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Rigid foams from cashew nut shell liquid: synthesis, characterization and evaluation of polyol and foam properties

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Abstract

In the past, polyurethanes were usually made with petroleum polyols. With the dwindling and non-renewable petroleum resource, some novel polyols made from vegetable and seed oil have been investigated for their potential of replacing the petroleum polyols. Of particular interest is a group of polyols derived from Cashewnut oil. These new polyols, however, have some major disadvantages limiting its applications when compared with petroleum polyols. Present work includes synthesis of novel polyols from CNSL as non-petroleum renewable resource and application in rigid polyurethane foam with better mechanical, thermal and fire performance.

Keywords: cashew nut shell liquid, mannich polyol, rigid foams, morphology, impact strength

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Introduction

Global efforts to find renewable feedstock for the chemical industry are aimed at replacing fossil reserves and a reduction in global warming by employing environmentally friendly technologies (green chemistry approaches) for specialty chemical manufacturing. Otto Bayer had studied the commercial development of polyurethane in 1937 but Rinkie and collaborators found its commercial use in 1938. The commercial production of polyurethane foams was started in the year 1954 [1] Cashew nut shell liquid (CNSL) is a product from cashew tree fruits. The cashew tree (Anacardium occidentale) is native to Brazil. [2–3] The cashew nut tree has a fruit with a very interesting structure, the nut is attached to the cashew apple, has two shells, a hard inner shell and an outer shell. Between these two shells, in a honeycomb structure, is oil known as CNSL. [4] CNSL is organic aromatic oil containing a variety of natural Phenolic components. The major component (approx. 90 %) is anacardic acid, and 10 % cardol.[5] Cardanol obtained from Cashew nut shell liquid (CNSL) is a renewable resource of immense potential. It is the alkyl Phenolic oil contained in the spongy mesocarp of the cashew nut shell (Anacardium occidentale L). [6-7] Cardanol has many applications in polymer chemistry, for example in epoxy resins, phenol–formaldehyde resins, nonionic surfactants and polyurethanes. [8-9] Renewable resources as a source of polyols in the preparation of Polyurethane foam has also been widely studied. [10-11] Soy-based polyol has recently been reported for the preparation of rigid foam with excellent mechanical strength. [12] Other vegetable oils like castor oil and palm oil were also used to synthesized polyether polyols either alone or as a blend to prepare to rigid PU foams. [13-14] In the present work, new bio-based mannich polyol was synthesized from renewable resource (cardanol) which was used for the preparation of rigid polyurethane foam. Mannich polyol and rigid foams were characterized by spectroscopic methods and physico-mechanical and fireproofing properties were evaluated.

Materials

Cardanol was obtained from CNSL by using de-carboxylation process. Castor oil was obtained from Aastha oil company (India). Diethanolamine, para-formaldehyde power 95% were purchased from sigma-Aldrich. Polymeric MDI (NCO=31.2 %) obtained from Dow chemical (Germany) and Sigma-Aldrich (Belgium). The surfactant TEGOSTAB B-8404 to achieve superior cell structure, which was donated by Evonic Company (Germany). The Amine catalyst Di methyl amino ethanol (DMAE) was obtained from Merck (india). Water was used as a Chemical blowing agent to generate foam.

Methods

^1H NMR spectra were recorded with a Hitachi 500-MHz spectrometer. Infrared spectra were recorded with a Jasco FT-IR spectrometer by the KBr pellet method. The hydroxyl value of the polyol was determined by pyridine‒acetic anhydride method (ASTM-1957-86). The GPC chromatograms were acquired on a Waters system consisting of a 510 pump and 410 differential refractometer. Tetrahydrofuran was used as the eluent at a flow rate of 1.00 mL/min. Four Phenogel columns from Phenomenex covering MW in range 10^2 to 5×10^5 were used. The test specimens ($50 \times 50 \times 30\ mm^3$) were weighed to determine the density in kilograms per cubic meter. Five specimens were tested and the average value was reported. Limiting oxygen index (LOI) was determined as minimum % of O_2 required to marginally support combustion according to ISO 4589-2, ASTM D 2863 (Atira, India). Impact testing was conducted according to ASTM D 256. Izod method was employed, using unnotched sample on a Zwick impact tester (model 5101 Atira, India), with a pendulum energy of 2 joule (J). The values of the obtained impact strength represented the mean of five specimen measurements.

