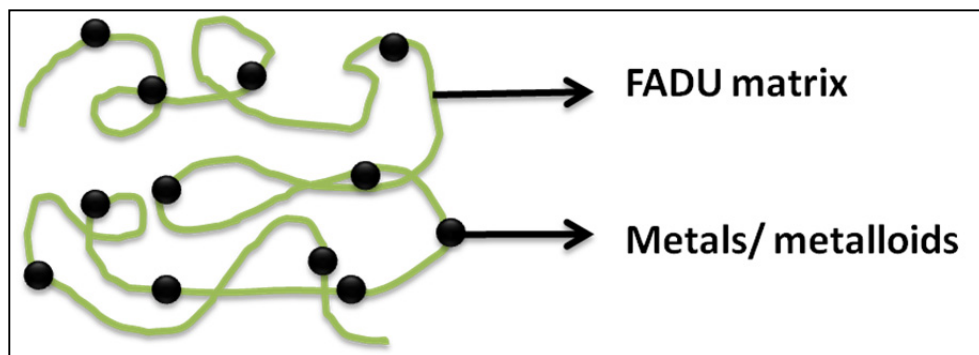
Figure 6. PU as hybrids

In one report, Zafar et al. have prepared organic-inorganic hybrids by using boric acid as inorganic content and PFADU as organic matrix [B-PFADU] [34]. B-PFADU was characterized by standard spectral techniques and physico-chemical methods. B-PFADU performed well as protective coatings in terms of physico-mechanical and chemical resistance tests. B-PFADU showed no change in water and xylene upto 15 days. However, slight deterioration in performance was observed in alkali and acid media, correlated to the presence of -O-B-O- which is susceptible to hydrolysis on exposure to these media. B-

PFADU showed high activity against *E. coli* (Zone of inhibition: 21-30 mm) and moderate activity against *S. aureus* (Zone of inhibition: 16-20 mm). The reason can be the presence of urethane, amide, and hydroxyl groups in the polymer backbone, which can presumably interact with the surface of microbes, causing antibacterial action. B-PFADU can be used as an antibacterial agent as well as coating material.

In another work, Ahmad and co-workers developed LFADU hybrid material with tetraethoxy orthosilane [TEOS] as inorganic constituent in the hybrid material [Si LFADU] by in situ silylation of LFAD with TEOS (at 80 ∘C) followed by urethanation with TDI (at room temperature) [35]. Along with the typical absorption bands for LFADU, additional absorption bands were observed at 484 cm^{-1} (Si–O–Si bending), 795 cm^{-1} (Si–O–Si sym str) and 1088 cm^{-1} (Si–O–Si assym str) in FTIR due to the presence of -Si–O–Si- bond in the hybrid backbone. Hydroxyl value decreases while refractive index and specific gravity increase with the loading of TEOS in Si LFADU, supporting the formation of the hybrid materials by insitu sylation and urethanation reaction. Optical micrograph of Si LFADU showed the presence of SiO$_2$ particles surrounded by LFADU (Figure 7).
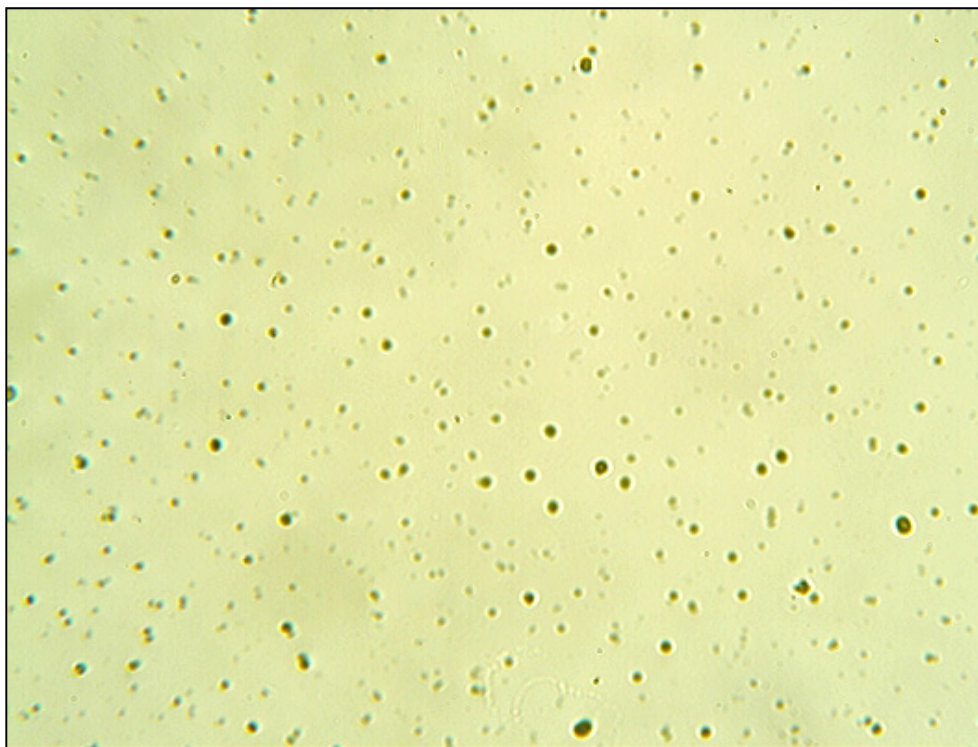
Figure 7. Optical micrograph of Si LFADU

Si LFADU formed hybrid coatings by simple curing route at ambient temperature, over mild steel panels of standard sizes with improved gloss and scratch hardness. SiO2 domains

also improved adhesion with the penal surface exhibiting good scratch hardness, bending ability (1/8 inch) and impact tests (150 lb/inch) correlated to the synergism showed by both the components, LFADU backbone imparting flexibility and gloss, while the inorganic domains conferring excellent adhesion and hardness [36].

The corrosion rate (CR) of Si LFADU is much lower (3.08 × 10^{-4} mm per year) relative to LFADU (3.124 mm/year) In 3.5wt% HCl, with inhibition efficiency (IE%) 99.77. In 3.5% NaOH, CR and IE% were found as 1.26 × 10^{-3} mm per year and 99.34, respectively. Si LFADU formed uniform and well adhered coating over the metal substrate which prohibits the permeation of corrosive media. The protection mechanism is purely through barrier action attributed to the hydrophobic inorganic content [37, 38]. Coating remained intact when subjected to corrosive media for 192 h as supported by the constant value of polarization resistance (Rp = 1.22 × 104 Ohm in NaOH and 7.7 × 105 Ohm for HCl). Thermal studies showed four step degradation, thermal stability increasing with higher inorganic content, with two glass transition temperatures (Tg) as observed at 115 ∘C and 155 °C in DSC thermogram with safe usage upto 200 °C.

3.3. PU as composites

Composite materials from FADU have not been prepared yet. In their recent research, Zafar et al have developed composites from FADU using metal oxides and organo-montmorillonite clay [OMMT] (Cloisite 30B; modified by an alkyl ammonium cation bearing two primary hydroxyl functions, alkyl group is tallow containing ≈65% C18, ≈30% C16, and ≈5% C14, Southern Clay product) as modifiers added in very lower amounts to FADU matrix (unpublished work). The sole aim behind the development of these composites was the improvement in performance of FADU materials in terms of thermal stability, physico-mechanical and corrosion or chemical resistance performance, and also antimicrobial behavior relative to the pristine material for high performance applications. MMT occurred as nano-sized aggregates with size ranging from 37 to 100 nm as observed by Transmission Electron Micrography [TEM]. The thermal stability of FADU/ MMT was found to increase with increased MMT loading. These composites may be used as protective coatings in future. Zafar et al have also developed FADU/MnO composites, with good antifungal behavior. MnO occurred as needles self-assembled in "lemon slices" morphology as observed in optical micrograph (Figure 8). The said composite material may find application as antimicrobial agent in coatings and paints.

PU composites were prepared by the dispersion of conducting polymer poly (1-naphthylamine) [PNA] in LFADU matrix in amount ranging from 0.5–2.5 wt% by conventional solution method as reported by Riaz et al [39]. At lower levels, the composites were very fragile in nature. The polymerization of PNA occurred through N–C(5) linkages of 1-naphthylamine units as confirmed by FTIR spectra. PNA also reacted with free isocyanate groups of TDI forming urea linkages, as also supported by spectral analysis. UV visible spectra also confirmed the formation of urea linkages between LFADU and PNA. TEM micrographs showed the average particle size as 17–27 nm. Nanoparticles appeared as

smaller aggregates which later on formed larger aggregates. XRD analysis revealed purely amorphous nature of composites. With the increase in the loading of PNA in the composites, the distortion and torsional strain increased in the composites due to higher urea linkages. It was found that as the percent loading of PNA in the composites increased, their electrical conductivity values also increased; however, these values fell in the semi-conducting range, which was much higher relative to the conductivity values obtained with very high loading of PNA in previously reported composites. The improved electrical conductivity values of LFADU/PNA composites can be correlated to the hydrogen bonding and urea type linkages formed between the two polymers, which provide the path to charge conduction [40,41].
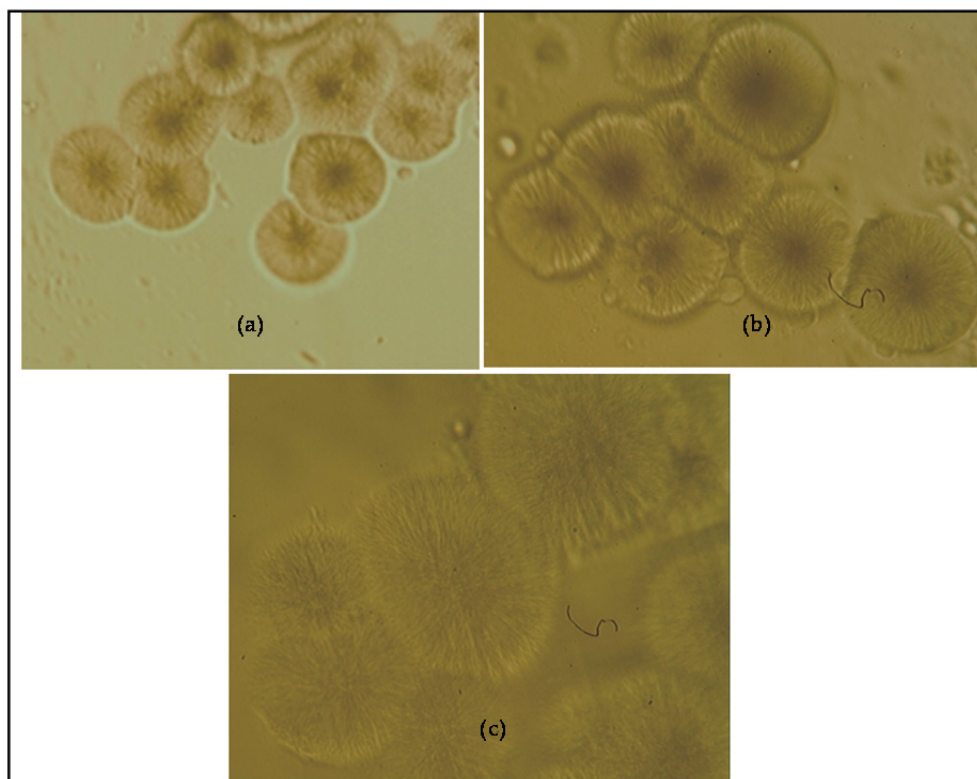
Figure 8. Optical micrographs of FADU/MnO (a) 100 X, (b) 200 X, (c) 500 X

4. SO based triol

Castor oil (CO) is obtained from seeds of *Ricinus communis* or Castor belonging to the family *Euphorbiaceae*. It is non edible oil. The crop is cultivated around the world because of the commercial importance of its oil. India is the world leader in castor production and dominates the international CO trade. Worldwide castor production was about 1.4 million metric tons during the year 2009 with an average yield of about 956 kg ha^{-1}. Ricinoleic acid

(12- hydroxy -9- octadecenoic acid), hydroxyl containing fatty acid, is the major component of CO, and constitutes about 89% of the total fatty acid composition. Castor seed products have widespread applications in many industries like paints, lubricants, pharmaceuticals and textiles. Today, the importance of these products has grown manifolds because of their biodegradable and eco-friendly nature.

Due to the inherent hydroxyl functionality, CO stands as an excellent natural raw material for the development of PU. CO derived PU are flexible due to long aliphatic triglyceride dangling chains [42]. CO has three hydroxyl moieties in one triglyceride molecule. On amidation, CO yields fatty amide triol or alkan-triol-amide [FAT], which bears two hydroxyl ethyl groups directly attached to amide nitrogen, as well as one hydroxyl group in the pendant fatty chain obtained from the parent CO. Thus, CO derived FAT [CFAT] acts as SO derived triol (Figure 9). Rao et al prepared acrylated CFAT as a multifunctional amide for photocuring [31, 43, 44].
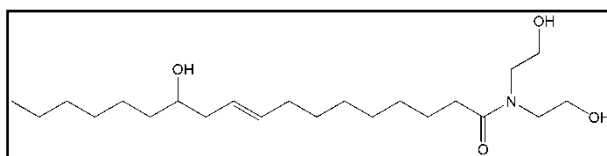
Figure 9. CO (87-90 % Ricinoleic acid) derived FAT [CFAT)

5. PU from SO FAT

CFAT on chemical reaction with TDI by one shot technique yields CFATU (Figure 10), with an additional crosslinking site (hydroxyl group) conferred by parent CO containing 89% ricinoleic acid. Contrary to LFADU and PFADU, where the permissible limit of TDI addition is 1.5 moles, in CFATU, at 1.2.moles of TDI addition, CFATU becomes highly viscous. The difference prevails due to the additional hydroxyl functionality in CFATU, which presumably makes possible higher inter and intra crosslinking sites relative to LFADU and PFADU. As also observed in LFADU and PFADU, the physico-chemical characteristics such as specific gravity, inherent viscosity and refractive index increase, while hydroxyl and iodine values decrease on increasing the content of TDI in PU. The thermal degradation occurred in the temperature range of 150–390 ºC. The decomposition observed at earlier temperature range may be attributed to the thermal degradation of urethane linkages followed by the volatilization of the decomposition products while that at higher temperatures is correlated to the degradation of amide bond, aromatic ring and aliphatic alkyl chain of the fatty acid, respectively, followed by the volatilization of the decomposition products [45, 46].

