

A review on advanced methods of polyurethane synthesis based on natural resources

N J Sangeetha, A Malar Retna*, Y Jasmala Joy and A Sophia

Department of Chemistry, Scott Christian College (Autonomous), Nagercoil-629003, K.K.District, Tamilnadu

*Corresponding author: E.Mail:malarscott@gmail.com.

ABSTRACT

This review presents the recent methods and synthesis of polyurethanes derived from natural resources such as natural fibers, natural fillers, natural oils and other natural resources. Polyurethanes are one of the most various plastic materials obtained by the reaction of a polyol with an isocyanate or diisocyanate in the presence of suitable catalysts and certain additives. The properties were examined by spectroscopic methods, thermo-mechanical methods, scanning electron microscopy (SEM) and x-ray fluorescence (XRF). This leads to high-performance products for building, furniture, bedding, automotive, ligature and industry due to their enduringness, lightweight, strength, tractability and chemical resistance.

Keywords: Polyurethanes, Natural resources, Diisocyanate, Catalyst.

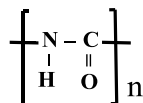
1. INTRODUCTION

Polymers are a group of materials constituting long covalently bonded molecules which are received either from natural or man-made (synthetic) sources. It is used in the form of plastics for making articles such as knobs, covers, shifts, tubes, heart valves and so on (Narine, 2005). Since, Bayer synthesized polyurethanes in 1937, its usage has become omnipresent (Sharma, 2008). Polyurethanes are formed by the reaction of diisocyanates with hydroxyl-containing materials such as oils, fabrics or with partial glycerides prepared from oil and glycerol (Guner, 2006). It has a class of polymers with great variety such as excellent abrasion resistance, hardness, flexibility, resistance to chemicals and solvents, high cohesive strength and tractable curing speed (Zhang, 1998).

Natural oils are viewed to be the most essential class of renewable sources. They can be received from naturally occurring plants such as linseed, sunflower, etc. It consists preponderantly of triglycerides (Guner, 2006). Fillers obtained from natural resources include wood flour, ash, rice husk, groundnut husk, rice straw, etc. (Soby, 2010) leads to improve mechanical properties of the composites and fibers also obtained from natural resources such as cotton, jute, etc. and cellulose is the most ample of all natural polymers (Fried, 1999). The products obtained by using these fibers have low-cost, increased impact strength and other mechanical properties such as tensile strength, percentage elongation, tear strength and hardness (Narine, 2005). They are used as reinforcing agents in plastic materials and have many substantial advantages over man-made fibers and fillers (Bledzki, 1999).

By incorporating fillers into a polymer matrix, composites can be oriented to have the desired properties with different applications (Soby, 2010). Still, incorporation of fibers will form elastomeric composites exhibit combined behavior of soft, elastic rubber matrix and firmly strong fibrous reinforcement (Petrovic, 2010).

1.1 Polyurethanes: Polyurethanes (PUs) are polymers containing urethane linkages in their repeat units.



Flexibility of PUs was increased by the presence of additional oxygen in the chain (Gowariker, 1986). It can be classified in the following major groups: flexible foams, rigid foams, elastomers, adhesives and coatings (Saunders, 1988). They exhibit versatile properties in all fields of polymer applications (Desroches, 2012) such as automobile, aerospace industry, etc (Sumaila, 2006).

2. Polyurethanes based on natural resources: Gopalakrishnan *et al.* (Gopalakrishnan, 2012; Gopalakrishnan, 2004) studied polyurethanes based on cardanol. First, they synthesized novalac resins (cardanol-formaldehyde resins) from cardanol reacted with formaldehyde and sebacic acid / glutaric acid as catalyst, such polyol has been condensed with diisocyanates using dibutyltin dilaurate to develop rigid polyurethanes. A commercially available polyol, polypropylene glycol-2000 (PPG-2000) also used for preparing tough polyurethanes. Differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) of rigid and tough polyurethanes in air and in nitrogen N₂ were determined. It shows that rigid polyurethanes possess higher degradation due to higher cross link density, more stable in chemical reagents and good thermal stability when compared to tough polyurethanes.