Thermo gravimetric analysis of rigid PU foams were carried out on a TGA Q50 thermo gravimetric analyzer (TA Instruments) in nitrogen stream, temperature range of 20–600 ^{O}C with heating rate of 10 ^{O}C/min. Scanning electron microscopy was performed on cut sections of the foam sample after coating the specimens with a thin layer of gold using a SEM Hitachi-S520 model from SVNIT, (India).

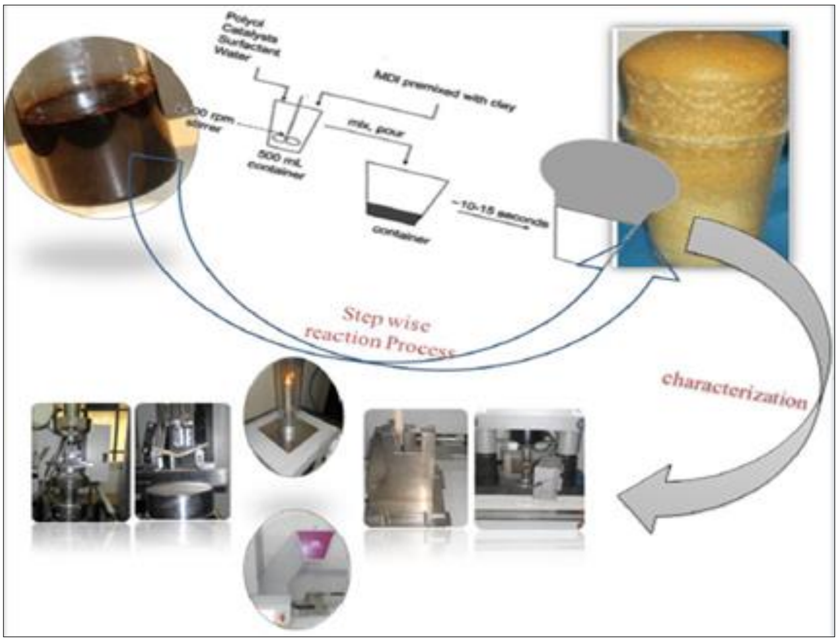


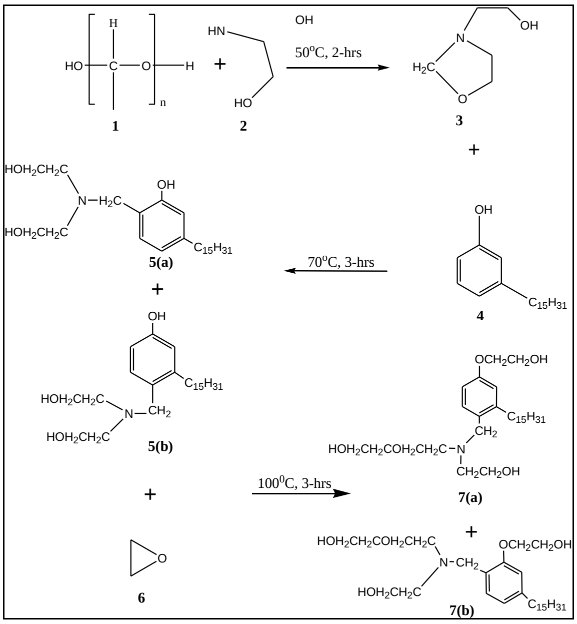
Fig 1

Experimental Procedures

The Synthesis of Mannich polyol from renewable resource (Cardanol) was carried out in step wise reaction and resulted polyol was utilized for the preparation of rigid foam. [15]

Synthesis of N-(2-hydroxyethyl)-1, 3-oxazolidine (Mannich precursor) and Mannich bases (5a and 5b) with Mannich polyols (7a and 7b)

Mannich Precursor **(3)** was synthesized the addition reaction between Para- formaldehyde with diethanolamine in the molar ratio of 1:1 for 2-hrs and reaction temperature was carried out not more than 50^{0}C. End of the reaction mannich precursor was light yellow liquid and low viscous as usually. The reactivity of N-(2-hydroxyethyl)-1, 3-oxazolidine is explained by the equilibrium between the cyclic form and the open chain form. The N-(2-hydroxyethyl)-1, 3 oxazolidine structure was confirmed by the IR spectrum. In 2nd step, Mannich base was synthesized by the reaction of cardanol and Mannich precursor in the mole ratio of 1:1 for 3-hrs shown in Scheme-1. The structures of the Mannich bases were confirmed by the IR and ^{1}H NMR spectra. In 3rd step Mannich polyol was synthesized by reaction of Mannich bases (5a) and (5b**)** and oxarine in the mole ratio 1:2 at 100^{O}C under auto-generated pressure (50 Psi) in a closed system for 3-hrs. The reaction is catalyzed by the tertiary nitrogen existing in the structure of Mannich base (self-catalysis).