5.1. PU as coatings

CFATU coatings have been prepared and their physico-mechanical, thermal as well as corrosion resistance behavior has also been investigated [31]. CFATU have been further modified for improvement in their performance as discussed in proceeding sections.
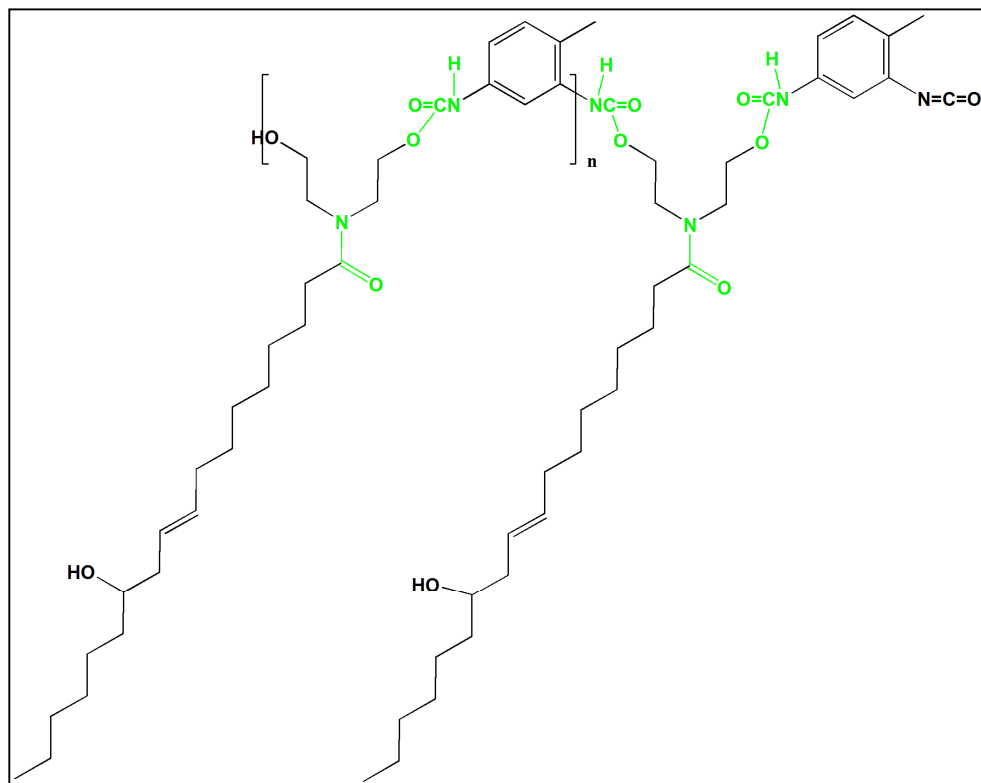
Figure 10. Chemical structure of CFATU

5.2. PU as hybrids

Ahmad et al have reported the preparation and characterization of metal containing CFATU [47]. They treated CFAT with zinc acetate (5, 10 and 15 wt%) and TDI (25–75 wt%) to prepare metal containing CFATU [MCFADU] ''in situ'' by microwave [MW] assisted preparation method in a domestic MW oven. During the preparation, it was observed that MCFATU with > 5wt% zinc acetate formed gel. While the conventional preparation method of LFADU, CFATU, PFADU and NFADU requires 8-12 hours, CFATU is obtained in 4 minutes by MW assisted preparation method. By molecular interactions with the electromagnetic field and heat generated by molecular collision and friction, the reaction is facilitated to occur in much reduced time periods under the influence of MW irradiations. In this reaction, hydroxyl groups of CFAT react with zinc acetate and TDI successively. Curing of MCFATU is a two step process occurring by solvent evaporation (physical phenomenon) followed by the second stage curing (a chemical process) where free –NCO groups of MCFATU react with the atmospheric moisture to form urethane and amino groups through addition reaction. MCFATU acted as good corrosion protective coatings for mild steel. The best physico-mechanical properties (scratch hardness 3.5 kg, impact resistance

150lb/inch, and bending ability 1/8 inch) were achieved at 5wt% loading of zinc acetate and 55 wt% of TDI, when evaluated by standard methods and techniques. The corrosion protection efficiency of the same was evaluated by potentiodynamic polarisation measurements [PDP] in aqueous solution of 3.5wt% HCl (CR 4.51 × 10-3 mm/year; IE% 96.23), 3.5wt% NaOH (CR 1.36 × 10-3 mm/year; IE% 90.81); 3.5wt%NaCl (CR 2.25 × 10-3 mm/year; IE% 94.50) and tap water (Cl- ion 63 mg/L; Conductivity 0.953 mS/A) (CR 3.56 × 10-3 mm/year; IE% 98.35).

5.3. PU as composites

CFATU composites were developed by the introduction of MMT clay [48] and nano sized ZnO by Zafar et al [unpublished work]. Morphology of the composites as studied by TEM revealed the presence of nanosized globules of size ranging between 15-120 nm in CFATU/OMMT (Figure 11), and ZnO in CFATU/ZnO composites occurring as nano-sized spindles of diameter 50-60nm (Figure 12). Both the composite materials may find application as corrosion protective coatings for mild steel. CFATU/ZnO composites also act as excellent antifungal agents against common fungal strains such as *Candida albicans*, *Candida krusei*, *Candida glabrata* and *Candida tropicalis*.
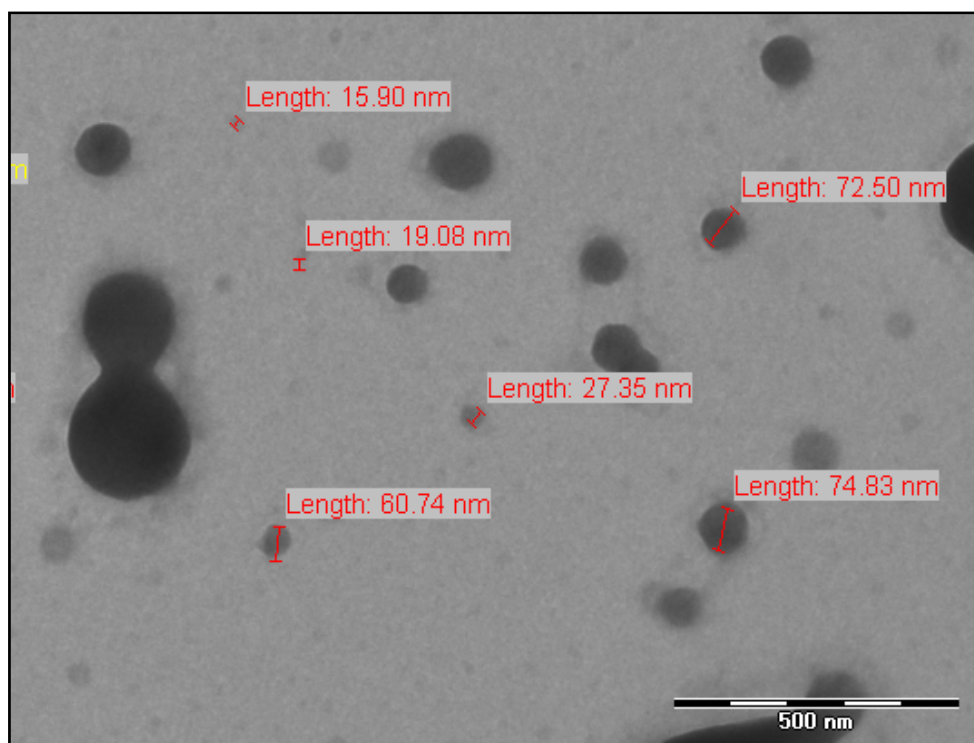
Figure 11. TEM of CFATU/OMMT
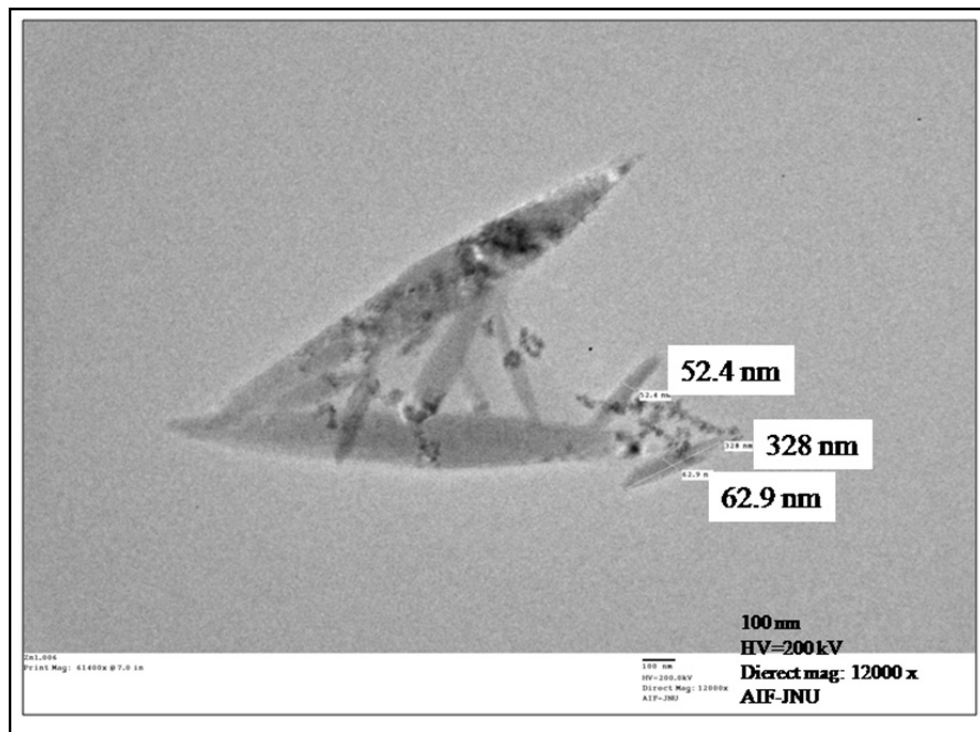
Figure 12. TEM of CFATU/ZnO composite

6. SO based polyols

SO derived polyols serve as the most important oleochemicals for PU production. Some of the SO polyols are derived through various chemical reactions such as epoxidation followed by hydration, ring opening by methanol, acids such as HBr, HCl, hydroformylation, ozonolysis of SO, others are naturally available polyols such as *Ricinus communis* or CO and Lesquerella oil. As discussed previously, the properties of PU also depend upon the type of polyol and the method by which the polyol is derived. In SO polyols, in general, hydroxyl groups are present in the middle of the triglyceride chains. Due to this, in cross linked polyols, the pendant or dangling chains provide steric hindrance to cross-linking, they do not support stress under load and act as plasticizers. In SO polyols, there is difference in the length of elastically active network chains (EANC) and elastically inactive network chains or dangling chains (DC). This variation is also passed onto their respective PU. The properties of PU thus also depend upon the content of EANC and DC, i.e., the number and position of hydroxyl groups. The number of hydroxyls on each chain in SO polyols and their stereochemistry are also variable depending upon the hydroxylating agents, hydroxylating method and other reaction conditions. For example, polyols obtained by ozonolysis and hydrogenation bear hydroxyl groups at terminal position.

SO polyols may also undergo amidation with diethanolamine to yield fatty amide polyols (FAP) [49]. Similar to FAD and FAT, FAP also house two hydroxyl ethyl amides directly attached to amide nitrogen and multiple hydroxyl groups located on the pendant fatty alkyl chains, which were part of the triglyceride molecule in parent SO bearing double bonds at the site of hydroxyl groups in FAP. The properties of SO polyols obtained by either method mentioned previously, also influence the properties of FAP. Hydroxylated, hydroxymethylated, carboxylated SO followed by their amidation yield polyols with higher number of hydroxyl groups with improved distribution [50-56]. These are ideal candidates to produce PU foams. The approach has been accomplished on CO, LO, PO, Rapeseed, Safflower, Soybean oils and refined bleached deodorized Palm Kernel Olein. These polyols have been used as non-ionic surfactants in the household and cosmetic industries and also to produce PU foams on treatment with suitable isocyanates. Such polyols prove to be advantageous over CO as they can be incorporated in higher amounts during PU formulations. Foams obtained show improvement in terms of high close cell contents, good dimensional stability and compression strength.

6.1. PU foams from SO FAP

Alkanolamide polyols serve as excellent starting materials for PU foams [50-56]. The variations in fatty acid components of starting SO, number and position of hydroxyl groups and also the presence of dangling chains in the polyol confer differences in performance and cellular structures in PU foams. The hydroxyl content of PU determines the suitability of PU foams ranging from flexible to rigid foams. A. Palaniswamy et al. produced PU foams from FAP derived from PO and Polymeric Diphenylmethane Diisocyanate (PMDI) by hand foaming. It was found that the decreased FAP content led to increase in compressive strength and density of PU foam [50]. In another research work, they have produced PU foams from PMDI and CO, in the presence of stannous octoate as catalyst and Tegostab by hand mixing process with carbon dioxide as the blowing agent generated from reaction between excess PMDI and water. PU foams with varying FAP content, catalyst and molecular weight of poly propylene glycol were studied with respect to their effect on density and compression strength [50, 51].

6.2. PU foams from SO based FAD epoxies

The epoxidized oil based alkanolamides are also classified as polyols for PU foams [56, 57]. PU show low thermal stability, thus with view to improve the thermal stability and mechanical properties of PU, heterocyclic groups such as isocyanurate, imide, phosphazene and oxazolidone, are incorporated in SO PU. The latter is formed by the chemical reaction between an oxirane ring and isocyanate in presence of a catalyst, the approach improving both thermal stability as well as stress-strain properties of the modified product with respect to the pristine material. PU foams derived from epoxidised alkanolamides show better compression strength, thermal conductivity, close cell contents

and dimensional stability relative to plain alkanolamide PU. However, in some examples, a part of epoxy content is lost during amidation reaction occurring at higher temperatures. Thus, it became imperative to determine ideal reaction conditions for amidation to retain maximum number of epoxidized rings, which was attempted by Lee et al and characterized by high performance liquid chromatography and gas chromatography [55, 56].

7. SO based polymers for PU production

As discussed earlier, SO undergo numerous transformations yielding various derivatives. Some of these derivatives bearing (inter or intra located) hydroxyls serve as excellent starting materials for PU production. A large number of PU are prepared from SO polymers such as polyesters, alkyds, polyesteramides, polyetheramides [Figure 1], which find profound applications in paints and coatings.

8. Summary

FAD, FAT and FAP serve as good starting materials for PU production. LFADU, PFADU, CFATU have similar structural characteristics; the difference being due to the pendant fatty amide chains attributed to the fatty acid composition of the parent SO. LFADU, PFADU,and CFATU are formed at a particular NCO/OH ratio. An astonishingly abnormal rise in viscosity was observed in LFADU and PFADU above 1.5moles and in CFATU above 1.2moles of addition of TDI, followed by the formation of lumpy aggregates. According to the general chemistry of PU, a particular NCO/OH ratio is required for a particular application. The best properties in PU are achieved when this ratio is kept as or closer to 1 or 1.1, i.e., when one equivalent weight of isocyanate reacts with one equivalent weight of polyol, to achieve the highest molecular weight. In certain applications this ratio is kept well below the stoichiometry (higher hydroxyl content relative to isocyanate) to obtain low molecular weight PU for applications as adhesives and coatings as described in the chapter. NCO/OH ratio is varied by the formulator based on the type of end use application of PU. Properties of PU mentioned here also depend on the chemical route of raw materials (polyol, isocyanate), functionality and type of the raw materials (diol, triol, polyol and isocyanates-aliphatic, aromatic), the number of urethane groups per unit volume, non-isocyanate PU, as well as other structural differences such as the presence of modifiers (acrylics, metals, nanosized metal oxides, MMT clay).

The preparation through MW technique offers advantages of reduced times and improved yield. Most of these PU are used for coatings and foams. The incorporation of inorganic constituent led to improved thermal and hydrolytic stability as well as coating performance of PU. Another area that is presently being explored is the preparation of green PU from fatty isocyanates or non-isocyanate PU. Due to their numerous applications and advantages SO PU have been extensively studied and extensive research is still going on.

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Polyglucanurethanes: Cross-Linked Polyurethanes Based on Microbial Exopolysaccharide Xanthan

Nataly Kozak and Anastasyia Hubina

Additional information is available at the end of the chapter

1. Introduction

Considering environmental protection and resolution a number of ecological problems (including problem of recourses for chemical synthesis depletion) synthesis of the biodegradable polymer materials becomes one of the most actual tasks of modern polymer chemistry. Among ways of environmental protection from polymer waste (keeping on waste deposits, burials, incineration, pyrolysis, recycling) there can be distinguished the method of minimization of ecological pollution due to creation of polymers able to be destructed under influence of natural factors such – chemical (oxygen, air, water), physical (sun light, heat), biological (bacteria, fungi) etc. These factors are very effective and lead to fragmentation of polymer as a result of macromolecule degradation and turning it into low-molecular compounds which become part of natural circuit of substance. In other words biodestruction is reliable and comparatively fast method of utilization. Usually it can be achieved by implication of natural compounds fragments into polymer structure. Other promising method is biopolymers modification with further creation of new synthetic polymers able for degradation under biological factors. Development of this method in future allows to resolve one of the most actual modern problems and to substitute petroleum refining products as the base of chemical synthesis with renewable source. It is also relevant using as reagents economically effective products which are cheaper than oil refining raw materials.