Suresh and Prasad (Suresh, 2005) prepared polyols from the monoglycidyl ether of cardanol, followed by ring opening to give diol or triol with diethanol amine. Polyurethanes were synthesized by these polyols with

diphenylmethane diisocyanate (MDI) at NCO/OH ratio of 1 using dibutyltin dilaurate catalyst. Polyurethanes based on diol (PUD) and glycard (PUG) showing higher thermal stability compared to triol (PUT) were determined by thermogravimetric analysis (TGA) under nitrogen atmosphere. Visco-elastic properties were analyzed by dynamic rheometry showing a linear increase in the Tg value with an increase in the polyol hydroxyl value.

Polyurethanes derived from castor oil studied by Corcuera *et al.* (Corcuera, 2010). They prepared novel segmented polyurethanes from soft segment (polyol deduced from castor oil) and hard segment derived from different chain extenders, petrochemical-based 1,4-butanediol (BD) and corn sugar-based 1,3-propanediol (PD) via a two-step polymerization changing hard segment ratio. Physico-chemical, mechanical and morphological properties were analyzed by FTIR spectra, DSC, AFM (atomic force microscopy) and TGA. This shows that hard/soft microdomain stage separation as well as the nature of hard segment and formed structure. The synthesized polyurethanes from biobased chain extender pointed a slightly lower crystallinity in the structure of hard segment than polyurethanes synthesized from BD as chain extender.

Santos *et al.* (Santos, 2012) synthesized polyurethane based polymers by mixing castor oil as polyol to diisocyanate at different NCO/OH ratios. Mechanical behavior was increased proportionally to content of diisocyanate were determined by uniaxial tests. Thermal behavior were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) showing Tg changes in the presence of plasticizers by its decreasing. Infrared microscopy utilized to investigate chemical groups.

Polyurethanes derived from soy-based polyols have been studied by Monteavaro *et al.* (Monteavaro, 2005). In this work, polyurethanes were prepared by reacting different diisocyanates and soy polyols. TGA was analyzed under nitrogen atmosphere indicating the thermal stability of polyurethanes depends strongly and an increase in the weight loss as a consequence of the increased amount of urethane groups. Degradation kinetics behavior of polyurethanes effects in nonparallel isothermals.

Ha and Broecker (Ha, 2002) prepared polyurethanes in one-step reaction by freezing starch granules in polycaprolactone diol, MDI and 1,4-butane diol in a majority stage at 175° C. FTIR spectra, SEM, DSC and swelling behavior of the products were analyzed and the DSC pointed that decreased average molecular weight of the homopolyurethane due to increased Tg with the starch content. About 20 wt% of starch, the polymers slightly increased or constant and then decreased rapidly as state gapping between the starch granules and the polyurethane stage and division of the starch granules under tensile strength and elongation.

Polyurethane based on yucca starch glycoside studied by Valero *et al.* (Valero, 2009). They prepared polyol-ethylene glycoside (PEG) and polyol-glycerol glycoside (PGG) from castor oil-polyols and glycosides (yucca starch is converted into glycol glycoside and glycerol glycoside through glycosylation reactions with ethylene glycol and glycerol respectively using sulphuric acid catalyst) under nitrogen atmosphere. Thus polyurethanes were synthesized by reacting PEG and PGG with isophorone diisocyanate (IPDI). Mass fraction of glycosides and polyol-glycosides were determined by MALDI TOF Mass spectroscopy. Mechanical properties, thermal properties and SEM micrographs were analyzed showing excellent resistance to chemicals, hardness and tensile strength.

Saralegi *et al.* (Saralegi, 2013) synthesized segmented polyurethanes from vegetable oil-based polyesters and corn sugar-based chain extender using a two-step polymerization process. It consists of a high-molecular-weight macrodiol called the soft segment (SS) and a low-molecular-weight diol called the hard segment (HS). Microphase segregation and phase-separated microstructure of the synthesized STPUs have been studied using infrared (IR) and atomic force microscopy (AFM). Hydrogen bonding occurs between HS carbonyl groups as well as SS carbonyl groups giving hard crystalline domains and soft crystalline domains respectively and contributes to phase mixing.

