PREPARATIONS AND PROPERTIES OF CASTOR OIL BASED POLYURETHANE ADHESIVES AND COATINGS

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The synthesis, characterization and study of 'tailor made' polymers are a center of attraction to scientist as well as technologist belonging to several disciplines such as chemistry, physics, biology etc. Some desirable properties of polymers are high strength, light weight, good flexibility, resistance to chemicals, special electrical properties, high temperature stability, ameanability to fabrications into complex shapes etc. Only some polymers do almost always meet our requirements. In recent years there has been considerable interest in synthesis of polyurethanes due to their exceptional properties like high mechanical strength, good chemical resistance, high dimensional stability etc. Polyurethanes find use in various fields of applications like coatings, foams, elastomers, adhesives, automotive industries etc. It can also be used in residential construction, for making flexible toys, furniture, wheels artificial limbs, shoe soles and orthopedic cast. However, use of renewable and biodegradable resources for synthesis of materials has always been stressed, which finds support from economic policies. Castor oil is unique among all renewable sources, in that it is the only source of 18 cabon-hydroxylated fatty acids with a single double bond.

Majority of coatings and adhesives exist in the form of a three-dimensional network produced by the cross linking of resins. Recent development of novel polyurethane coatings led to high quality product for surface coatings. The demand of biodegradability and economic policies stress the use of castor oil for the synthesis of polyurethanes.

The research work in this thesis mainly deals with the synthesis, characterizations, properties and applications of polyurethanes. Different polyols were reacted with different isocyanate adducts to form Polyurethanes (PU's). This PUs could be efficiently used as surface coating material and as wood to wood and metal to metal adhesives. Also the effect of chain length as well as NCO/OH ratio on performance properties of polyurethanes were determined.

Polyester polyols were synthesized by Fusion process. Novel polyol (EpxR) were synthesized by solution condensation polymerization process. A series of acrylated polyols were also prepared by grafting of 2-hydroxy ethyl methacrylate (HEMA) on a polyol (EpxR) backbone. Grafting was carried out by free radical polymerization mechanism on conjugated double bond. They were characterized by spectroscopic technique FTIR, Hydroxyl value, Acid value, percentage non-volatile matter, viscosity, GPC etc.

These polyols were reacted with different isocyanate adducts viz. Aromatic isocyanate adduct, aliphatic isocyanate adduct and R60-isocyanate adduct. This R60 isocyanate adduct was synthesized in our laboratory by simple addition reactions and characterized.

These PU resins synthesized by varying NCO/OH ratio for coating application and were applied on test panels and its coating properties evaluated in terms of drying time, flexibility, adhesion on substrates, pencil hardness, scratch hardness, impact resistance, chemical resistance etc. These PUs were also characterized by FTIR spectroscopy and by TGA. The effect of chain length of different polyols, NCO/OH ratio and the presence of catalyst on coating performance was also studied.

These PU resins could be used efficiently as adhesives for wood to wood and metal to metal substrates and evaluated by measuring the adhesion strength in terms of lap shear strength. Effect of variety of chemicals such as an acid, alkli, salts solutions on adhesive strength and green strength of adhesives were also studied.

Swelling properties of some PUs and the effect of use of diffeent chain length polyols, PEG 200, PEG 400 and PEG 600 and crosslink density (NCO/OH ratio) on swelling behavior of PUs was investigated. Molecular weight between two cross-link points, sorption coefficient and diffusion coefficient was calculated by using Flory Rehner theory.

Synthesis:

(i) *Synthesis of Polyester polyol:*

Three different polyols were synthesized from castor oil derivative ricinoleic acid by esterification with ethylene glycol, diethylene glycol and triethylene glycol respectively by Fusion process (ii*) Synthesis of novel polyol (EpxR)*:

The novel polyol *EpxR* was synthesized from epoxy resin and castor oil derivative ricinoleic acid in the presence of a catalyst triethylamine by solution condensation polymerization technique.

(iii) *Synthesis of Acrylated Polyol:*

A series of acrylated polyol were also prepared by grafting of 2 hydroxy ethyl methacrylate on a conjugated double bond present in polyol (EpxR) backbone through free radical mechanism on a polyol presence of AIBN as initiator.