Purpose of our study was to create new polymerizing systems possessing above metioned attractive features. Therefore new polyglucanurethane (PGU) networks were obtained on the base of microbial polysaccharide xanthan and blocked polyisocyanate (PIC) using environment friendly method. Biopolymer application as reagent provides both preserving advantages of initial materials and developing new advanced properties of obtained biodegradable materials due to chemical modification. Replacement of toxic compounds

with latent isocyanate-containing reagent blocked polyisocyanate is also a prominent advantage of developed technique. PGU were obtained via interaction of xanthan hydroxyl groups and isocyanate groups of deblocked above 125°C PIC (Kozak & Nizelskii, 2002).

Microbial polysaccharide xanthan is produced by xanthomonas campestris pv. Campestris bacteria (Gzozdyak et al., 1989). Xantan is well known and most widely used microbial exopolysaccharide. It is used in light industry (textile), heavy industry (drilling and oil production) and food industry as well as in agriculture, forestry, pharmaceutics, medicine and cosmetics. The water solutions of xantane have unique rheological properties due to metal cation complexing ability and formation of primary, secondary and higher levels of structure. The main chain of the polysaccharide is alike to cellulose and its side-chains (pendants) consist of glucose, mannose and glucuronic acid residues.

Blocked polyisocyanate is latent reagent which is able to produce reactive isocyanate groups under elevated temperature. It is multifunctional latent reagent that can consist of 40 to 70 % of dimeric compound , 20 to 60 % of tetramer and 1 to 5 % of trimer and hexamer. Melting temperature interval of blocked PIC is from 80 to-95 °C, NCO-group unblocking temperature ranges from 125 to 130 °C. PIC is soluble in most of organic solvents and can be used both in powder and liquid form.

2. Synthesis

The reaction was provided in solid. Fig. 1 describes the scheme of PGU synthesis. There occur both deblocking of polyisocyanate groups and urethane bonds formation.

There were obtained powdered PGU, hot-pressed samples and reinforced PGU with calculated degree of polysaccharide hydroxyl group substitution of 20, 40, 60, 80 and 100%. As far as obtained polymer is quite new and unexplored polymer material, not full range of the hydroxyl/urethane ratio was studied by methods presented in this Chapter. The obtained materials are acid-, alkali- and thermo resistant.

The reaction path was controlled using sampling procedure and sample analysis with FTIR spectroscopy.

Characteristic band at 2276 cm^{-1} which appears after heating the reactive mixture up to 130°C demonstrates the process of isocyanate groups deblocking. On the initial stages of reaction all of PGU samples show increasing intensity of this band due to active isocyanate group formation.

Interaction of N=C=O groups with the nearest primary and secondary hydroxyl groups of polysaccharide leads to decreasing intensity of characteristic band 2276 cm^{-1} during next 10 min. Diffusion limitations of this reaction are determined by heterogeneity of reactive mixture and results in retarding of urethane bonds formation. Mechanic stirring of reactive mixture allows improve reactive centers contact and leads to total disappearance of isocyanate groups in the system. (Fig 2.a). Consumption of hydroxyl groups is accompanied by disappearance of the band at 3165 cm^{-1} and decreasing of intensity band at 1209 cm^{-1} (valence vibrations and deformation vibrations of O-H bond in glucuronic acid residue

respectively) and by intensity reduction of the band at 3215 cm^{-1} (valence vibrations of primary OH-groups in mannopyranose cycles) (Fig 2 c).
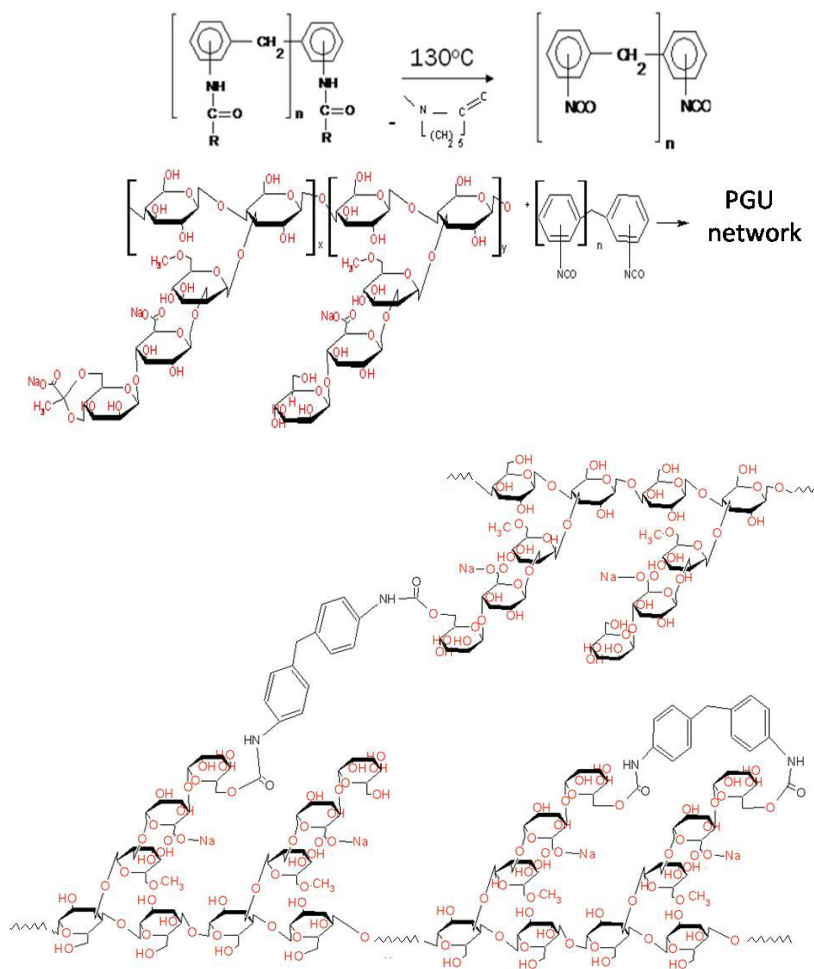
Figure 1. Scheme of PGU synthesis

Increasing intensity of the band at 3364 cm^{-1} (in characteristic doublet of N-H valence vibrations), appearance of the 1635 cm^{-1} band in the region of NH deformation vibrations (amide II) and changes of intensity of 1650 and 1590 cm^{-1} bands respond to formation of urethane bonds and releasing of blocking agent (Fig 2b).

In the wave numbers range from 3000 to 3500 cm^{-1} redistribution is observed of the intensities of absorption bands corresponding to hydrogen linked OH-groups. That points on redistribution of intermolecular bonds in the system during polysaccharide cross-linkage and PGU formation.
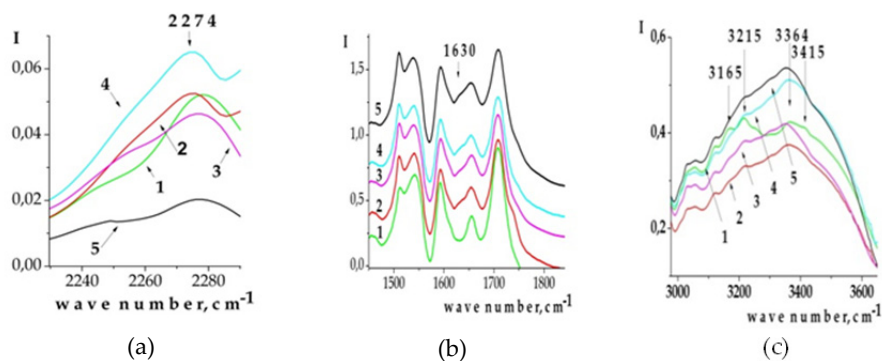
Figure 2. IR spectra of reactive mixture for PGU60 at temperature 130°C(1), 150°C (2), at 150°C after 10 min (3), after 20 min (4) after 30 min(5)

According to FTIR spectra of various PGU (PGU40, PGU80 and PGU100) the number of isocyanate groups released at the initial stage of reaction correlates with the polyisocyanate content in the system. During the first 10 min the process of polyisocyanate deblocking dominates. At the same time the urethane group formation occurs via interactiom of NCO groups and polysaccharide hydroxyl groups in acid residue of glucuronic acid and/or hydroxyl groups of mannose. The time when the urethane group formation begins to dominate depends on balance of the reagents in reaction mixture.

3. Polyglucanurethane chemical and thermal resistance

Obtained PGU networks possess advanced thermal and chemical (both alkali and acid) resistance. Chemical resistance of PGU was analyzed using standard method…[State Standart 12020-72]. Thermal resistance of initial reagents and PGU of various composition were studied with the thermogravimetry. Table 1 shows the results of PGU20 exposure in water, acid- and alkali media. Fig 4. illustrates the TGA curves: mass loss (TG), differential mass loss (DTG) and differential thermal analysis (DTA) that characterize the dependence of thermooxidative destruction character of PGU on the degree of substitution of xanthan hydroxyl groups.

As it can be seen from table 1 data the mass of PGU20 samples remains practically unchanged after the 7 and 13 days exposure in aggressive alkali end acid medium. The initial stages of PGU interaction with water, alkali- and acid media are characterized with ignificant swelling of polysaccharide component.

According to TGA data thermooxidative destruction of the systems analyzed consists of several stages. TGA curves of xanthan are typical for polysaccharides. TGA curves character for PGU networks and number of stages in temperature interval from 20 to 700°C depend on the balance of hydroxyl and urethane groups in PGU. Stage of weight loss in temperature interval 60-140°C is accompanied with endothermal peak on DTA curve and responds to absorbed water removal.

Time, day	Sample weight, g		
	H₂O	*H₂SO₄*	*NaOH*
1	0,081	0,085	0,081
2	0,213	0,205	0,431
3	0,217	0,213	0,489
7	0,250	0,224	0,485
13	0,425	0,241	0,489

Table 1. The weight change of PGU20 exposed in deionized water, concentrated sulphuric acid (V=20 ml, 30% wt.) and concentrate alkali solution (V=20 ml, 40% NaOH).

Presenting mass of absorbed water in modified and non-modified samples of exopolysaccharide as mass loss at the first stage (temperature interval 45 – 150°C) we can see that amount of absorbed water correlates with balance of hydroxyl and urethane groups in the system (Fig.3). It corresponds with the fact that system hydrophilic properties correlate with amount of hydroxyl groups. Weight loss at this stage is 1,5; 2,5; 8,5 % wt. for PGU80, PGU40, PGU20, respectively.
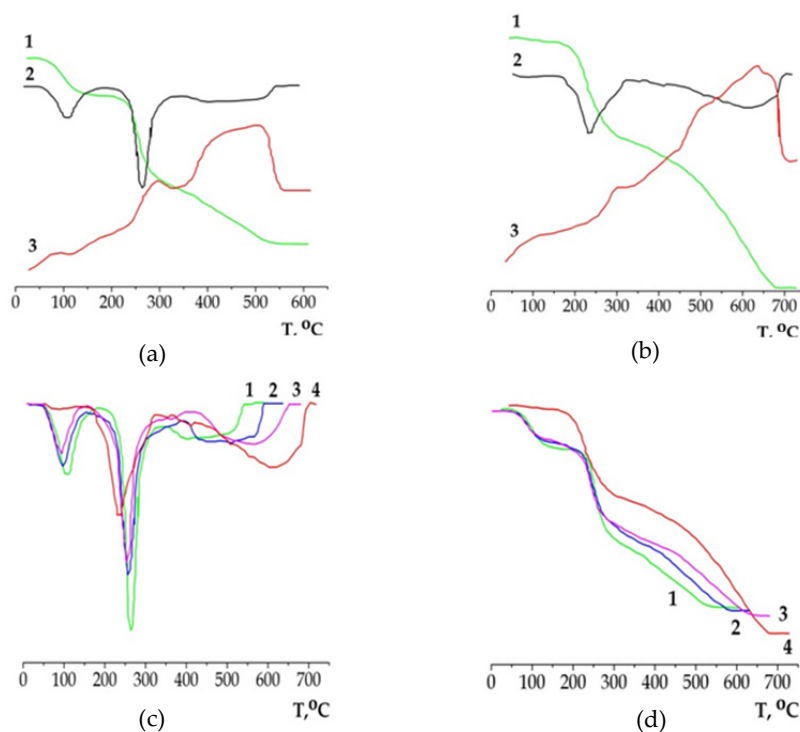

Figure 3. TGA curves - TG (1), DTG (2), DTA (3) of initial reagents: xanthan (a), blocked PIC (b); curves DTG (c) and TG (d) for initial reagents and PGU of various composition: xanthan (1), 2- PGU20 (2), PGU40, PIC (4)

Intensive thermal-oxidative destruction is observed in 200 – 400°C temperature interval. The characteristic temperature responding to maximum speed of weight loss at the stage shifts toward the higher temperatures with increasing of urethane groups amount in the system. Weight loss at this stage is 35, 30, 35 % wt. for PGU80, PGU40, PGU20, respectively.

Wide peak on DTG curves in temperature interval from 500 to 700°C mainly corresponds to destruction of carbon base of polymer. With growth of urethane group content in the system the carbon residual decreases.

As it can be seen thermal resistance of PGU grows with increasing of urethane group amount. For instance, for PGU40 high temperature stage is allocated 40°C lower than for the PGU 80. The degree of hydroxyl substitution also influences the system capacity of water absorbance. With growth of urethane group content in the system the amount of absorbed water declines

4. PGU interaction with water solutions of phenol and transition metal salts

It is known that microbial polysaccharides are considered as prospective raw materials for obtaining effective sorbents for extracting organic compounds and metal ions from water solution (Crini, 2005). Application of water-soluble polysaccharides (eg. xanthan) as sorbents is difficult. Using of PGU allows both keep sorption properties of polysaccharide and eliminate a number of disadvantages (water solubility, low chemical resistance etc.). Study of properties of cross-linked PGU (Hubina, 2009) revealed its ability to quantitative extraction of phenol and bivalent metal ions from water solution, while controlling capacity of the material with cross-linking degree.

To analyze ability of PGU to phenol sorption from its water solution the pollutant concentration was controlled before and after exposure of PGU20 and PGU60 films in 10^{-4}M phenol water solution during 24, 48 and 120 hours. Phenol concentration was monitored using UV electron spectroscopy by the change of band intensity near 256 nm. Experiment conditions were as follows: T=18 °C, $m_{sorbent}$=7 g, $V_{solution}$=50 ml. Calibration curve was plotted for 0,05; 0,075; 0,1; 0,15 and 0,2 M phenol water solutions.

According to UV-spectroscopy data after 24 hours of exposure PGU in phenol solution increasing of phenol concentration is observed both for PGU20 and PGU60 (Fig.4). Further exposure of PGU in solution leads to essential decreasing of phenol concentration. Such phenol concentrating during PGU interaction with phenol solution can be explained by the preferable swelling of polysaccharide component of the polymer in water.