Polyurethanes derived from glucose and xylose based polyols have been synthesized by Donnelly *et al.* (Donnelly, 1993). They prepared polyurethanes by blending ethylene glycol glucoside (alkoxylated to a low level in a reaction solution) with polytetrahydrofuran diol, gives high carbohydrate content polyols of low viscosity. Tensile strength shows that the solid polyurethanes ranged from weak elastomers, soluble, linear to those of decreased solubility and lower extension, increased transition temperature and stiffness. These consequences are ascribable to the rigidity of the glucose unit increases hydrogen bonding and potential for crosslinking.

Achary *et al.* (Achary, 2012) synthesized polyurethanes from glycerol modified linseed oil and diphenyl methane-4,4'-diisocyanate (DPMDI) and cardanol based dyes with aminophenols. The thermal stability of the

polyurethanes was investigated by thermogravimetric analysis (TGA), the rate of thermal degradation was determined by derivative thermogravimetry (DTG) and the exothermic and endothermic behavior of thermal degradation was determined by differential thermal analysis (DTA). The kinetic parameters such as activation energy and order of reaction of thermal degradation of polymer blends were calculated by Freeman-Anderson's method. The significant effect of NCO/OH molar ratio of polyurethanes was analyzed showing thermally stable.

3. Polyurethane composites based on natural resources: Merlini *et al.* (Merlini, 2011) synthesized polyurethane composites from short random banana fibre (modified with 10 wt% sodium hydroxide solutions) and castor oil. SEM, dynamic mechanical analysis (DMA), FTIR spectra, tensile strength and pull-out tests of the composites were determined. The treated banana fibre composites depicting higher tensile strength and young's modulus values than the untreated fibre composites due to stronger interfacial interactions between the treated fibers and the polyurethane matrix.

Polyurethane composites based on curaua fibre have been studied by Mothe *et al.* (Mothe, 2009). They prepared polyurethane composites with curaua fibre as reinforcement at 5, 10 and 20% mass/mass proportions by melt-mixing method. Dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) were determined showing the thermal behavior and polymer cohesiveness in polyurethane matrix. At low temperatures upto 70°C, PU80 was much stiffer and resistant than other composites.

Okiemen and Bakare (Okieimen, 2007) synthesized polyurethane composites from rubber seed oil monoglyceride (rubber seed oil reacting with glycerol) and different diisocyanates by compression moulding using sisal, jute and banana fibers. The tensile and flexural properties of the polyurethane composites depicted a 3-fold higher than the unreinforced polyurethane samples using fibers as good reinforcement. The fractured surface provides better adhesion between the fibers and the polyurethane matrix on scanning electron micrographs without fibre. The thermal stability of the polyurethane composites shows that lower for the fibre but higher for the unreinforced polyurethane samples.

Polyurethane composites based on sisal fibre have been studied by Milanese *et al.* (Milanese, 2012). They synthesized polyurethane matrix from castor oil reacted with 4,4'-methylene diphenyl diisocyanate (MDI) using woven sisal fibre. Flexural tests were determined by scanning electron microscopy (SEM) exhibiting the scattering of flexural strength decreases and deflection increases as using sisal reinforcement.

Bakare *et al.* (Bakare, 2010) studied rubber seed oil-based polyurethane composites using sisal fibre. They prepared polyurethane composites from rubber seed monoglyceride deduced from glycerolysis of oil and reinforced with unidirectional sisal fibers and the result shows that good thermal and mechanical properties. The polyurethane composites were more than tenfold and about twofold higher than unreinforced rubber seed oil-based polyurethane suggested by the values of tensile strength and flexural moduli. Scanning electron micrographs of the fracture surface of the sisal fibre reinforced rubber seed oil-based polyurethane composites were assigned to good fibre-matrix interaction.

Sumaila *et al.* (Sumaila, 2006) synthesized polyurethane composites from lignocellulosic material such as groundnut husk powder varied between 2 and 10 weigh percent of matrix. Properties were analyzed showing that tensile strength increased and impact strength decreased with increased filler content. These consequences are ascribable to the poor interfacial interactions between fibre and matrix.