(iv) Synthesis of R60 Isocyanate Adduct:

R60 isocyanate adduct was synthesized by simple addition reaction method. With continuous stirring TDI was added dropwise into R60 ,in a three-necked flask equipped with nitrogen inlet, mechanical stirrer and the reaction mixture was stirred continuously for 5h resulting into a viscous product of R60 isocyanate adduct.

Polyurethane Coatings:

Synthesis of polyurethane for coating was carried out by reacting various polyols with aromatic isocyante adduct, aliphatic isocyanate adduct as well as R60 isocyanate adduct with or without catalyst at room temperature having different NCO/OH ratio viz. 1, 1.3 and 1.7. Then PU resin was diluted with appropriate solvent mixture to have viscosity for particular application of coating with brush on cleaned mild steel and tin panels (size 15 cm × 2.5 cm × 0.1 cm).

Drying Time:

After application of PU resin on test panels, the panels are kept vertical. Drying time of all coated panels were measured. PU systems having higher NCO/OH ratio dried faster compare to PU systems obtained from relatively lower ratio. The aromatic isocyanate adduct system dried faster than aliphatic systems. The drying speed of the coating was also accelerated by the presence of catalyst. The effect of chain length also affect the drying time. Compared to PU B and PU C which contained diethylene glycol and triethylene glycol in polyol respectively the system PU A, containing shorter chain length of ethylene glycol in polyol, dried faster.

Adhesion:

Adhesion test of coated materials was by cross hatch adhesion to determine unacceptable adhesion. Results show almost 100% adhesion on all PU system.

Flexibility:

Flexibility test of coated materials was done on tin panels by bending mendrel 1/8". Results showed that aliphatic isocyanate adduct was more flexible compare to aromatic isocyanate adduct. From PU A to PU C flexibility increased. Also, as the NCO/OH ratio increased, the flexibility decreased.

Pencil Hardness:

The coatings are related according to their resistance to be scratched or marked by pencil of various hardness. During testing uniform pressure was applied at an angle of 45^0.Results indicate that at a given NCO/OH ratio, aromatic system shows better pencil hardness compared to aliphatic system. This may be due to increase in the rigidity provided by more crosslinked structure.

Scratch Hardness:

From the results it can be inferred that all the compositions were found to show good scratch resistance. This may be due to higher crosslink density in the coating resulted from the more number of functional group.

Impact resistance:

The determination of impact resistance involves indention by an object of specified weight on a panel from the varying height. PU coating systems consisting of aromatic isocyanate adduct at the same NCO/OH ratio showed poor results compared to aliphatic isocyanate adduct, because aromatic isocyanate produces aromaticity in the polymer network, so the film could be easily broken under sudden impact.

Water and Moisture resistance:

Coatings are invariably designed to control the action of water by functioning as a barrier between the substrate and the aqueous environment. When the effect of water on coated film was studied, all PU systems show a very good resistance to water.

Chemical resistance:

For this we dipped the coated panels into acid solution (5% H_2SO_4), alkali solution (5% NaOH) and salt solution (10% NaCl) and measured the performance of coated materials.

The results showed that PU system based on polyester polyol have poor chemical resistance in acid solution at lower NCO/OH ratio, while as NCO/OH ratio increased it gave excellent resistance to acid solution. It also gives a very good resistance to alkali and salt solution.

Another series of synthesis of PU coatings were carried out by reacting novel polyol with aromatic isocyanate adduct, aliphatic isocyanate adduct and R 60 isocyanate adduct (NCO/OH ratio viz. 1, 1.3 and 1.7) with or without catalyst. It showed better chemical and mechanical properties. Also it can be inferred that the combination of aromatic and aliphatic moieties in an isocyanate adduct, provides higher degree of cross-linking and uniformity in network.

The above observations indicate that castor oil based isocyanate adduct based PU coatings of various NCO/OH ratio show better chemical and mechanical properties than all other PUs discussed in this thesis.