The same character of concentration change is observed while extracting Cu^{2+} ions from copper sulfate solution. (Fig.5). Its concentration change was controlled using electron spectroscopy in Vis-region by the change in band intensity near 810 nm. That band corresponds to d-d transitions in $[Cu(H_2O)6]^{2+}$aqua ion. Exposure of PGU60 sample in copper sulfate water solution during 10 min. is accompanied by sufficient growth of

solution absorbance and shows copper ions concentrating. Increasing time of interaction with sorbent to 60 min leads to absorbance reduction.
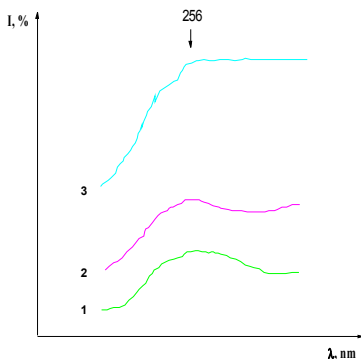
Figure 4. The electron spectra of phenol water solutions: 1 – initial; 2 – PGU60 after 10 min exposure; 3 – PGU20 after 10 min exposure
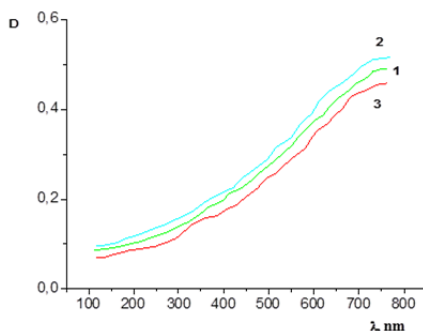
Figure 5. The electron spectra of copper salt water solutions: 1 - initial, 2 - after 10 min of PGU exposure and 3 - after 60 min of PGU exposure

Interaction of PGU40 and PGU80 with water solution of Cu^{2+} and Co^{2+} salts with concentration of 50 and 500 mg/dm^3 was studied in static conditions using conductometry. Solution conductivity was fixed after 2, 12 and 74 hours of PGU exposure. Experiment conditions were as follows m_{PGU}=1,25 g; $V_{solution}$=50 cm^3 ; permanent stirring frequency=2 Hz; room temperature. Intermediate and final concentrations were calculated from calibration curve. Fig 7 demonstrates conductivities of cobalt and copper salt solutions of various concentrations (50 and 500 mg/dm^3) depending on the time of interaction with PGU40 and PGU80. In the table 2 there are the results of concentration changes of copper(2+) sulfate and cobalt(2+) chloride solutions respectively *vs* time of exposure PGU40 and PGU80. Fig 6 shows that conductivity of cobalt chloride and copper sulfate solutions grows on the initial stages of sorbent exposure for both high (500 mg/dm) and low (50 mg/dm) concentrations.

1 – CuSO₄ 500 mg/ dm³ in PGU80,
2 - CuSO₄ 500 mg/ dm³ in PGU40,
3 - CuSO4 50 mg/ dm³ in PGU80,
4. - CuSO₄ 50 mg/ dm³ in PGU40

1 - CoCl₂ 500 mg/ dm³ in PGU80,
2 - CoCl₂ 500 mg/ dm³ in PGU40
3. - CoCl₂ 50 mg/ dm³ in PGU80,
4. - CoCl₂ 50 mg/ dm³ in PGU40
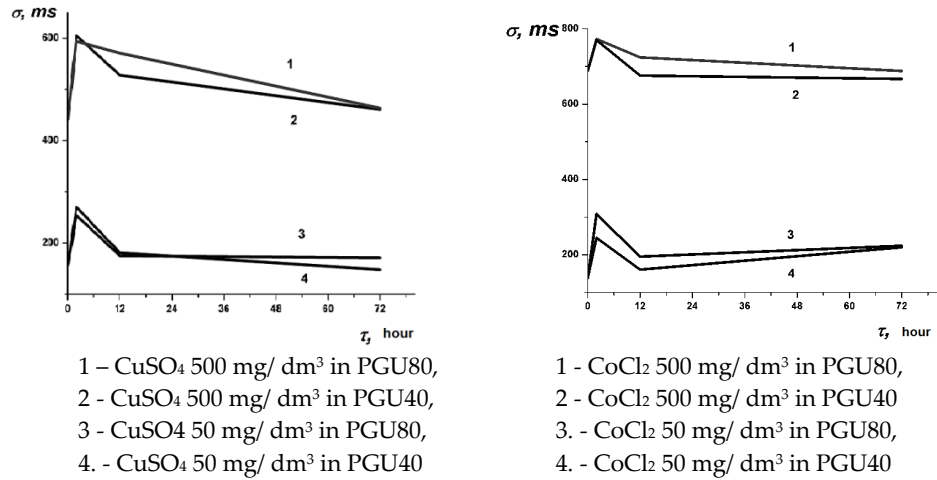
Figure 6. Dependence of solution conductivity *vs* time of sorbent exposure

Similar effect was observed for hot-pressed samples of PGU while interacting with water solutions of phenol and transition metal salts due to predominant swelling of polysaccharide component on the initial stages. Next 12 and 74 hours of PGU exposure result in sufficient solution concentration decreasing due to metal ions capture by the functional groups of sorbent. Equilibrium was achieved both for PGU40 and PGU80 in solutions of high cobalt salt concentration (500 mg/ dm³) while for copper salt solutions equilibrium was achieved for low concentration (50 mg/ dm³).

As table 2 and Fig 6 show the efficiency of metal ions extraction depends on both concentration of solution and the balance of hydroxyl and urethane groups in PGU. The highest concentration fall was observed for PGU80. The solutions of low concentration aren't sensible to hydroxyl and urethane balance in PGU. Besides, the best ion extraction of cobalt ions from low concentration solutions is achieved with short-time exhibition of sorbent. For cobalt salts solutions of high concentration and copper salts solutions of low concentration the best effect is achieved during 74 hours of exhibition.

PGU	C, mg/dm³	Cu SO₄			CoCl₂		
		ΔC_{2h}, %	ΔC_{12h}, %	ΔC_{74h}, %	ΔC_{2h}, %	ΔC_{12h}, %	ΔC_{74h}, %
40	50	20,0	45,3	55,0	11,2	43,4	33,1
80	50	24,2	47,2	48,3	29,2	53,6	36,4
40	500	73,2	84,7	86,4	55,0	58,0	60,0
80	500	63,2	83,2	86,3	55,2	60,7	61,2

Table 2. Concentration change of cobalt chloride and copper sulfate solutions.

The results of PGU sorptive properties research in static conditions correspond with the research results obtained under dynamic conditions. Ability of synthesized powdered PGU materials to sorb metal ions in dynamic conditions was examined for $CoCl_2$ and $CuSO_4$ water solutions of various concentration. PGU60 sorbent was used. Concentration of initial and final solutions was controlled using electron spectroscopy in Vis-region by the change of band intensity responding to d-d transitions in aqua ion $[Co(H_2O)_6]^{2+}$ and d-d transitions in aquaion $[Cu(H_2O)_6]^{2+}$ (near 510 nm and 810 nm respectively). Calibration graphs were plotted for 0,05; 0,075; 0,1; 0,15, 0,2 M concentrations of $CoCl_2×6H_2O$ and $CuSO_4×5H_2O$. Experiment was carried out at 18 °C. Solutions of copper and cobalt salts with initial concentrations of 0,1 M and 0,05 M were pumped through the column filled with the sorbent powder. m_{PGU}=7 g; $V_{solution}$=50 cm³. Under dynamic conditions the time of interaction ranged from 60 to 120 seconds. Fig. 7 illustrates the character of Co^{2+} and Cu^{2+} ion sorption.

After dynamic contact of copper salt with sorbent during 60 seconds absorbance of filtrate (D) falls to 1,08 in comparison with the initial solution absorbance value of 1,4. It responds to 40% decreasing of copper ions in solution. For 0,1M solution of cobalt chloride after dynamic contact with PGU40 there is observed absorbance fall from 0,52 to 0,48 that responds to extracting of 20% metal ions. For 0,05M solution of cobalt chloride is achieved 40% decreasing of cobalt ion concentration after 60 sec contact. Calculated concentration of cobalt ions in final solutions was 0,08M for initial 0,1M and 0,03M for initial 0,05M. The dynamic sorption of metal ions with PGU40 sorbent is more effective for solutions with lower concentration.

(a)	(b)	(c)

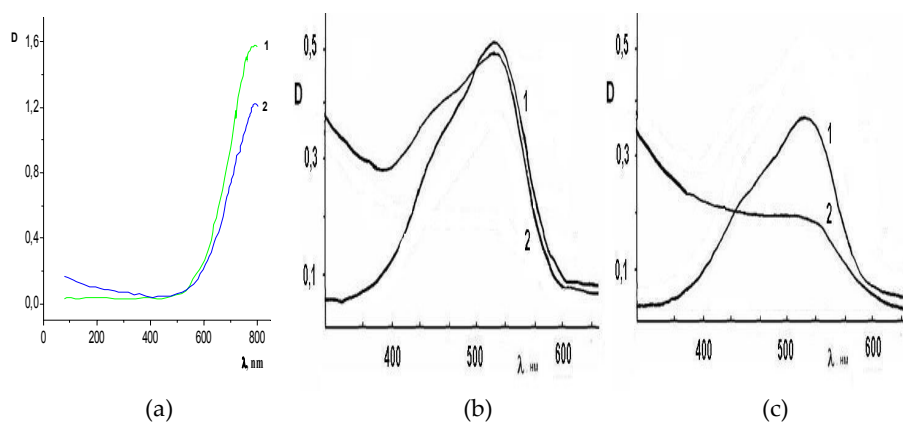**Figure 7.** The electron spectra of water solutions of metal salts before (1) and after (2) passing through the column filled with powdered PGU40

According to (Bergmann et al., 2008) the mechanism of ion capture by water soluble polysaccharides mainly related to formation of complexes of chelate structure. Research of complex formation of PGU with metal ions allows conclude of chelate structure of formed

complexes. In particular chelate structure of copper ion (2+) complexes with PGU is confirmed in (Hubina et al., 2010). Using results of (Bergman et al., 2008; Hubina et al., 2010) we can assume that cobalt ions also form chelate structures with PGU.

Analysis influence of cross-linking degree of PGU on complexing metal ions with functional groups of PGU demonstrated that variation of hydroxyl and urethane groups balance in the system allows to achieve effective control over holding metal ions in PGU matrix.

Peculiarities of "PGU-copper ion" complex formation were studied using electron paramagnetic resonance method (EPR). Copper ions were introduced into PGU matrix via pumping of 0,1M water solution of CuSO4 through column filled with PGU60 (the way it described above for dynamic sorption conditions). Then metal-containing PGU sample was dried and the EPR spectra of bivalent copper were recorded. Fig. 8 demonstrates EPR spectrum of dried PGU60 after interaction with copper sulfate water solution.

Recorded spectra are characterized with anisotropy of g-factor and appearance of hyperfine structure in the region of $g_{\parallel}$ that is usually concerned to tetragonal chelate complexes of bivalent copper. Hyperfine structure components are broadened as a result of superposition of signals from tetragonal copper complexes which can differ both in symmetry distortion and in nearest chemical surrounding. Integral intensity of obtained EPR spectra depends on the balance of hydroxyl and urethane group in PGU while electron spin parameters are almost unchanged. That points on preferable interaction of metal cation with one of the components of PGU. This conclusion corresponds with the regularities of bivalent copper ion complexing with mono saccharides.
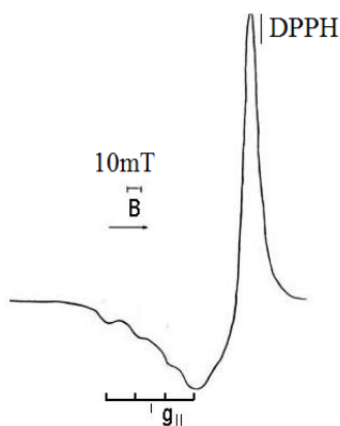
Figure 8. The representative EPR spectrum of copper containing PGU

Experimental analysis of influence of metal ions on water molecules self diffusion process in swelled polysaccharide gel was carried out by the method of quasi-elastic neutron scattering.

For description of experimental dependences there was calculated the values of general coefficient of water self diffusion in swelled gel $D = D_{singl} + D_{col}$ as well as values of its D_{singl} (single particle) component and D_{col} (collective) component. (Fig 9b).
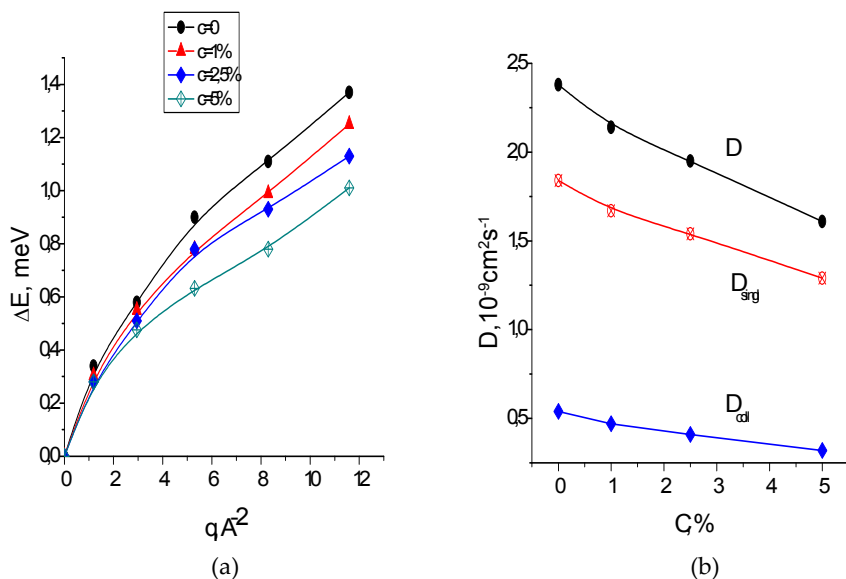
Figure 9. Dependence of energy broadening of quasi-elastic peak ΔE *vs* squared transferred kinetic moment q for various polymer–metal salt ratio (a) and concentration dependencies of D, D_{singl} and D_{col} (b).

Obtained data demonstrate that addition of metal salt to water and increasing of solution concentration decreases the coefficient of water molecules self diffusion in swelled xanthan gel both for general coefficient and for its components.

That indicates the swelled polymer density growth in presence of metal ions. Such condensation effect can be explained taking into account ability of transition metal chelates to form charge-transfer complexes with electron-donor centers of polymer resulting in creation of additional 'coordination juncs' both in swelled linear polysaccharide and in chemically cross-linked PGU.

Thus, polyglucanurethanes based on water soluble polysaccharide xanthan and blocked polyisocyanate are able to extract heavy metal ions from their salt water solutions. Variation of hydroxyl and urethane groups balance at the cross-linking stage provides effective regulation of complexing and capturing of metal ions with polyglucaneurethanes.

5. Biodestruction

Used plastics utilization had become an important problem. One of the ways of polymer and in particular of polyurethane waste reclamation is biodegradation of plastic. The ability

to biodegradation was analized on the PGU exposed in the medium of common soil microorganisms association as well as into the medium of resistive microbial association isolated from soils polluted by chlorine-organic pesticides. (Hubina et al., 2009). There were explored biodegradable properties of two types of PGU20: based on microbial polysaccharide xanthan (PGU20) and methylcellulose (PGU20-cellulose).

The resistant microbial association with working name "Micros" was isolated from soil polluted by chlorine-organic pesticides. This association has high destructive activity with respect to chlorine-organic, organic-phosphorous, simm-triazine and other pesticide groups. It was supposed, that "Micros" is able to specialize to exotic substratum and could decompose polyglukanurethane systems due to utilization of this polymer as carbon or nitrogen source. To compare destruction of the PGU by common soil microorganisms the soil native-born microbial association was isolated from pollution-free chernozem soil. It has never contacted with pollutants in soil.