Polyurethane composites based on rice husk (RH) with commercially available, polypropylene glycol-400 (PPG-400) and diisocyanate have been studied by Rozman *et al.* (Rozman, 2003). The flexural, tensile and impact properties were analyzed showing the effect of percentage of RH (by weight), RH hydroxyl (OH) groups and RH size. This leads to the properties increased as the percentage of RH or RH OH groups were increased and decrease on exceeding threshold value. Scanning electron microscope (SEM) analysis observed that interaction between the OH groups from the RH and NCO groups from MDI is due to the greater surface area.

3. Polyurethane nanocomposites: Pradhan and Nayak (Pradhan, 2012) synthesized polyurethane nanocomposites from castor oil using hexamethylene diisocyanate (HMDI) and modified clay. The properties of polyurethanes and their nanocomposites were analyzed by FTIR, SEM, XRD (x-ray diffraction), TGA and mechanical testing. The FTIR spectra exhibited that the polymer chains have added into the gallery of cloisite 30B (C30B). After modification with HMDI, the nanocrystals become pseudospherical and the size increases or decreases depending on diisocyanate concentration compared to the ungrafted particles as exhibited by SEM results. The XRD result shows

that the diffraction peak for modified clay (SM-15) seems at $20.3A^\circ$, when compared to $18.48A^\circ$ for pristine C30B, indicating the constitution of intercalated tactoids.

4. Polyurethane foams based on natural resources: Silva *et al.* (Silva, 2013) synthesized polyurethane foams from modified tung oil and reinforced with rice husk ash (RHA) as rigid filler. Addition of RHA leads to detectable changes in properties such as thermal conductivity, density and foam morphology even using low filler content. Thermal stability was unaffected by ash content.

Polyurethane foams synthesized from castor oil-based polyol (castor oil by alcoholysis with triethanolamine) and wood flour as filler have been studied by Mosiewicki *et al.* (Mosiewicki, 2009). Mechanical, thermal and physical properties of the neat and reinforced foams were assessed, examined, and equated to a reference commercial system. Thermogravimetric tests were studied proves that the chemical reaction between wood flour and isocyanate strongly affected the composites. As wood flour content increased then compression modulus and yield strength decrease.

Ogunniyi and Fakayejo (Ogunniyi,1996) studied polyurethane foams based on castor oil. They prepared polyurethane foams from a mixture of castor oil and polyol (hydroxyl-terminated polyether) using toluene diisocyanate (TDI). Mechanical properties were determined that increased tensile strength and elongation-at-break will be decreasing.

Polyurethane foams based on soy-derived phosphate ester studied by Firdaus (Firdaus, 2010). In this study, polyurethane foams (PUF) were formed by the reaction of polyol and isocyanate. The polyol was synthesized by ring-opening hydrolysis of epoxidized soybean oil using phosphoric acid as catalyst. The properties of the polyurethane foams were determined by the effect of the amount of solvents, phosphoric acid and their derivatives. SEM analysis exhibited that the cells of these foams were opened cells.

4.a Polyurethane microfoams: Polyurethane microfoams based on flax and jute fibers have been studied by Bledzki *et al.* (Bledzki, 2001). They synthesized polyurethane-based composites using woven flax and jute fabrics with an equally disseminated microvoid foam structure. Mechanical properties of the composites were analyzed that slenderly dependent on microvoid content. Still, microvoid content increases leads to decreased shear modulus and impact strength. The flax fibre composites ensued in better mechanical strength than jute fibre composites.

4.1 Flexible polyurethane foams based on natural resources: Shan *et al.* (Shan, 2012) studied flexible polyurethane foams reinforced with coir fibers. SEM micrographs of flexible PU foam composites indicating open-cells cellular structure formed by small cells hence depicts higher cell density. X-ray fluorescence (XRF) results exposed that 99% in coir is organic compounds and thermal analysis shows that high decomposition temperature at $250^\circ C$, coir fibers were used as fillers.