Thermogravimetric analysis:

Thermal stability of polyurethanes synthesized was studied by TGA. PU synthesized from castor oil showed two stage decompositions and reasonably good thermal stability though the second stage was not quite well distinct. Activation energy of decompositions was evaluated by well known Broido's method. The equations used for the calculations of activation energy (Ea) was,

$\ln \ln(1/y) = (-Ea / R)(1/T) + \text{constant}$, where y has been discussed earlier.

The activation energy of decompositions of polyurethanes synthesized from polyester polyols were in the range of 71-94 kJ/mole and for polyurethanes synthesized from EpxR are in the range of 51-76 kJ/mole.

Swelling Study:

In the present study, the sorption and diffusion of various organic solvents through polyurethane elastomers have been discussed. The equilibrium swelling were performed in various solvents in order to determine solubility parameter of PUs. The kinetics of swelling of the PU samples was also studied in dioxane, in which PUs showed maximum swelling.

The uptake capacity of PUs varied with change in compositions (ratio of the components) used and NCO/OH ratio. Increase in NCO/OH ratio in PU system had a negative effect on the uptake capacity of solvents.

Swelling parameters like diffusion coefficient, sorption coefficient and permeability were also calculated from the swelling data. The molecular weight between two crosslink points was computed using by Flory Rehner equation.

$$M_c = -\frac{\rho V_1 (V_p)^{1/3}}{\ln(1 - V_p) + V_p + \chi_{12} V_p^{\,2}}$$

The sorption of solvents under swelling study was inversely proportional to the crosslinking density and directly proportional to the chain length of polyethylene glycols in the PU series. Diffusion process from the sorption kinetic study was found to be not much different from the normal Fickian behavior. The value of diffusion coefficient (D) and sorption coefficient (S) are found to be directly related to the function of flexibility and rigidity of polyurethane networks

Mechanical Testing:

The tensile properties of some of PUs in terms of tensile strength and % elongations were evaluated from stress/ strain curve. The data showed a gradual increase in all mechanical properties studied with decrease in molecular weight of polyethylene glycol incorporated with polyol (EpxR). For PUs made from EpxR and R 60 isocyanate adduct, the tensile strength increased with increase in NCO /OH ratio and the % elongation also decreased. If PEG was then incorporated into PUs tensile strength as well as % elongation decreased. The tensile strength of PU system having NCO/OH 1.3 was also measured. EpxR with R 60 isocyanate adduct showed maximum tensile strength and PEG 600 with R60 isocyanate adducts show minimum tensile strength value.

Polyurethane Adhesives:

The polyols synthesized were mixed with isocyanate adduct at different NCO/OH ratio. Adhesives for wood to wood, metal to metal bonding, were formulated as evaluated in terms of lap shear strength, chemical resistance of these adhesives in terms of change in lap shear strength was also measured . Polyester polyol based adhesives showed good adhesive property for wood to wood and acrylated polyol based adhesives were found to be more effcient for metal to metal adhesives. Lap shear strength of adhesives for wood pieces and metal pieces was measured by standard methods.

The above polyols and polyurethanes were characterized by FTIR spectroscopy. The FTIR spectrum of PU showed the strong band at 1537 cm^{-1} and 1539 cm^{-1} indicating the presence of –NH bending. Also absence of 3400cm^{-1} spectrum indicated the absence of OH stretching. In case of higher NCO/OH ratio the band observed at 2200 cm^{-1} indicated the presence of free NCO groups in the PUs.

The FTIR spectrum of novel polyol (EpxR) the particular band of epoxy group was absent at 920 cm^{-1} which indicated that the terminal epoxy ring reacted with acid group with formation of ester linkage. The strong band at 3400 cm^{-1} indicated the free hydroxyl groups present in the polyol.

FTIR spectrum of acrylated polyols showed a broad peak at 3400 cm^{-1} due to –OH stretching and medium intensity absorption peak at around 2295 cm^{-1} due to the –CH stretching of aliphatic methylene group. The spectrum of acrylated polyol showed a broad peak of ester group at about 1740 cm^{-1}.