Changes in polymer structure after exposure in microbial medium were analyzed by FTIR spectroscopy, optical microscopy and thermogravimetry. Fig presents IR – spectra of PGU20 after contact with aggressive and natural microbial medium. Evaluation of redistribution of bonds in destructed PGU was provided by analysis of the location, width and intensity of valence vibrations band of C-O-C intercycle group of polysaccharide (805 cm^{-1}) and also by analysis of location and intensity of band amide II) in PGU urethane bridges (1600 ÷ 1660 cm^{-1}).

In PGU spectrum after the sample contact with aggressive medium (spectrum 3 fig 10) it is seen resolving of complex band at 1600 – 1660 cm-1 (N-H vibrations) comparing to initial PGU20 spectrum (Fig.10 spectrum 1). This may be caused by destruction of essential part of urethane bonds of PGU in aggressive medium.
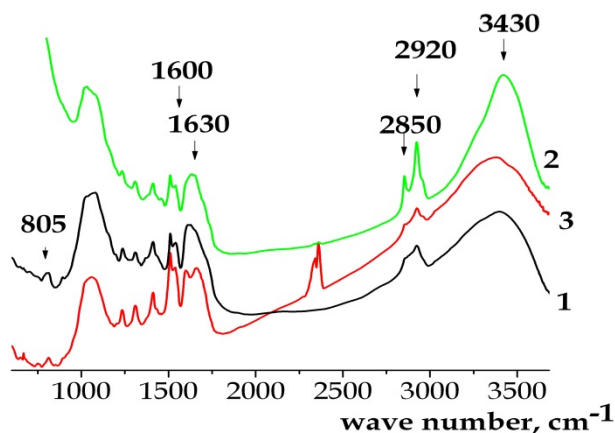

Figure 10. IR spectra of PGU20 based on xanthan 1 – initial PGU, 2 – PGU after contact with natural microbial medium, 3 – PGU after contact with aggressive microbial medium

Other type of PGU destruction is observed in natural medium (fig. 10 Spectrum 2). It is approved by redistribution of intensities of valence vibrations of C-O-C groups comparing with initial PGU and by absence of prominent changes in area of amide II. The band at 805 cm-1 responding to intercycle C-O-C bonds disappears. It is accompanied by increasing of intensity of the band responding to free OH-group (3430 cm-1) and C-H bonds (2850 and 2920 cm-1).

Another evidence of sufficient urethane bonds destruction in PGU20 in aggressive medium is seen on microphoto of PGU films after aggressive destruction (Fig. 11). There can be distinguished fibrous polymer elements, usual for fibrous of initial polysaccharide xanthan, which formed after urethane destruction. This effect is absent on the micro photos of PGU sample after destruction in natural microbial medium .

1 – initial polysaccharide fibers; 2 - effect of aggressive microbial medium; 3 – effect of natural microbial medium.

Figure 11. Micro images of PGU films after contact with natural and aggressive microbial mediums

IR spectra of PGU20-cellulose present the difference between this polymer biodestruction and biodestruction of PGU20-xanthan (Fig. 12)

In particular, the intensity of the band in area 1600 – 1660 cm-1 falls both for natural medium and aggressive one. (Fig.13 stectra 2 and 3). Intensity of 809 cm-1 band decreases (valence vibrations of intercycle bonds C-O-C) after exposure of PGU20-cellulose in natural microbial medium (Fig.12 spectrum 2) differing from intensity of this band in PGU20-cellulose spectrum after contact with aggressive medium. Bands corresponding to symmetric and asymmetric vibrations of saccharide groups C-O-C are nearly unchanged.

Efficient difference in biodestruction character of PGU20-xanthan and PGU20-cellulose allows conclude that xanthan based PGU is destructed mainly in its saccharide side-chains (containing D-mannose, D- glucuronic acid and D-glucose).

IR data correlate with results of TGA analysis. Table 3 shows difference in character of TG, DTG and DTA curves for PGU20-cellulose after contact with aggressive and natural medium. On DTG curves of PGU20-cellulose after natural and aggressive medium it is seen that stage of thermal destruction in temperature interval 200 – 300 oC is moved into district of higher temperatures while in PGU40-xanthan this stage is splitted and differs for natural and aggressive medium.
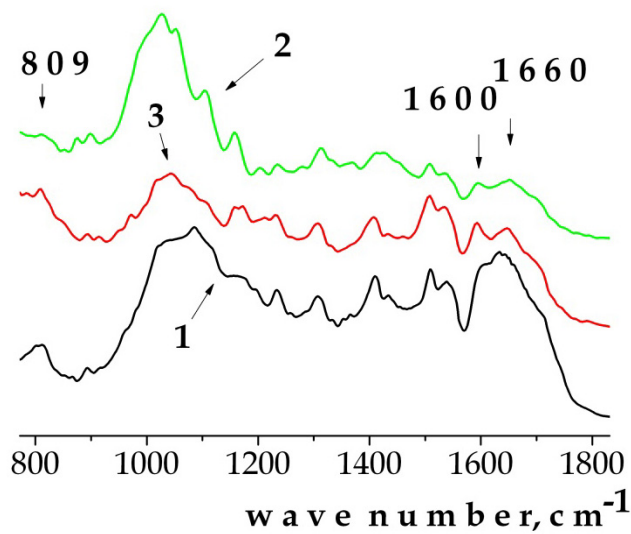
Figure 12. IR spectra PGU20-cellulose 1 – initial PGU20-cellulose; 2 – PGU after contact with natural microbial medium, 3 – PGU after contact with aggressive microbial medium.
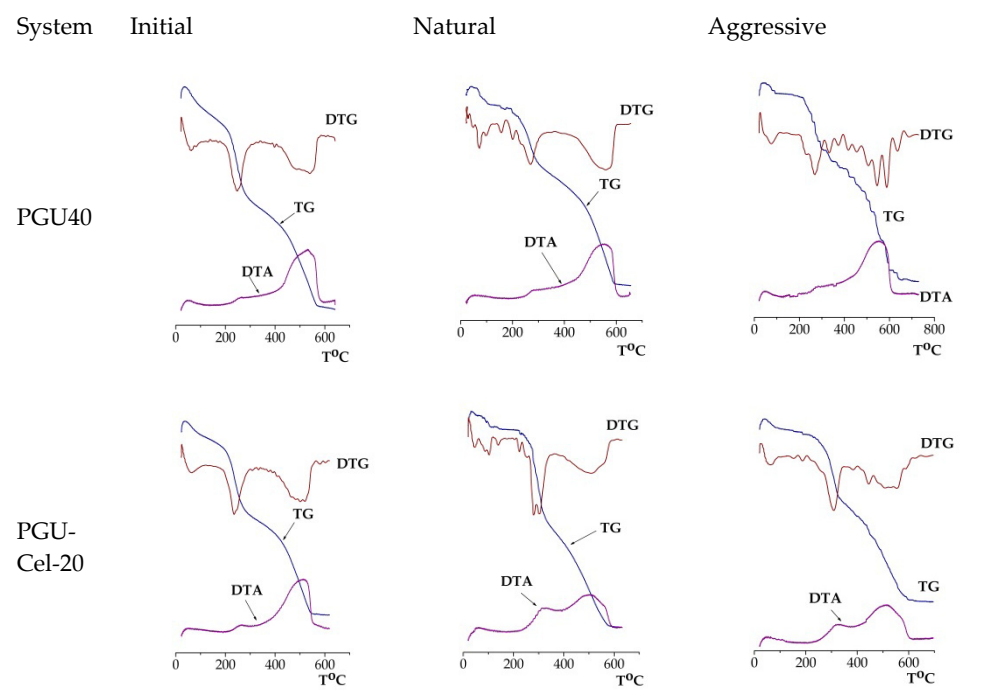
Table 3. IR spectra of PGU40 and PGU-cellulose-20 after biodestruction

6. Conclusions

New hydroxylcontaining polyurethane networks (polyglucanurethane) with various urethane group content were obtained based on microbial exopolysaccharide xanthan and latent blocked polyisocyanate using environment friendly technique. Obtained polyglukaneurethanes possess advanced thermal and chemical (both alkali and acid) resistance. Thermal resistance of PGU grows with increasing of urethane group amount. Were as with growth of urethane group content in the system the amount of absorbed water declines.

Study of properties of polyglucanuretanes reveals their ability to quantitative extraction of phenol and bivalent metal ions from water solution, while controlling sorption properties of the material with polysaccharide cross-linking degree. According to electron spectroscopy and EPR data the main mechanism of ion capture by polyglucanurethane consists in formation of "polymer-metal ion" chelate complexes.

Biodestruction research demonstrate that polyglucanurethane degradation in aggressive microbial media occurs via polysaccharide fragmentation due to urethane bonds cleavage. On the contrary microbial association that was isolated from pollution-free chernozem disintegrate the polysaccharide chains predominantly.

But both in aggressive microbial association and in natural microbial association that was isolated from pollution-free soil the direct relation was observed between destruction process intensity and percentage of polysaccharide OH-group substitution in PGU. The lower percentage of OH-groups was substituted, the more intensive destruction process was observed.

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Biobased Polyurethane from Palm Kernel Oil-Based Polyol

Khairiah Haji Badri

Additional information is available at the end of the chapter

1. Introduction

Polyurethanes are block copolymers containing segments of low molecular weight polyester or polyether bonded to a urethane group (-NHCO-O). Traditionally, these polymers are prepared by reacting three basic materials; polyisocyanates, hydroxyl-containing polymers (polyester or polyether polyol) and chain extender, normally low molecular weight diol or diamine (such as 1, 4-butanediol or 1, 4-dibutylamine).

Polyols are generally manufactured by one or two possible chemical routes, namely alkoxylation and esterification. Alkoxylation, by far is the most common route, involves the reaction between a hydroxyl or an amine-containing initiator (such as sucrose, glycerol) and either propylene- or ethylene oxide. A molecular weight of up to 6000 can be obtained by extending the polymer chain with the addition of alkylene oxide. This product is suitable for more flexible polyurethanes in cushioning and elastomeric applications. The alkylene oxide used in this process is derived from mineral oil via the petroleum industry. Propylene for instance, is derived from the petroleum cracking process and is then converted to propylene oxide before being further converted to polyol by reaction with an amine or hydroxyl-containing initiator such as glycerol.

At present, most polyols used in polyurethane industry are petroleum-based where crude oil and coal are used as starting raw materials. However, these materials have been escalating in price and rate of depletion is high as well as required high technology processing system. This necessitates a look at utilizing plants that can serve as alternative feed stocks of monomers for the polymer industry. Moreover, with increasing annual consumption of polyurethane, its industrial waste is a serious matter. In Europe and the United States of America for instance, government regulations encouraged recycling of materials to avoid excessive usage of landfill area. However, with thermosetting behavior of polyurethane the recycling activity is difficult and limited. The best alternative is

biodegradation. Biodegradable polymers have widely been used in pharmaceutical industry such as suture usage, wound-dressings, surgical implants and medicine delivering system. But there are still some usage limitations either due to high production cost or its low performance. This performance can be achieved by chemical and physical modification of these materials through combination of biodegradable and non-biodegradable materials.

Polyurethane based on polyester has been known to be more biodegradable than from polyether. Utilization of renewable resources to replace petrochemicals in polyurethane industry has attracted attention of many technologists. Most of these renewable resources are forest products. Palmeri oil, vernonia oil, castor oil and cardanol oil (extracted from the cashew nut shell) have been used to synthesize polyurethane polyols with multiple functionality to replace the petrochemical-based polyols (Pourjavadi et al. 1998 and Bhunia et al. 1998). Castor oil has long been used in the polyurethane industry. Relatively, it is stable to hydrolysis due to its long fatty acid chain but sensitive to oxidation due to the present of unsaturated fatty acid. Commercially, it can only be used in the coating and adhesive industries.

Polyester polyols are generally consisted of adipic acid, phthalic anhydride, dimer acid (dimerized linoleic acid), monomeric glycol and triol. It has low acid number (normally 1-4 mg KOH/g) and low moisture content (less than 0.1%). These properties are not easily achieved unless a high-technology processing method is applied. Due to these industrials requirements, polyester polyols are usually supplied at higher price compared to polyether polyols. Polyether polyols on the other hand, are commercially produced from catalytic reaction of alkylene oxide i.e.propylene oxide or ethylene oxide to di- or polyfunctional alcohol. Its functionality is four and above and is useful in the production of rigid foam. It can also be produced with the presence of di- or polyfunctional amine i.e. diethanolamine when high reactivity is required (such as laminated continuous panel production). Important properties specified in polyurethane industry for polyols are as summarized in Table 1.

Classification	Flexible foam / Elastomer	Rigid / Structural foam
Molecular Weight	1,000 to 6,500	400 to 1,200
Hydroxyl value, mgKOH/g	28 to 160	250 to 1,000
Functionality	2.0 to 3.0	3.0 to 8.0

Table 1. Technical requirements for polyols used in polyurethane industry (Wood 1990).

The lower the equivalent weight of polyol is, the higher the rigidity of the polyurethane. These contributed to higher compressive strength, modulus, thermal stability and dimensional stability polyurethanes. If the equivalent weight is excessively low, the resulting polymer becomes more friable and required more isocyanate especially for the production of rigid polyurethane foam (Berlin and Zhitinkina 1982).

Natural occurring oils and fats are water-insoluble substances originated from vegetable, land or marine animal known as triglycerides. A triglyceride is the reaction product of one molecule of glycerol with three molecules of fatty acids to yield three molecules of water

and one molecule of a triglyceride. The molecular weight of the glycerol portion (C_3H_5) of a triglyceride molecule is 41. The combined molecular weight of the fatty acid radicals (RCOO-) varies. Natural oils can undergo a number of chemical reactions such as hydrolysis, esterification, interesterification, saponification, hydrogenation, alkoxylation, halogenation, hydroxylation, Diels-Alder reaction and reaction with formaldehydes. Polyester is a high molecular weight chemical with ester group –O-C=O- as repeating unit. It is achieved by polycondensation and esterification of carboxylic acid with hydroxyl-containing compounds.

Lauric oil or better known as lauric acid is the main source of fatty acids. The only lauric oils available to the world market are coconut oil and palm kernel oil. The oil palm is a monocotyledon belonging to the Elaeis Guiness species. Palm kernel oil (PKO) is obtained from the kernel part of the oil palm fruit. The percentage of unsaturated fatty acids is much lower compared to palm oil as shown in Table 2. PKO consist of 80 percent saturated fatty acid and 10% of each polyunsaturated and unsaturated fatty acid. Palm oil on the other hand, consist of 53% saturated fatty acid, 10% polyunsaturated and 37% unsaturated fatty acids. The higher the unsaturated fatty acid contents the unstable it is when exposed to heat. The reactivity increases substantially if the double bond are conjugated (separated by one single bond) or methylene-interupted (separated by a –CH_2 unit). PKO contains only traces of carotene.

Vegetable Oil	Saturated Fatty Acid, %							Unsaturated Fatty Acid, %					
								Enoic				Dienoic	Trienoic
Carbon Chain	C8	C10	C12	C14	C16	C18	>C18	<C16	C16	C18	>C18	C18	C18
Palm Oil				1-6	32-47	1-6				40-52		2-11	
Palm Kernel Oil	2-4	3-7	45-52	14-19	6-9	1-3	1-2		0-1	10-18		1-2	

Table 2. Fatty acid contents in palm oil and palm kernel oil (Khairiah Haji Badri 2002).

Two major reactions occurred during polymerization of polyurethane. First, the reaction of isocyanate with water yields a disubstituted urea and generates carbon dioxide. This is called the blowing reaction because the carbon dioxide is acting as an auxiliary-blowing agent. The second reaction is between the polyfunctional alcohol (polyol) and the isocyanate (Fig. 1).