Flexible polyurethane foams based on palm oil have been studied by Pawlik and Prociak (Pawlik, 2012). Initially, palm oil was epoxidized using hydrogen peroxide as an oxidizing agent and then hexamethylene glycol was applied to open oxirane rings. Thus the obtained palm oil-based polyol was reacted with toluene diisocyanate using amine catalyst, water and Niac silicone L-627(surfactant) to synthesis polyurethane foams. Physical-mechanical properties of polyurethane foams were analyzed exhibiting enhanced properties such as apparent density, tensile strength, resilience, compressive stress and thermal stability.

4.2. Rigid polyurethane foams based on natural resources: Kuranska and Prociak (Kurska, 2012) studied polyurethane foams based on natural fibers. In this study, rigid polyurethane foams prepared from rapeseed oil-based polyol and natural fibers such as flax and hemp. Cell structure, closed cells content, apparent density, thermal conductivity and compression strength of the rigid polyurethane composites were determined. It shows that the application of fibre in the amount of 5% php (per hundred polyols) the polyurethane composites have highest values of compressive strength and lowest thermal conductivity.

Rigid polyurethane foams based on coconut coir fibre have been synthesized by Azmi *et al.* (Azmi, 2012). They prepared polyurethane foams by mixing polyol and isocyanate, followed by coir fibers. Density test was analyzed showing the density of foam decreases as fibre content increased. Scanning electron microscopy (SEM) shows that morphological changes in the surface of treated fibre also have more clefts and imperfections at 75x magnification when compared to untreated fibre.

Guo *et al.* (Gopalakrishnan, 2012) studied rigid polyurethane foams based on soybean oil. They synthesized rigid polyurethane foams from soybean oil-based polyols and isocyanate using catalyst. These foams were detected to have comparable thermoinsulating and mechanical properties to foams of petrochemical source. The thermal and thermo-oxidative behaviors of soy-based foams exhibited that more stable toward both thermal degradation and thermal oxidation than PPO-based foams and hence reveals that the lack of ether linkages in the soy-based rather than in PPO-based polyols.

5. Polyurethane elastomers based on natural resources: Polyurethane elastomers based on agar filler have been studied by Opera (Oprea, 2010). In this work, polyurethane elastomers were prepared from castor oil with hexamethylene diisocyanate and agar polysaccharide (obtained from seaweeds). Mechanical and morphological properties were examined for finding the intermolecular interactions between polyurethane and agar, optic micrograph exhibits a random dispersion of the agar filler in the composites respectively. Pure polyurethane shows hydrophilic character when compared to polyurethane-agar elastomers.

Narine *et al.* (Narine, 2007) synthesized polyurethane elastomers from seed oil polyols. First, they prepared polyols by ozonolysis and hydrogenated in tetrahydrofuran (THF) with Raney Nickel as catalyst. Thus, the canola-oil based polyols and commercial soybean oil-based polyols reacted with 1,6-hexamethylene diisocyanate (HMDI) to prepare polyurethane elastomers. The elastomers were determined by dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), modulated differential scanning calorimetry (MDSC) and thermogravimetric analysis (TGA). The glass transition temperatures (T_g) values of the elastomers found from TMA were lower than DMA and MDSC but T_g increased with decreasing OH/NCO molar ratio.

6. Polyurethane films based on natural resources: Polyurethane films based on starch have been studied by Kim *et al.* (Kim, 2007). They synthesized polyurethane films with toluene 2,4-diisocyanate using starch as the main polyol. FTIR spectra was carried out for confirming the formation of a urethane linkage between the -OH present in starch and -NCO present in toluene 2,4-diisocyanate. Polyurethanes ensued in two endothermic peaks under differential scanning calorimetry (DSC) which shifted to higher temperatures with increasing starch content and -NCO/-OH molar ratio and also leads to breaking stress and elastic modulus under tensile testing.