< Scheme 1.>

Fig 2

Foam Formation

Rigid foams were prepared by a free-rise method according to the formulation listed in Table-1. Cashew mannich polyol and castor oil was mixed with the additives (catalysts, surfactant, and blowing agent) using a spatula at ambient temperature for 5 minutes. The polymeric isocyanate mixed with the filler as used (0 to 40 %) than after both mixtures were mixed for around 20 s by using high speed agitator (1000 rpm). Afterwards, the resultant mixture was quickly transferred into a teflon mold (150 mm x 150 mm x 25 mm) for foaming to obtain the rigid foam. Finally resulting rigid foam was removed from the mold and allowed to post cure for 1 day at room temperature before cutting into the test specimens.

Table 1: Formulation used for rigid foams based on cashew Mannich polyol

Components	Weight of components in grams
Castor oil	21
Cashew based mannich polyol (Mw-672.9), (OH number-331 mg KOH/g)	11
Silicon B-8404	0.33
DMAE	0.19
Water	0.33
Polymeric MDI	Index 110
Fillers (Fly ash)	0 to 40 percentage

Results and Discussion

Generally, the synthesis of Mannich polyols is based on the reaction of phenol or p-nonyl phenol with diethanolamine and aqueous solutions of formaldehyde. [8, 16] After the reaction, water is removed under vacuum. This synthetic pathway has a big disadvantage an increase in viscosity of the product during vacuum distillation of water. We reported new pathway for polyol synthesis where of Cardanol (phenolic) with N-(2-Hydroxyethyl)-1, 3-Oxazolidine has a big advantage because Cardanol is not contact with formaldehyde but only contact with oxazolidine. An interesting question is why N-(2-hydroxyethyl)-1, 3-oxazolidine reacts with cardanol and leads to the same Mannich bases as from the direct reaction of cardanol with formaldehyde and diethanolamine. The explanation is that oxazolidine have the cyclic form in equilibrium with the open chain.. The open chain form has the structure of an iminium cation which is the well-known intermediate of Mannich reactions. [17-18] In the presence of bases (in our case oxazolidine, a tertiary amine) cardanol dissociate to cardanol anions with the negative charge distributed at equilibrium in resonance effect at oxygen and in the positions ortho and para of aromatic ring. The alkylation of the aromatic ring with the iminium cation is carried out by reacting oxazolidine open chain form with the cardanol anions, in the positions ortho and para. The final step is the rearrangement of intermediate with regeneration of the aromatic phenolic substituted rings, in fact the Mannich base.

Mannich polyol from cardanol, are very reactive due to the presence of the tertiary nitrogen in their structure, exerting a strong catalytic effect in the reaction between hydroxyl and isocyanate groups. Mannich polyol from cardanol (Cashew Mannich polyol) was used for formulation of rigid polyurethane foams, which require very reactive polyol. Formulations presented in Table-1 produced rigid polyurethane foams with good physico-mechanical and fire retardant properties.