R-N=C=O + R'-O-H   →   R-NH-C(O)-O-R
Isocyanate   Polyol   Polyurethane
R-N=C=O + H-O-H   →   R-NH-C(O)-O-R' + R-N-H + CO_2
Isocyanate   Water   Polyurethane
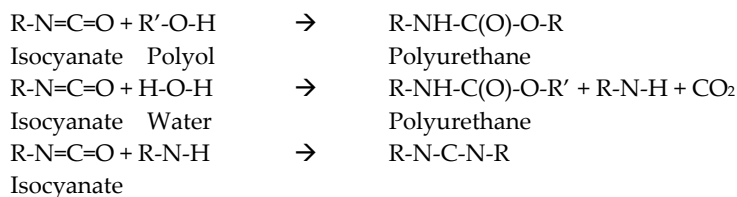R-N=C=O + R-N-H   →   R-N-C-N-R
Isocyanate

Figure 1. Addition polymerization of polyurethane

It generates a urethane linkage and this is referred to as the gelation reaction. The isocyanate reacts slowly with alcohols, water and the unstable amino products without the present of catalyst. However, for most commercial requirements the acceleration of these reactions is required.

One characteristic of amorphous polymeric systems is the glass transition temperature, T_g that defines the point where the polymer undergoes a change from glassy to rubbery behavior. Considerable attention has been devoted over the last several years to these studies: synthesis of polyurethane polyol from PKO and the production of oil palm empty fruit bunch fiber-filled PU composites (Badri et al. 1999, 2000[a], 2000[b], 2001; Khairiah Haji Badri 2002; Badri et al. 2004[a], 2004[b]; Badri et al. 2005; Badri & Mat Amin 2006; Badri et al. 2006[a], 2006[b]; Mat Amin et al. 2007, Norzali et al. 2011[a], 2011[b]; Liow et al.; Wong & Badri 2010, Badri & Redhwan 2010;). These include intensive evaluation on the chemical, mechanical, thermal and environmental stress on the synthesized polyol and PU foam by looking at various scopes:

- Synthesis of the palm kernel oil-based polyol from refined, bleached and deodorized (RBD) palm kernel oil via esterification and polycondensation.
- Preparation of the polyurethane foam from the RBD PKO-based polyol and evaluation of its chemical, mechanical and thermal decomposition and glass transition temperature of the foam.
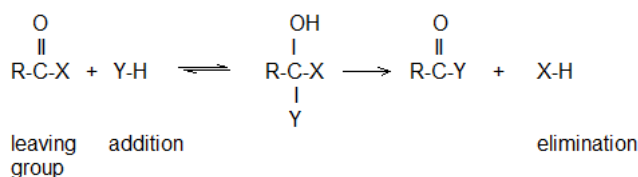
2. Vegetable oil-based polyurethane polyol

Several reports have been published in producing polyurethane from vegetable oils and some of them have even been patented (Arnold 1983, Chittolini 1999 & Austin et al. 2000). Focus was given to utilization of mixture of vegetable oils in the polyurethane system and not as raw materials to produce the polyurethane. Vegetable oils that are frequently used are soybean oil, safflower oil, corn oil, sunflower seed oil, linseed oil, oititica, coconut oil, palm oil, cotton seed oil, peritta oil, olive oil, rape seed oil and nuts oil. Researches carried out using these oils were focusing on full usage of materials found abundance in certain area such as production of polyurethane foam from mixture of starch and triol polycaprolactone (Alfani et al. 1998) and mixture of starch, soybean oil and water *(Fantesk)* (Cunningham et al. 1997). Polyurethane products based on vegetable oils like nuts oil, soybean oil, corn oil, safflower oil, olive oil, canola oil and castor oil (Nayak et al. 1997, Bhunia et al. 1998, Mohapatra et al. 1998, Javni et al. 1999) exhibited high thermal stability. In Malaysia, the Malaysian Palm Oil Board (MPOB) has taken the initiative to produce polyol from the epoxidation and alcoholysis of palm oil (Ahmad et al. 1995, Siwayanan et al. 1999). An early finding has indicated that when natural oils or fats are epoxidized, they react with polyhydric alcohols to produce polyols. A study by Guthrie and Tait (2000) has successfully produced an ultraviolet (UV) curable coating from epoxidized and unprocessed palm oil, and epoxidised palm olein.

These researches however, are pointing to one direction that is synthesizing polyester. Polyester may be defined as heterochain macromolecules containing repeating ester groups (-

COO-) in the main chain of their skeletal structures. Most useful routes to polyester synthesis of carboxylic acids are step growth or direct polyesterification (condensation polymerization) and ring opening polymerization of lactones. The former is suitable for synthesis of aliphatic polyester where it utilizes primary and secondary glycols where the primary hydroxyl groups being esterified more readily. The removal of liberated water from the process is carried out by stirring and percolation of inert gas such as nitrogen, N_2. If a volatile monomer is used (i.e. glycol), an excess amount with respect to dicarboxylic acid (10 %w/w) should be added to compensate for losses caused by evaporation at high temperature. Side reactions may occur usually at 150°C and above which leads to changes in polymer structure and reduces molecular weight distribution of the polyester (Jedlinski 1992).

Esterification is one of many substitution reactions of carboxylic acids and their derivatives that involve tetrahedral addition intermediates. The extension of mechanism of carbonyl addition is as shown below. The best leaving group is the weakest base. In addition, reaction of ester with hydroxylamine (:NH₂OH) gives N-hydroxyamides (known as hydroxamic acids). This is the point where it is vital to add some reactivities to the existing polyester by addition of the amide group to form polyesteramide (Loudon 1988).

$$\underset{\text{leaving group}}{R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}X} + \underset{\text{addition}}{Y\text{-}H} \rightleftharpoons R\text{-}\underset{\underset{\displaystyle Y}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}\text{-}X \longrightarrow R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}Y + \underset{\text{elimination}}{X\text{-}H}$$

Polyurethanes are possible to decompose by prolonged contact with water, diluted acids or moist heat (causes swelling and slow hydrolysis, particularly in some ester-type polyurethanes), chlorine bleach solutions (may cause yellowing and decomposition) and prolonged exposure to light (discoloration of derivatives of aromatic isocyanates) (Roff et al. 1971). The dimensional stability of foams is a time-dependent property that receives considerable attention. Disregarding cold aging at -15±2°C, humid aging (70± 2°C at 95±5% relative humidity) is usually a prime property. Humid aging requirements (specifications) are determined by the end use of the foam. A foam that has expanded and the shrunk is considered, as a first approximation, to be caused by the effect of plasticization by heat and moisture that would allow the stresses built into the foam at the gel to relax, which will then allow the foam to return to a lower energy state. For urethane foams specifically, high thermal stability results in excellent dimensional stability over a large temperature range.

3. Green material and technology

The RBD palm kernel oil (viscosity of 65 cps, specific gravity of 0.99 g/ml, and moisture content of 0.02%) was obtained from Lee Oilmill Sdn Bhd, Kapar, Klang, Malaysia and was used as received without further purification. Polyhydric compounds consisted of dietanolamine, DEA (purity of 99.8%, hydroxyl value of 1057 mg KOH/g and functionality

of 2, with viscosity of 236 cps and moisture content of 0.05%) and ethylene glycol, MEG (hydroxyl value of 1122 mg KOH/g) were supplied by Cosmopolyurethane (M) Sdn Bhd, Pelabuhan Klang, Malaysia with the inclusion of potassium acetate which was manufactured by Merck (M) Sdn Bhd, Shah Alam Malaysia. Chemicals used for the preparation of polyurethane foam were crude MDI (2,4-diphenylmethane diisocyanate), tetramethylhexanediamine (TMHDA) and pentamethyldiethyltriamine (PMDETA) (Cosmopolyurethane (M) Sdn Bhd, Port Klang, Malaysia) and silicon surfactant (Tegostab B8408, Th. Goldschmidth, Singapore). The blowing (foaming) agent used was tap water.

DEA, MEG and potassium acetate were mixed homogeneously with a ratio of 90:7:3 to form the polyhydric compound. A mixture of this polyhydric compound with RBD PKO at stochiometric ratio was continuously stirred in a 2-L glass reactor and was reacted separately at three different temperature ranges: 165-175°C, 175-185°C and 185-195°C, each for 30 minutes. The nitrogen gas was flushed into the system throughout the process. The reflux flask was connected to a condenser and a vacuum pump to withdraw the water and excess of reagent from the system. The progress of the reaction was monitored by sampling at intervals. The samples collected were then analyzed. At the end of the reaction, the polyol produced was kept in a sealed cap glass jar for further analysis. 140 g of crude MDI was poured into 100 g mixture of resin (Table 3 and Appendix A).

Composition	Part by weight, pbw
RBD PKO Polyol	100
Tegostab B8408	2
TMHDA	0.3
PMDETA	0.15
Water	4.5
Total pbw	106.95
Ratio of 100 parts to MDI	100:140

Table 3. Formulation of palm-based polyurethane foam system.

The mixture was agitated vigorously using a standard propeller at a speed of 200 rpm for 10 seconds at 20°C (Fig. 2).

Figure 2. Polymerization of the palm-based polyurethane

The reaction time: cream time (CT), fiber/gel time (FT), tack-free time (TFT) and rise time (RT) was noted (Appendix B). The free-rise density (FRD) was calculated using equation (1).

$$\text{Free - rise density, FRD (kg / m}^3) = \frac{(\text{mass of foam and cup - mass of cup), kg}}{\text{capacity of cup, m}^3} \tag{1}$$

The mixture was poured into a waxed mold, covered and screwed tight. The foam was demolded after 10 minutes. The molded density was determined using equation (2). The molded foam was conditioned for 16 hours at $23 \pm 2°C$ before further characterization of the polyurethane foam.

$$\text{Molded density, MD (kg/m}^3) = \frac{\text{mass of molded foam, kg}}{\text{volume of molded foam, m}^3} \tag{2}$$

Fourier Transform Infrared analysis of the RBD PKO polyol and palm-based PU was carried out on the Perkin Elmer Spectrum V-2000 spectrometer by Diamond Attenuation Total Reflectance (DATR) method. The samples collected during the intervals were scanned between 4000 and 600 cm^{-1} wavenumbers. For the former, two selected peaks (designated as peaks A and B) were used to monitor the progress of the reaction (derivatization).

Chromatography analyses were carried out on the former by thin layer chromatography followed by gas chromatography. A sample of 1 pph (part per hundred) by dilution in methanol was dropped on the silica plate with minimal diameter of about 0.5 mm and was applied 2 cm from the edge of the silica plate. The plate was removed once it traversed 2/3 of the length of the plate (normal length of a silica plate is 20 cm). The plate was placed in a chamber containing iodine crystals (iodine reacts with organic compounds to yield dark stain) after the methanol has all evaporated. The molecular weight was determined using gas chromatography coupled with mass spectrometer, GC-MS model Bruker 200 MHz with splitless inlet and HP5 (polar) column with flow rates of 1.0 µl/min. The oven was programmed to a temperature range of 100 to 280 °C at 6 °C/min.

Standard method ASTM D4274-88 (Standard Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols) was used to determine the hydroxyl value of the polyol. The value calculated would be able to verify the FTIR peak ratio method for completion of derivatization process. The water content of the polyol was determined using the Karl Fischer Titrator model Metrohm KFT 701 series (ASTM D4672-00(2006) e1: Standard Test Methods for Polyurethane Raw Materials: Determination of Water Content of Polyols) while the viscosity of the polyol was determined using the Brookfield digital viscometer model DV-I (ASTM D4878-88: Standard Test Methods for Polyurethane Raw Materials- Determination of Viscosity of Polyols). The viscosity of the polyol is important in determining the flowability of the polyurethane resin in the foaming process where it is advantageous in the material consumption. The specific gravity was determined following ASTM D4669–07: Standard Test Method for Polyurethane Raw Materials: Determination of Specific Gravity of Polyols. Other physical characterizations were determination of cloud point, pH and solubility of polyol in methanol, benzene, acetone, ether and water.

The PU foams were characterized for their apparent molded and core densities, compression strength, dimensional stability and water absorption following standard method BS4370: Part 1:1988 (1996) Methods 1 to 5: Methods of test for rigid cellular materials. Foam samples were cut using into cubes of 100 mm × 100 mm × 100 mm in dimensions. A replicate of five specimens were used and carefully weighed using an analytical balance. The dimensions were measured following BS4370: Part 1:1988 (1996): Method 2. The apparent molded density was determined by using a simple mathematical equation, mass (kg)/volume (m^3). The core density is determined by the same method but using skinless foam. The compressive strength test was carried out on a Universal Testing Machine Model Testrometric Micro 350 following BS4370: Part 1:1988 (1996): Method 3 at 23 ±2°C. The specimens were cut into cubes of 50 mm × 50 mm × 50 mm in dimensions. The foam rise direction was marked and a crosshead speed of 50 mm/min was applied. The compression stress at 10% deflection, compression stress at 5% strain and compression modulus was noted. For the dimensional stability test, the specimens were cut into dimensions of 100 mm × 100 mm × 25 mm. The specimens were then put into a controlled temperature-humidity chamber each at −15 ± 2°C and 70 ± 2°C, 95 ± 5% relative humidity for 24 hours. Method 5A of BS4370: Part 1:1988 (1996) standard was followed. The specimens were remeasured and percentage of change in dimensions was calculated. These are then converted to percentage in volume change. The water sorption was carried out using method in Annex D BS6586: Part 1:1993. The specimens were cut into dimension of 50 mm × 50 mm × 50 mm.

The thermal decomposition of the polyurethane foam was measured using a thermogravimetric analyzer model Shimadzu TGA-50 with temperature ranging from room temperature to 600°C at heating rate of 10°C/min under nitrogen gas atmosphere. Samples were placed in alumina pan holders at a mass ranging from 5 to 15mg. The thermal property of the foam was determined using a Perkin Elmer Model DSC-7 differential scanning calorimeter interfaced to the Model 1020 Controller. The samples were analyzed from room temperature to 200°C at a heating rate of 10°C/min. Standard aluminum pans were used to analyze 10 mg samples under nitrogen gas atmosphere. The insulation value (k-factor or λ-value) of the polyurethane foam was determined using the Thermal Conductivity Analyzer model Anacon at testing temperature for cold plate at 25°C and hot plate at 35°C. The thickness of the specimens was 20-30 mm and method 7 of BS4370: Part 2: 1993 standard was followed.