Lee *et al.* (Lee, 2009) investigated castor oil/polycaprolactone-based polyurethane (CPU) films and polyurethane biocomposites reinforced with hemp fibers (HCPU). By adding polycaprolactone diol (PCL) to the polyol mixture, the mechanical properties of CPU and HCPU was controlled. The thermal and mechanical properties of CPU and HCPU samples were analyzed using FTIR, DSC, DMTA, Minimat and SEM on varying the mixing ratio of castor oil and PCL. When hemp fibre was reacted with MDI, interfacial adhesion between fibre and matrix biocomposites improved showing the surface of the hemp fibre became smoother revealed by SEM micrographs.

7. Biobased polyurethanes based on natural resources: Biobased chain extended polyurethane composites with silk fibre have been studied by Manjula (Manjula, 2010) *et al.* In this work, they prepared biobased polyurethane in two-steps. First they synthesized pre-PU by reacting diisocyanates (TDI and HMDI) with castor oil in methyl ethyl ketone under nitrogen atmosphere followed by glutaric acid and incorporating the silk fibre with synthesized pre-PU to obtain biobased polyurethane composites. The mechanical properties such as tensile strength, modulus and surface hardness of neat TDI PU sheets found to be higher than that of HMDI-PU and a substantial enhancement in the mechanical properties was detected after the incorporation of a small amount of silk fibre into neat PU. SEM studies also exhibited that the composites have better interfacial bonding which leads to the improved mechanical properties.

Dwan'isa *et al.* (Dwan'isa, 2004). prepared biobased polyurethane from soy oil polyol and diisocyanate using glass fiber as reinforcement loading from 15, 30 and 50-wt%. On using 50wt% glass fibers, the storage modulus of biobased polyurethane showing 14-fold increase as well as enhancement in strength and modulus of biobased polyurethane more than 260 and 480% respectively. The impact fractured samples exhibits the efficiency of wetting and distribution of glass fibers on environmental scanning microscopy (ESEM) analysis. Thermal stability of the biobased polyurethane improved on reinforcement with glass fiber by thermogravimetric analysis (TGA).

CONCLUSION

Plastic materials are the major pertains of environmentalists. Thus, the natural sources are now greatly favored for the production of polymers and the natural oils provide a large kind of options for the preparation of

polyurethanes. The mechanical and morphological properties find wide range of applications. The incorporation of fillers and fibers into polyurethanes provides intermolecular interactions between them. The solid polyurethanes obtained from natural sources such as glucose and xylose draws increased transition temperature and stiffness due to the rigidity of the glucose unit increases hydrogen bonding and potential for cross linking.