The N-(2-hydroxyethyl)-1, 3-oxazolidine and cashew based mannich polyol structure were confirmed by the spectral analysis. [20] IR spectrum of N-(2-Hydroxyethyl)-1, 3-Oxazolidine, the peak at, IR (KBr, ῡ cm^{-}), strong absorption at 1654 cm^{-1} (C=N imines group) as shown in Fig. S1.The Mannich base from cardanol contained peaks at ^{1}H-NMR (400 MHz-DMSO), 1.53-1.56δppm (3H, -CH_3), 2.56-3.75 δ ppm (2H, =N-CH_2), 5.29-5.38δppm (6H –C=C-), 6.5δ ppm (1H-Ar-OH),6.5-7.87 (Ar-H) as shown in Fig. S2 and Fig. S3 shows the IR spectrum of the Mannich base from cardanol contained peaks at (m,cm-1): 3349 (-OH), 2925 (-C=C-), 2854 (-C-H), 1584 (Phenyl ring), 1378(-C-N), 1274 (-C-O), and 1074(Conjugated double bond). Fig. S4 and Fig. 5 display the IR and ^{1}H-NMR Mannich polyol from mannich base with ethylene oxide, the peak at IR and ^{1}H-NMR (400 MHz-DMSO), 0.88-1.27 δppm (3-H,-CH_3), 1.30-1.55 δppm (-CH_2-CH_2-linkage),2.75-2.84 δppm (6H,=N-$(CH_2)_3$), 3.30-3.74 δppm (-CH_2-CH_2-OH), 5.41-5.86 δppm (Ar-H),6.52-6.62 δppm (Branch -OH) and the peak at IR (KBr, V cm^{-}), 3367 (-OH), 3009 (-C-H), 2923 (-C-C-), 2852 (-C=C-), 1585 (Phenyl ring), 1454 (-C-N), 1270 (-C-O-), 1070 (Conjugated double bond).

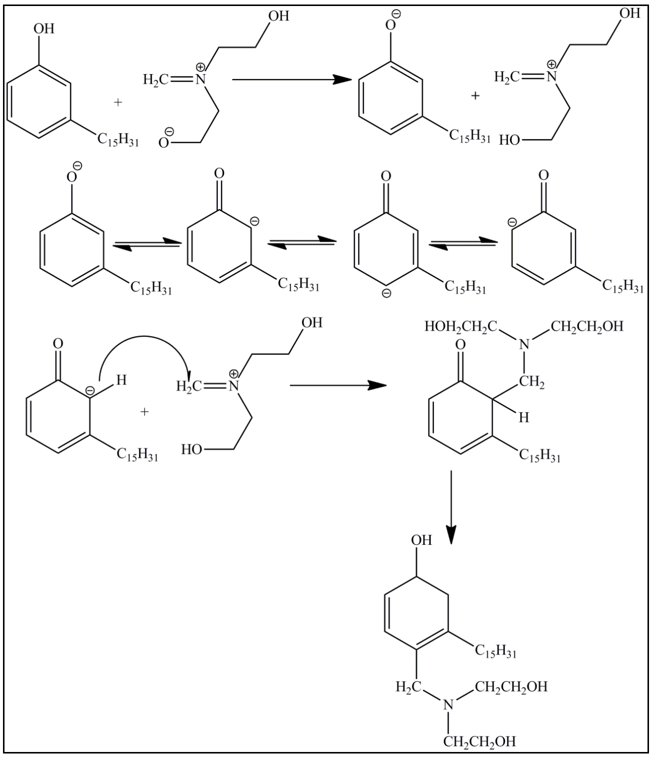


Fig 3: The mechanism of reaction of N-(2-Hydroxyethyl)-1, 3-Oxazolidine with Cardanol>

Mechanical, thermal and fire properties of all synthesized cardanol based rigid foam were measured with variation in filler content. The impact strength was decreased with increasing of the fillers as shown in Fig. 4. Impact strength results shows better strength up to 10% filler ratio, due to interfacing bonding between fillers and PU-matrix but more than 10%filler ratio causes brittleness due to weak. For PU-matrix, we use 0 to 40 % filler ratio, up to 10% impact strength was gradually increase than after 10% its becomes gradually decrease.

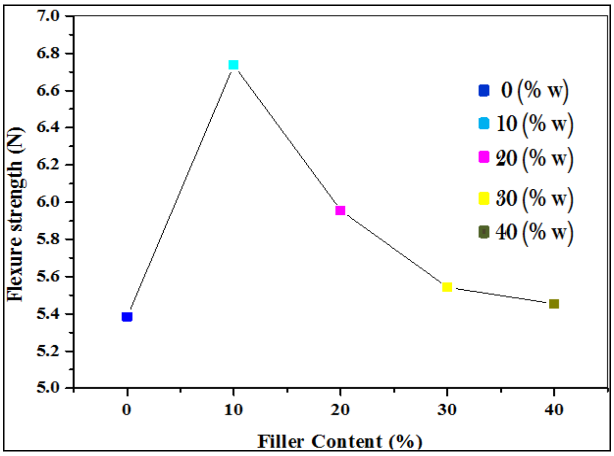


Fig 4: The impact strength- fillers plots showing the density behavior of the foams

Numbers of parameter responsible for fire properties of synthesized materials such as limiting oxygen index (LOI) [19]. Effect of fillers additive on the LOI value of foam has been examined as as shown in Fig. 5. It can be seen that 10 % filler-based foam shown high LOI value as compared to others.