The RBD PKO consists of triglycerides that when undergoes esterification form by products such as glycerol and other possible polyester network (Loudon 1988) as shown in Scheme 1 and Scheme 2. During the reaction, the acetate ion forms an intermediate, the carboxylic acids. These acids attack the lone pair in nitrogen atom in diethanolamine, DEA and formed the probable structure of the esteramide with hydroxyl terminal (Scheme 2)

R_1, R_2 and R_3 generally are represented by R and it is very common to have lauric-lauric-oleic composition of fatty acid in the carbon chains (Scheme 2).
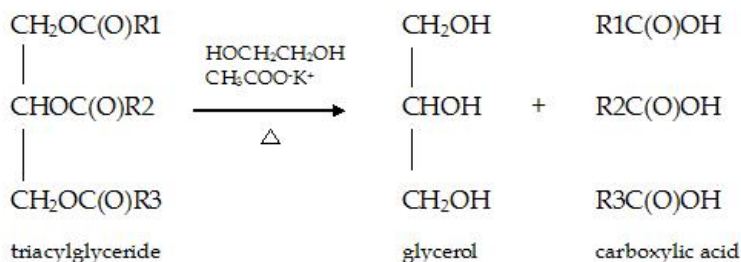
Scheme 1. Probable reaction mechanism between the RBD PKO and the hydroxyl-containing compound
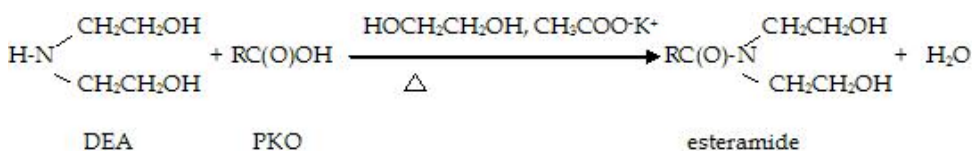
Scheme 2. Conversion of RBD PKO to the esteramide (RBD PKO-based polyol)

RBD PKO reacts with the polyhydroxyl compound in an alkaline medium (contributed by the potassium acetate). The alkalinity of the system ensured that the RBD PKO is fully reacted. The selection on polyhydroxyl compound being used is the critical part where it should offer highest hydroxyl value and functionality polyol possible to fully converting the RBD PKO into polyol (highest yield). Methods used in this study involved polycondensation and esterification where these are the only routes that offered low reaction temperature and short reaction time. It produced polyol (compound with functional group –OH) at high yield (almost 100%), low moisture content and no toxic vapor. The esteramide or PKO-based polyol is a monoester with OH terminal.

4. Properties of the PKO-based polyol

The derivatised RBD PKO-based polyol is a golden yellow liquid with a cloud point of 13°C. It has very low moisture content of 0.09% and low viscosity of 374 cps and specific gravity of 0.992 g/cm^3 at room temperature. Low water content and liquidy nature of the polyol are advantageous in formulating the polyurethane system especially when processing of end product is concerned. Less viscous polyol offers less viscous polyol resin which leads to system with good flowability. The viscosity increases as the degree of polycondensation and branching increases (Wood 1990). The physical properties of the PKO-based polyol are summarized in details in Table 4. It is important to note that raw RBD PKO solidified at room temperature with cloud point of about 23-24°C whilst the derivatized polyol solidified only at 13°C (cloud point). Polyol heating system is not required here as what is being used by other studies (Parthiban et al. 1999 and Ahmad et al. 1995).

Parameters	Result
State at 25°C	Liquid
Color	Golden yellow
Odor	Odorless
Density at 25°C, g/cm^3	0.992
Solubility	Alcohol, Ketone, Ether, Alkane, Water
Cloud Point, °C	13
Viscosity at 25°C, cps	374
pH	9-10
Moisture content at 25°C, %	0.09

Table 4. Physical properties of the derivatised RBD PKO-based polyol.

4.1. Chemical analysis

a. Fourier Transform Infrared Spectroscopy (FTIR)

The RBD PKO, a chain of fatty acid with carboxylic acid group displays intense C=O stretching bands of acids absorb at 1711 cm^{-1} as shown in Fig. 3 (a). The C-H stretches at 2932 and 2855 cm^{-1}. Two bands arising from C-O stretching and O-H bending appear in the spectra of RBD PKO near 1320-1210 and 1440-1395 cm^{-1} respectively. Both of these bands involve some interactions between C-O stretching and in-plane C-O-H bending. The C-O-H bending band near 1440-1395 cm^{-1} is of moderate intensity and occurs in the same region as the CH$_2$ scissoring vibration of the CH$_2$ group adjacent to the carbonyl (Silverstein et al. 1991).

The FTIR spectrum of the derivatized RBD PKO was obtained from samples taken at 175-180°C (Fig. 3(b)) during the esterification process. The spectrum was evaluated at peak 3351 cm^{-1} (designated as peak A) and 1622 cm^{-1} (designated as peak B). Peak A and B, which are the hydroxyl (-OH) and carbamate (O=C=N-) peaks respectively (assigned by IR Mentor Pro Classes, Sadtler Division Bio-Rad Laboratories 1990 and Silverstein et al. 1991). These peaks do not appear in the spectra of the raw RBD PKO (Fig. 3(a)). A vague trace of the hydroxyl peak was observed when PKO is mixed with the hydroxyl compound. Further increase in the reaction temperature and reaction time changed the percentage of transmittance for both peaks A and B significantly. It also indicated a formation of ester cleavage at 1710 cm^{-1}. The sharp absorption bands in the region of 1750-1700 cm^{-1} are characteristic of carbonyl group of ester (C=O) stretching vibrations (Silverstein et al. 1991).

Transmittance ratio of both peaks, the OH and the carbamate peaks (% transmittance of peak A divided by the % transmittance of peak B) was plotted as in Fig. 4. It was used to

identify the progress of the derivatization process (Chian and Gan 1998). Fig. 4 also showed that the hydroxyl value (OHV) reached to a constant at 350-370 mg KOH/g sample at intervals of 175-180°C for 15-30 minutes of reaction time. The FTIR spectrum and hydroxyl value (OHV) curves both demonstrated that 175-180°C at 15-30 minutes as optimum temperature and reaction time respectively. Both methods are advantageous in the identification of optimum processing parameters assuming that Beer's Law is applicable here. However, OHV determination method is slow and time-consuming. Therefore, FTIR method is more preferable in determining the completion of reaction for the RBD PKO-based polyol (Chian and Gan 1998).
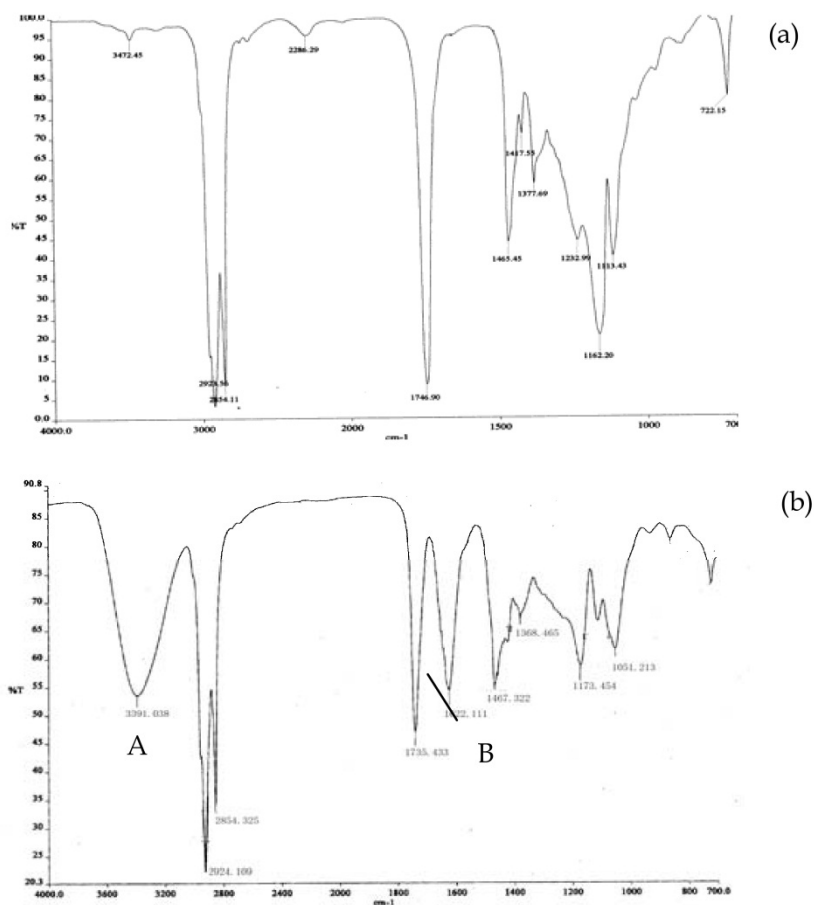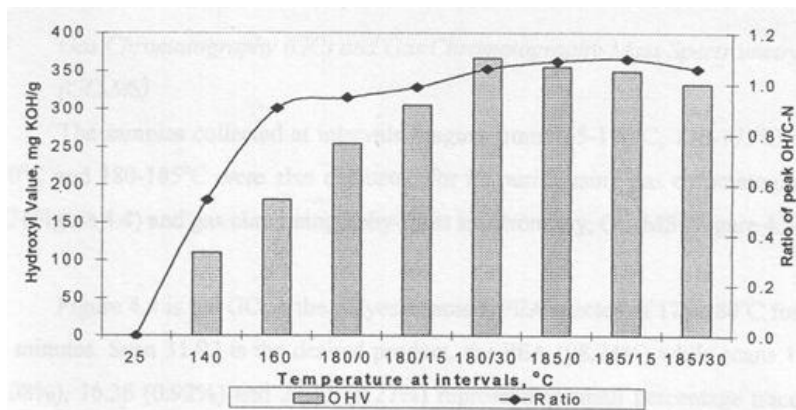

Figure 3. FTIR spectra of (a) the raw RBD PKO and (b) the palm-based esteramide

Figure 4. Curve of ratio of OH peak to the C-N peak and the OHV curve of the blend at intervals

b.   Thin Layer Chromatography

The thin layer chromatography (TLC) test on the desired products obtained at intervals of reaction time at 175-180°C (0, 15 and 30 minutes) indicated a clear qualitative separation. These separations were compared to TLC carried out on individual ingredients: The RBD PKO, diethanolamine (DEA), the catalyst-potassium acetate in monoethylene glycol and standard lauric acid (Athawale et al. 2000). There were three separation peaks, identify as the PKO, DEA and small trace of the catalyst up to 175-180°C at 0 minute. At 175-180°C for 15 minutes, only two separation peaks were observed and finally at 175-180°C for 30 minutes, only one separation peak was observed (Fig. 5). The result is parallel to the gas chromatography (GC) peaks of the final product, the RBD PKO-based polyol (Fig. 6)).

c.   Gas Chromatography-Mass Spectrometry (GC-MS)

The samples collected at intervals ranging from 165-170°C, 170-175°C, 175-180°C and 180-185°C were also evaluated for its purity using gas chromatography, GC coupled with mass spectrometry, GC-MS. Fig. 6 is the GC of the RBD PKO-based polyol reacted at 175-180°C for 15-30 minutes. The signal at retention time of 31.92 min is the desired product, the RBD PKO-based polyol (98.24%) while signals at retention time of 13.37 (0.08%), 16.36 (0.92%) and 27.91 (0.27%) representing small percentage traces of MEG, glycerol (by-

product of esterification) and DEA (C:\ DATABASE\WILEY275.L). Others (0.49%) are traces of oligomeric polyester components from C_{14} and C_{18} chains. The GC-MS scan of the RBD PKO-based polyol showed an estimated molecular weight of 477. Molecular weight obtained at 165-170 and 170-175°C of reaction temperature was 296 and 355 respectively. Thus, molecular weight obtained at 175-180°C is considered to be the most desirable molecular weight for this study. The functionality of the RBD PKO-based polyol derived from this molecular weight and the determined hydroxyl value (OHV of 350 to 370 mg KOH/g) is 2.98 to 3.15 calculated using the mathematical equation in equation 3.

$$\text{Functionality} = M_w \times OHV / 56100 \qquad (3)$$

Note: M_w is the estimated molecular weight of the RBD PKO-based polyol obtained from GC-MS which is 477 OHV is the hydroxyl value of the RBD PKO-based polyol obtained using ASTM D4274-88 method, which is about 350-370 mg KOH/g sample
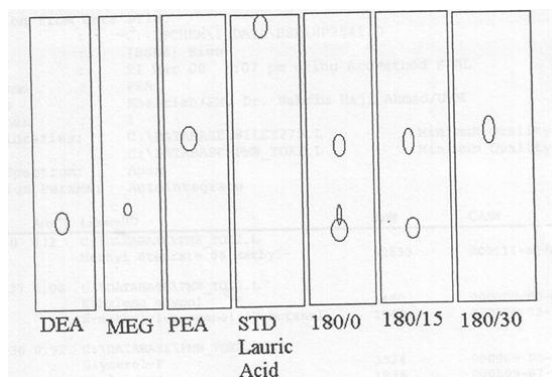
Note:

PEA   RBD PKO-based polyol
DEA   diethanolamine
MEG   monoethylene glycol
STD   standard lauric acid
180/0   derivatised RBD PKO at starting of 180°C
180/15   derivatised RBD PKO at 180°C for 15 minutes
180/30   derivatised RBD PKO at of 180°C for 30 minutes

Figure 5. The thin layer chromatography of the ingredients

This range of functionality is suitable for rigid foam application (Wood 1990).

Both FTIR (IR Mentor Pro 1990) and GC-MS approaches (Wiley MS-database) could be used to estimate the most probable molecular structure of the RBD PKO-based polyol at 175-180°C/30 minutes (optimum temperature and reaction time) as 2-hydroxy-undecanoamide as in Scheme 2 (library search on Wiley MS-database giving 98% quality match). There is no intention of purification of the synthesized RBD PKO-based polyol as all these hydroxyl-containing compounds would react with crude MDI.
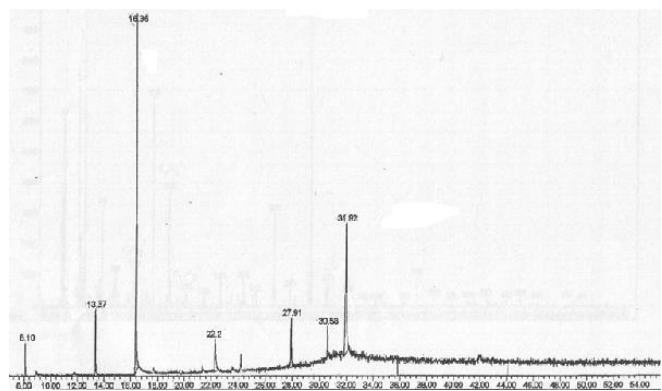
Figure 6. GC chromatogram of the RBD PKO-based polyol obtained at 175-180ºC for 30 minutes.