REFERENCES

- Achary PGR, Mohanty N, Guru BN, Pal NC, Synthesis and Thermal Degradation Study of Polymer Blends from Polyurethanes of Linseed Oil and Cardanol based Dyes with Aminophenols, *J. Chem. Phar. Res.*, 4(3), 2012, 1475-1485.
- Azmi MA, Yusoff MFC, Abdullah HZ, Irdi MI, Rigid Polyurethane Foam Reinforced Coconut Coir Fibre, *Inter. J. Inte. Engi*, 4(1), 2012, 11-15.
- Bakare IO, Okieimen FE, Pavithran C, Khalil HPS, Brahmakumar M, Mechanical and Thermal Properties of Sisal Fibre-Reinforced Rubber Seed Oil-based Polyurethane Composites, *Mat. Des.*, 31(9), 2010, 4274-4280.
- Bledzki AK, Gassan J, Composites Reinforced with Cellulose based Fibers, *Prog. Poly. Sci.*, 24(2), 1999, 221-274.
- Bledzki AK, Zhang W, Chate A, Natural Fibre-Reinforced Polyurethane Microfoams, *Comp. Sci. Tech.*, 2001, 2405-2411.
- Corcuera MA, Rueda L, Arlas BF, Arbelaiz A, Marieta C, Mondragon I, Eceiza A, Microstructure and Properties of Polyurethanes Derived from Castor Oil, *Poly. Deg. Stab.*, 95(11), 2010, 2175-2184.
- Desroches M, Escouvois M, Auvergne R, Caillol S, Boutevin B, From Vegetable Oils to Polyurethanes: Synthetic routes to Polyols and main Industrial Products, *Poly. Revi.*, 2012, 52:1-96.
- Donnelly MJ, Stanford JL, Still RH, Polyurethanes from Renewable Resources-1: Properties of Polymers derived from Glucose and Xylose based Polyols, *Poly. Inte.*, 32(2), 1993, 197-203.
- Dwan'isa L, Mohanty LP, Misra M, Drzal LT, Kazemizadeh M, Biobased Polyurethane and its Composites with Glass Fibre, *J. Mate. Sci.*, 39(6), 2004, 2081-2087.
- Firdaus FE, Property of Polyurethane from Soy-derived Phosphate Ester, *Wor. Aca. Sci. Eng. Tech.*, 52, 2011, 235-238.
- Fried JR, *Polymer Science Technology*, second edi., Prentice Hall, New Delhi, 1999, 251-309.
- Gopalakrishnan S, Fernando TL, Influence of Polyols on Properties of Bio-based Polyurethanes'. *Bull. Mate. Sci.*, 35(2), 2012, 243-251.
- Gopalakrishnan S, Mythili CV, Retna AM, Synthesis, Mechanical, Thermal and Chemical Properties of Polyurethanes based on Cardanol'. *Bull. Mate. Sci.*, 27(3), 2004, 235-241.
- Gowariker VR, Viswanathan NV, Sreedhar J, *Polymer Science*, first edi., New Age International Publishers, New Delhi, 1986, 215-262.
- Guner FS, Yagci Y, Erciyas AT, Polymers from Triglyceride Oils, *Prog. Poly. Sci.*, 31, 2006, 633-670.
- Guo A, Javni I, Petrovic Z, Rigid Polyurethane Foams based on Soybean Oil, *J. App. Poly. Sci.*, 77, 2000, 467-473.
- Ha S, Broecker HC, Characteristics of Polyurethanes Incorporating Starch Granules, *Poly.*, 43(19), 2002, 5227-5234.
- Kim D, Kwon O, Yang S, Park J, Preparation of Starch-based Polyurethane Films and their Mechanical Properties, *Fib. Poly*, 8(3), 2007, 249-256.
- Kuranska M., Prociak A, Porous Polyurethane Composites with Natural Fibers'. *Comp. Sci. Tech.*, 72(2), 2012, 299-304.
- Lee N, Kwon O, Chun BC, Cho JW, Park J, Characterization of Castor Oil/Polycaprolactone Polyurethane Biocomposites Reinforced with Hemp Fibers, *Fib. Poly*, 10(2), 2009, 154-160.

Manjula KS, Kumar MN, Soare BG, Picciani P, Siddaramaiah, Biobased Chain Extended Polyurethane and its Composites with Silk Fibre, *Poly. Engi. Sci.*, 50(4), 2010, 851-856.

Merlini C, Soldi V, Barra GMO, Influence of Fibre Surface Treatment and length on Physico-Chemical Properties of Short Random Banana Fibre-Reinforced Castor Oil Polyurethane Composites, *Poly. Tes.*, 30(8), 2011, 833-840.

Milanese AC, Hilario MO Voorwald JC, Flexural Behavior of Sisal/Castor Oil-based Polyurethane and Sisal/Phenolic Composites, *Mat. Res.*, 15(2), 2012, 191-197.

Monteavaro LL, Riegel IC, Petzhold CL, Samios D, Thermal Stability of Soy-based Polyurethanes, *Poli.*, 15(2), 2005, 151-55.

Mosiewicki MA, Dell'Arciprete GA, Aranguren MI, Marcovich NE, Polyurethane Foams obtained from Castor Oil-based Polyol and filled with Wood Flour, *J. Comp. Mate.*, 43(25), 2009, 3057-3072.

Mothe CG, Araujo CR, Wang SH, Thermal and Mechanical Characteristics of Polyurethane/Curaua Fibre Composites, *J. Ther. Anal. Calo.*, 95(1), 2009, 181-185.

Narine SS, Kong X, Vegetable Oils in Production of Polymers and Plastics, *Bail. Indu. Oil. Fat. Prod.*, 6, 2005, 279-306.