This indicates that 10% filler more efficient as a flame retardant in foam. LOI results shows good value up to 10 % filler ratio, due to higher efficiency between fillers and PU-matrix but more than 10 % filler ratio causes less efficient. Fig. 6 displays thermo gravimetric curves of rigid polyurethane foams based on synthesized Cashew Mannich polyols. All TGA data observed that weight decrease in the range of 150-200 ^{O}C is probably explained by the evaporation of some low molecular components. The thermal degradation of foam based initial starts at around 350^{O}C.

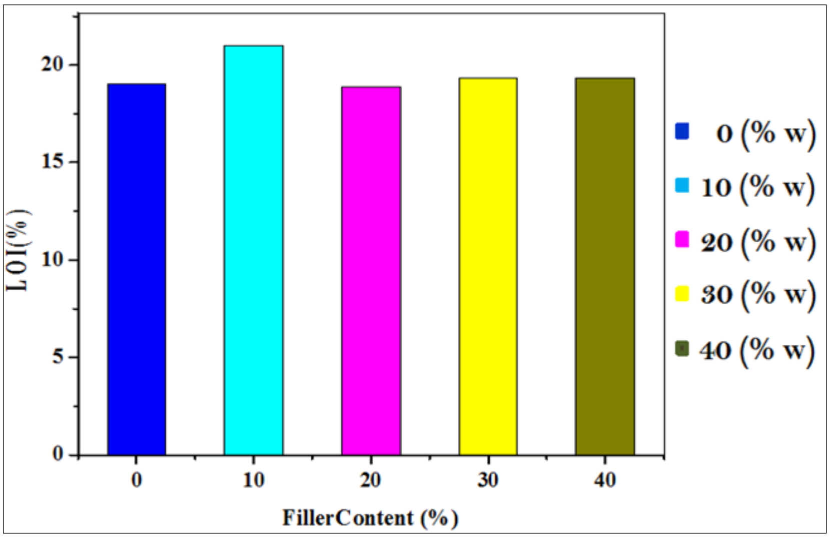


Fig 5: LOI-Filers plots showing the Limiting Oxygen Index behavior of the foams.

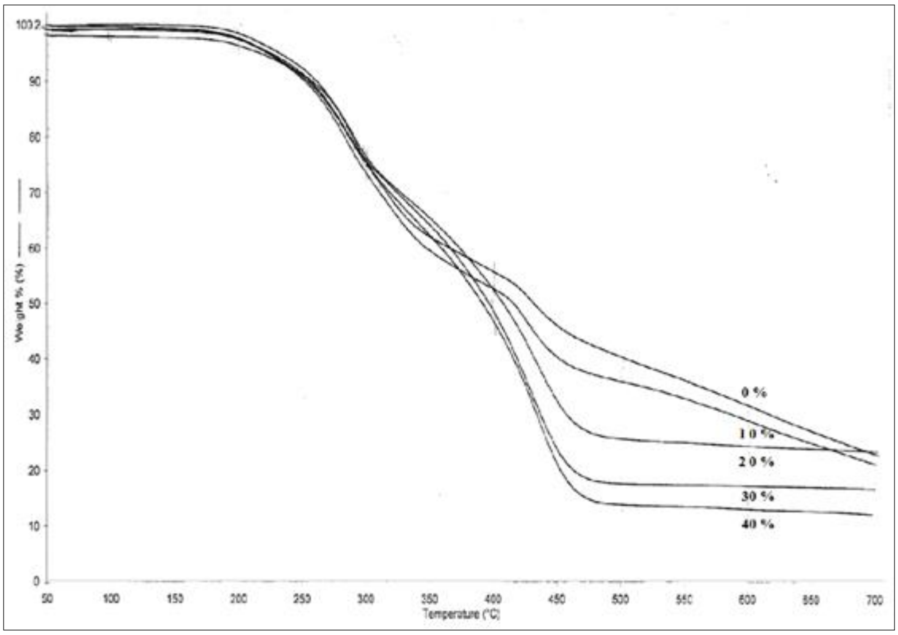


Fig 6: Thermo gravimetric curves of foam based on cashew mannich polyol

Cell structure of the foams was analyzed by scanning electron microscopy shown in Fig. 7. SEM results shows uniform cell structural like pentagon up 10 % filler ratio but increasing amount of filler ratio cell structural was damage and foam becomes to brittle. This could be reason for the increasing the filler decrease the impact strength.