4.2. Thermal testing

The thermogram of the resulted RBD PKO-based polyol is as shown in Figure 7. Thermally, it is stable up to 167.6ºC and undergoes two stages decomposition at 167.6 to 406.3ºC with total weight loss of 99.41%. The initial 3.34% weight loss is contributed to the moisture content and other volatile impurities in the RBD PKO-based polyol (Oertel 1993). The initial decomposition is contributed by the degradation of RBD PKO-based polyol and traces of glycerol supported by the DTA curve which representing the softening temperature at 385ºC. Charred residue was obtained after testing.
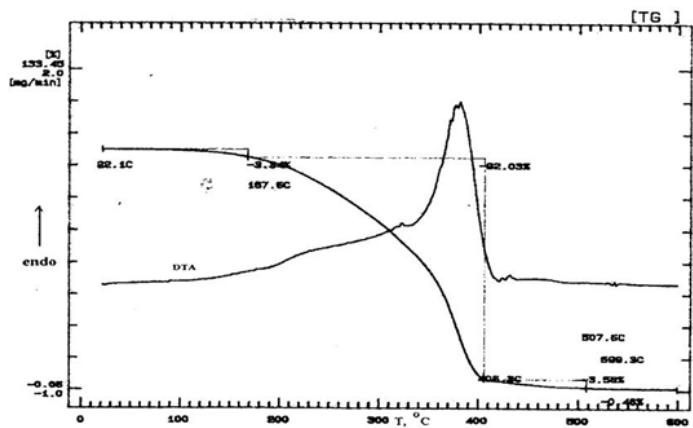

Figure 7. TGA thermogram of the RBD PKO-based polyol obtained at 175-180ºC for 30 minutes

5. Properties of the PKO-based polyurethane foam

5.1. Physical properties

The PKO-based polyurethane foam (PUF) produced is a light yellow solid with skin thickness of about 1.5 mm. It is a stiff/rigid but brittle solid at 43-44kg/m^3 molded density and core density of 38-39 kg/m^3 with average void size of 0.10-0.15 mm (Fig. 8).
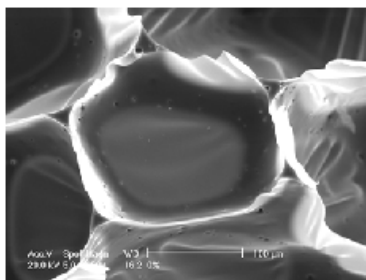

Figure 8. Scanning electron micrograph of the PUF at 250× magnification

5.2. FTIR analysis

The PUF is analysed by FTIR spectroscopy which showed the absence of the free OH groups and indicates a complete conversion of both –OH groups of the PEA to the urethane moiety (NH-C(O)-O). Typical FTIR spectrum of the PU is as shown in Fig. 9. The characteristic –NH stretching vibration of the –NH$_2$- (amide) is located at 3405 cm^{-1}, overlapping with the OH peak as a broad band. Bands at 2932 and 2894 cm^{-1} are the synchronous reflection of asymmetric and symmetric of CH$_2$ bridges, from the linkage of the urethane with the PEA. Bands at 1650 cm^{-1} is the overlapping of –N=C=O (urethane) and ester linkage of the PEA. Obviously, bands 1550, 1650 and 3350 cm^{-1} indicate complete conversion to urethane moiety (Silverstein et al. 1991).
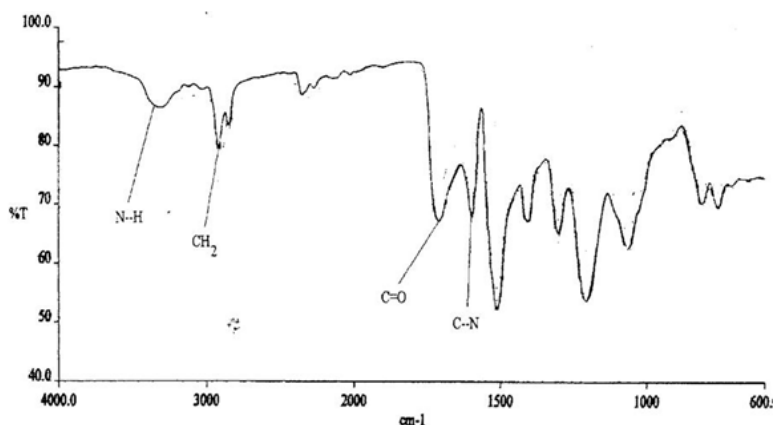

Figure 9. FTIR spectrum of the RBD PKO polyurethane foam

5.3. Thermal properties

The thermal instability of a PU may be defined as the ease by which heat produces changes in the chemical structure of the polymer network. These may involve simple bond-rupturing dissociation or reaction reversals and provide more volatile components, or they may result in extensive pyrolysis and fragmentation of the polymer. This characteristic provides a measure of fire hazard in that a more thermally stable polymer is less likely to ignite and contribute to a conflagration than a less stable one (Burgess, Jr. & Hilado 1973). Thermodynamic parameters such as decomposition temperatures, percentage of weight loss, melting temperature, T_m and glass transition temperature, T_g were determined by thermal analyses of the PU.

TGA thermogram of the PU is as shown in Fig. 10. Presence of three degradation stages implying the presence of three thermal degradation temperatures. It was thermally stable at 191.9ºC, a common stability temperature for PU (Hepburn 1991). The initial weight loss of about 41.24% commences at 191.9 to 396.9ºC. T_{max} from the DTA curve occurred at 275ºC attributed by carbon dioxide trapped in the sample. Degradation started at 396.3 to 498.4ºC, which was initially a fast process. The total weight loss up to 500ºC is 74%. This second stage of degradation rationalized the urethane linkage reported by Hepburn (1991).
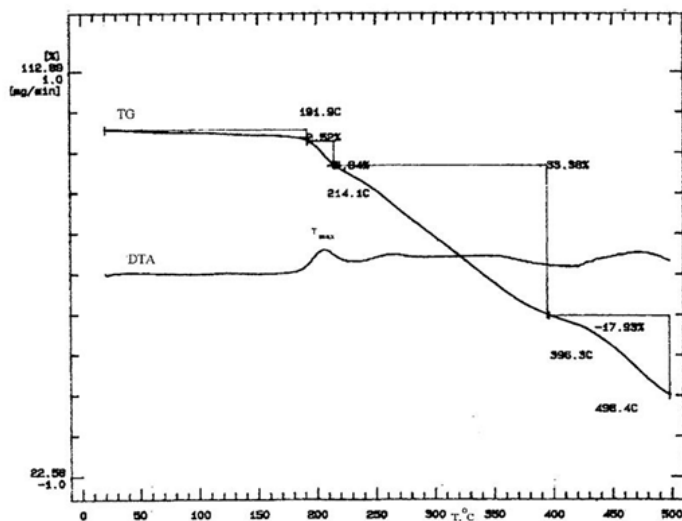
Figure 10. TGA thermogram of the RBD PKO PU foam

There is no indication of melting and crystallization temperatures curves in the DSC thermogram of the PU foam. Therefore, this polymer could be identified as an amorphous polymer (Badri et al. 2000). The glass transition temperature is 39.74ºC, a regular glass transition temperature for thermosetting polymers, with heat capacity of 33.0 J/g. Since the heat of evaporation of water is 2300J/g, moisture content of the PU was detected to be 1.43%.

However, the initial thermal conductivity of PU foam is found to be 0.0244 W/m-K. This is expected since it is a water-blown PU system where water has poor properties i.e. boiling point and k-factor compared to its industrial counterpart, chlorofluorocarbon, CFC (Crawford & Escarsega 2000). Low thermal conductivity is normally contributed by the low boiling point of the blowing agent such as CFC and finer cell structure of the foam (Hardings 1965, Frisch 1985, Hepburn 1991). However, another fact to be remembered is that water is a chemical blowing agent compared to CFC, a physical blowing agent. Water is capable of interfering in the polymerization of polyurethane by producing by-product such as urea and large amount of carbon dioxide when being used I larger quantity. Functionality of polyols also plays an important role in producing good insulated material (Wood 1990, Hass and Uhlig 1985).

5.4. Mechanical properties

The mechanical properties of the foam produced from the derivatized RBD PKO show comparable results (Table 5) to the British Standard requirement (practiced by industry such as building construction industry). It is expected for water-blown PU foam to have lower compressive stress at 5% strain and the compression due to irregular formation of cellular structure. This decreased the strength upon higher percentage of strain. Table 5 showed the summary of the mechanical properties of the PU foam.

The dimensional stability which is described in percentage of volume change indicated changes of -0.090% and 0.012% at -15±2ºC and 70±2ºC at 95±5% relative humidity for 24 hours respectively. A very minimum shrinkage and expansion problem was observed on the foam prepared from this palm oil-based polyurethane polyol in a water-borne system. Identical resin formulation was used using petroleum-based polyol to substitute the palm-based polyol. Major shrinkage and expansion problems were observed. Shrinkage and expansion problems are normally used as indicators of how good the foam is as an insulator. The mechanical properties could be enhanced by using low or high pressure dispersing machines (Oertel 1993). Better mechanical properties could also be achieved by introducing filler in the PU system (Rozman et al. 2001[a], 2001[b], 2000, 1998).

5.5. Rheological and kinetic properties

The PU system is polymerized kinetically using tetramethylhexadiamine, TMHDA as a gel/blow catalyst and pentamethyldiethylenetetramine, PMDETA as a blow catalyst. The addition of both catalysts is very minimum (0.05-0.10 pbw) in achieving an optimum kinetic reaction time (Tamano et al. 1996) especially when reactive RBD PKO-based polyol (Scheme 2) is used in the formulation. The cream time, gelling/fiber time, tack-free time and rise time (Appendix B) were 23, 71, 105 and 156 seconds respectively at 20ºC. The PUF is demolded after 10 minutes of mixing with skin thickness of about 1.5 mm. It has a flow index of 1.050 cm/g, a moderate flowability PU system (Colvin 1995). This is assumed to be helpful in reducing the consumption of raw materials, especially the RBD PKO-based polyol.

5.6. Resistance to environmental stress

The chemical resistance of the PU with normal closed-cell structures of rigid urethane foam prepared from the crude MDI and RBD PKO-based polyol is carried out to investigate the limitation of the interactions with surroundings to the surface layer in order to produce a chemically and physically stable material. Effects produced by chemical agents depend both on the chemicals and on the permeability of cell membranes. Solubility of the chemical in the foam affects both permeability and swelling. Results obtained are not representative of other temperatures, concentrations or exposure times.

Parameter	Method	Standard	Results
*Apparent molded density, kg/m^3	BS 4370:Part 1:1988 (Method 2)	Min 38	43.6 ±0.85
*Apparent density (core), kg/m^3	BS 4370:Part 1:1988 (Method 2)	Min 35	38.9 ±0.53
*Compressive strength to foam rise at 10% deflection, kPa	BS 4370:Part 1:1988 (Method 3)	Min 180	185.7 ±8.22
*Compressive stress at 5% strain, kPa	BS 4370:Part 2: 1993 (Method 6)	Min 140	105.4 ±2.41
Compressive modulus, N/m^2	BS 4370: Part 1: 1988 (Appendix A)	Not available	8.52 ±0.46
*Dimensional stability,%	BS 4370: Part 1: 1988 (Method 5B)		
	At -15 ±2°C for 24h	Maximum 1.0	Length: -0.151 ±0.03 Width: -0.433 ±0.03 Thickness: 1.373 ±0.06
	At 70 ±2°C, 95 ±5% r.h. for 24h	Maximum 3.0	Length: 0.359 ±0.25 Width: 0.017 ±0.04 Thickness: 1.654 ±0.09
*Apparent water absorption,%	BS 6586: Part 1: 1993 (Annex D)	Maximum 6.5	2.25 ±0.89
Shore A Hardness	ASTM D 2240	Not Available	29.0 ±1.4

Note: * Physical property requirements following BS6586: Part 1: 1993 industrial standard.

Table 5. The mechanical properties of the PU foam synthesized from the RBD PKO-based polyol.

Fig. 11 illustrates the compressive strength at 10% deflection and 5% strain as well as its compression modulus upon exposure to stress. All resistivity test medium being used result

in a major increment in the strength at 10% deflection. Readings of above 0.20MPa (compared to the control foam) with maximum compressive strength are observed in benzene at about 0.34MPa, followed by PUF at ambient temperature (0.30MPa), freeze-thaw condition (0.26MPa), 10% NaOH (0.25MPa), saltwater (0.20MPa) and finally 10% HNO$_3$ (0.19MPa). The same trend is observed in compressive strength at 5% strain where the maximum value is encountered at freeze-thaw condition followed by at ambient temperature, 10% NaOH and finally benzene. The compression modulus reaches as high as 11.0MPa and others are in the range of 8.0 to 9.0MPa.
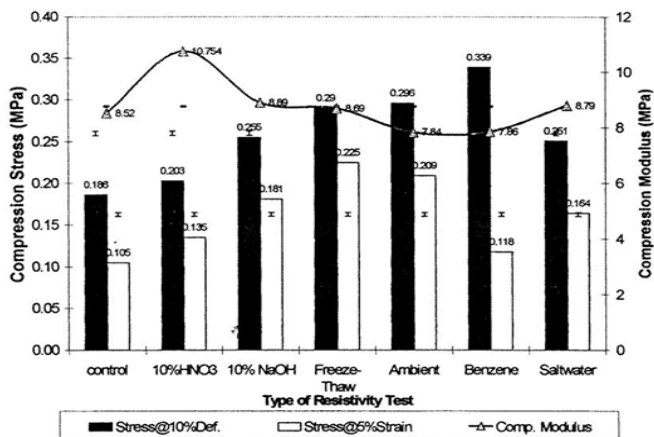

Figure 11. Effect of various environmental stresses on the compressive strength and compression modulus of the RBD PKO-based PU foam

Practically, the absorption of chemicals into the foam results in swelling of the cell faces, which apparently increases the compressive strength. Weathering conditions (ambient and freeze-thaw) however are very much dependence on the diffusion rate of carbon dioxide being replaced by the air which causes expansion of the foam and increases the compressive strength (Wood 1990). The foams are found to be unaffected by the test medium basically due to the mixture of organic components (RBD PKO-based polyol and MDI). Rigid PU foam is stable in the present of most solvents such as found in binders and sealers (Oertel 1993).

Physically, the foam becomes spongy with the formation of waxy material on the surface of the foam, as a result of prolonged exposure to benzene as an aromatic hydrocarbon. It is important to note that ester-based polyurethanes are easily attacked by hot aqueous alkali or moderately concentrated mineral acids, swollen by aromatic hydrocarbons and decomposed by prolonged contact with water, diluted acids and moist heat (causes swelling and slow hydrolysis) (Roff et al 1971).

The compression modulus of the PUF ranges from 7.8 to 10.8MPa. the compression modulus for the control PUF is at 8.5MPa which is lower compared to the modulus in 10%HNO$_3$,

10%NaOH, under freeze-thaw condition, and in saltwater but higher if compared to the modulus of the rest of the resistivity test.

Rigid PU prepared has high resistivity to the action of most organic solvents and are seriously degraded only by strong acid, oxidizing agent and corrosive chemicals. Only stronger polar solvents, which significantly swelled the polymer, led to shrinkage of the foam structure. Evaporation of the solvent normally returns the polymer to its original state (Oertel 1993).

6. Conclusion

Several advantages are foreseen from this study. Some important advantages are being identified through this method of polyol production. Firstly, it is attractive and economical. RBD PKO-based polyol is a naturally formed macromolecules found in Malaysia. It is extremely plentiful, easy to process and refine, capable of being cultivated with minimum capital investment and suitable for conversion to quality polyols using an inexpensive reaction process. Secondly is the simplicity of the process, which requires only a few reactors for producing the polyol as well as formulating the resin. Commercially, the process acquires only a few personnel to produce consistently good quality polyols. Thirdly, compare to the manufacturing of the petrochemical-based polyols, the process is relatively safe, where it involves the usage of hazardous chemicals. Generally, it is non-toxic and of low volatility.

Two major environmental advantages can be realized. Firstly, the source of oil is truly renewable, where it does not lead to permanent depletion of resources which has a limited global availability. Secondly, the amount of energy required to convert the natural oils to polyol is considerably less than using the conventional process. The foam made from this RBD PKO-based polyol is low in density, light in color, high in strength but low in water sorption. The produced RBD PKO-based polyurethane foam in this study also has other advantages as tabulated in Table 6.

Property	Rating	Consequence	Benefit
Thermal Insulation	Highest	Thinnest Section	Space
Rigidity	High	Added Strength	Structural
Adhesion	High	No glue-line	Manufacturing
Dimensional Stability	High	Non-sag, non-heave	Maintenance
Density	Low	Lightweight	Handling
Water Vapor Transmission	Low	Less Condensation	Construction

Table 6. The advantages of producing RBD PKO-based polyurethane.

The PUF meets the British Standard requirements in any medium of the tested environmental stress test. This ester-type polyurethanes are easily attacked by prolonged contact with water, diluted acids and moist heat (causes swelling and slow hydrolysis) and swollen by aromatic hydrocarbons. These rigid PUs either the PUF, are resistant to the

action of most organic solvents and are seriously degraded only by strong acids, oxidizing agents and corrosive chemicals. Only polar solvents, which significantly swell the polymer, lead to shrinkage of the foam structure. Evaporation of the solvent normally returns the polymer to its original state.

In terms of application, these composites are most suitable in structures where stiffness and dimensional stability are of prime importance but is only a secondary choice to areas where structural strength is more vital than the component rigidity.

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