Narine SS, Kong X, Bouzidi L, Sporns P, Physical Properties of Polyurethanes Produced from Polyols from Seed Oils, *J. Amer. Oil Chem. Soc.*, 84, 2007, 55-63.

Ogunniyi DS., Fakayejo WRO., Ola A, Preparation and Properties of Polyurethane Foams from Toluene Diisocyanate and Mixtures of Castor Oil and Polyol, *Iran. Poly.J.*, 5(1), 1996, 56-59.

Okieimen FE., Bakare IO, Rubber Seed Oil-based Polyurethane Composites, Fabrication and Properties Evaluation *Adv. Mat. Res.*, 18, 2007, 233-239.

Oprea S, Preparation and Characterization of the Agar/Polyurethane Composites, *J. Com. Mate.*, 2010, 1-7.

Pawlik H, Prociak A, Influence of Palm Oil-based Polyol on the Properties of Flexible Polyurethane Foams, *J. Poly. Envi.*, 20(2), 2012, 438-444.

Petrovic ZS, Polymers from Biological Oils, *Cont. Mate.*, 1(1), 2010, 39-50.

Pradhan KC, Nayak PL, Synthesis and Characterization of Polyurethane Nanocomposite from Castor Oil-Hexamethylene Diisocyanate, *Adv. App. Sci. Res.*, 3(5), 2012, 3045-3052.

Rozman HD, Ang LG, Tay GS, Abubakar A, The Mechanical Properties of Rice Husk-Polyurethane Composites, *Poly. Plas. Tech. Engi.*, 42(3), 2003, 327-343.

Santos DJ, Tavares LB, Batalha GF, Mechanical and Physical Properties Investigation of Polyurethane Material obtained from Renewable Natural Source, *J. Ach. Mate. Manu. Engi.*, 54(2), 2012, 211-217.

Saralegi A, Rueda L, Arlas BF, Mondragon I, Eceiza A, Corcuera MA, Thermoplastic Polyurethanes from Renewable Resources: Effect of Soft Segment Chemical Structure and Molecular Weight on Morphology and Final Properties, *Poly. Inte.*, 62, 2013, 106-115.

Saunders KJ, Organic Polymer Chemistry, second edi., Chapman and Hall, New York, 1988, 358-359.

Shan CW, Idris MI, Ghazali MI, Study of Flexible Polyurethane Foams Reinforced with Coir Fibers, *Inte. J. App. Phy. Mat.*, 2(2), 2012, 123-130.

Sharma V, Kundu PP, Condensation Polymers from Natural Oils, *Prog. Poly. Sci.*, 33, 2008, 1199-1215.

Silva VR, Mosiewicki MA, Yoshida MI, Silva MC, Stefani PM, Marcovich NE, Polyurethane Foams based on Modified Tung Oil and Reinforced with Rice Husk Ash1: Synthesis and Physical Chemical Characterization'. *Poly. Tes.*, 32(2), 2013, 438-445.

Soby MS, Tammam MT, The Influence of Fibre length and Concentration on the Physical properties of Wheat Husk Fibers Rubber Composites, *Inte. J. Poly. Sci.*, 2010, 1-8.

Sumaila M, Ugheoke BI, Timon L, Oloyede T, A Preliminary Mechanical Characterization of Polyurethane filled with Lignocellulosic Material, *Leo. J. Sci.*, 9, 2006, 159-166.

Suresh KI., Krishanprasad VS, Synthesis, Structure and Properties of Novel Polyols from Cardanol and Developed Polyurethanes, *Ind. Eng. Chem*, 44, 2005, 4504-4512.

Valero MF, Pulido JE, Hernandez JC, Posada JA, Alvaro R, Cheng Z, Preparation and Properties of Polyurethanes based on Castor Oil Chemically Modified with Yucca Starch Glycoside, *J. Elas. Plas.*, 41, 2009, 223-244.

Zhang Y, Hourston DJ, Rigid Interpenetrating Polymer Network Foams prepared from a Rosin-based Polyurethane and Epoxy resin, *J. Appl. Poly. Sci.*, 69(2), 1998, 271-281.