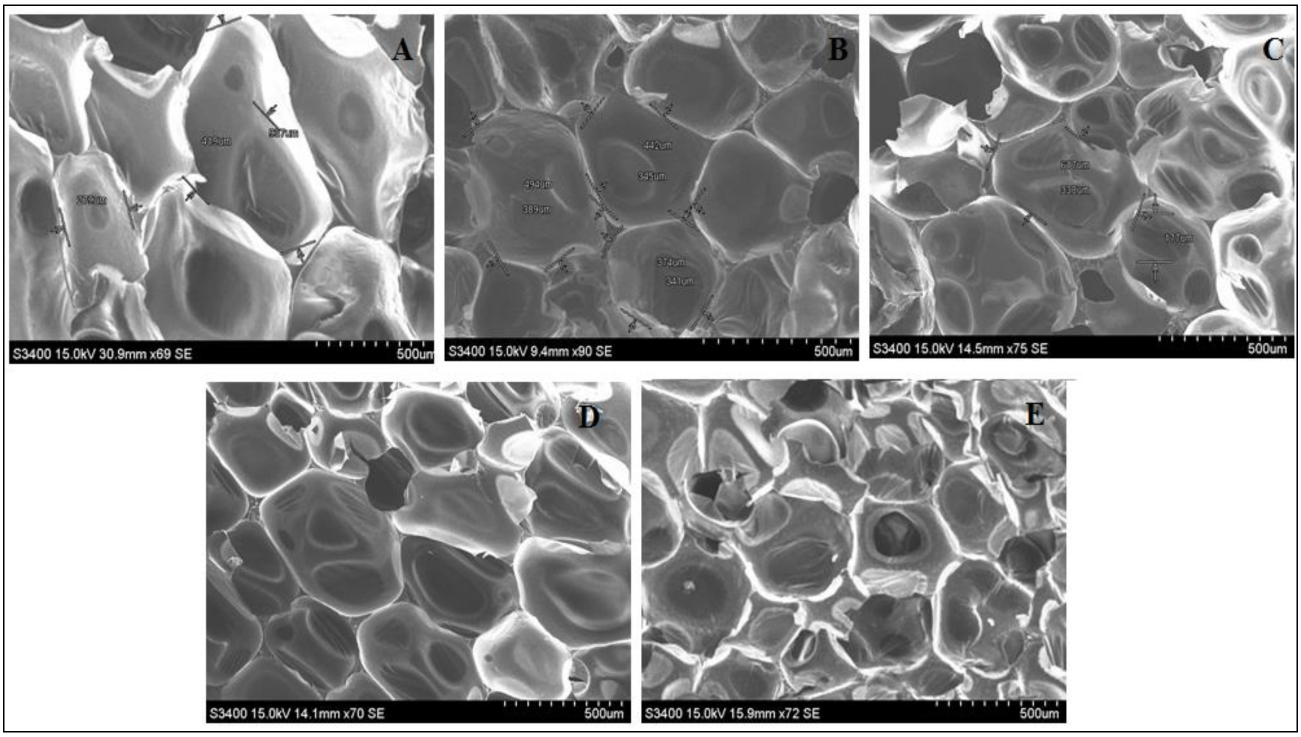


Fig 7: scanning electron micrograph of a rigid polyurethane foams from cashew mannich polyol [without filler to 40 % A to E]

Conclusions

Cashew mannich polyol was successfully synthesized from cardanol via oxazolidine route for the preparation of the rigid foams with good physico-mechanical, thermal and fire properties. Cost effective polyurethane based rigid foam can be prepared by using fly ash as filler (0-40%). Rigid PU foam containing 10 % fly ash as filler shows good mechanical, thermal and fire properties. There is decrease in mechanical and fire properties and increase in brittleness with increase in filler content due to poor interfacing bonding between filler and PU- matrix and due to damage in cell geometries.

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