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Improvement in the Flame Retardancy of Flexible Polyurethane Foam by addition of nano-silica

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Abstract: Flexible polyurethane foam (PUF_F) is beneficial and a multipurpose product used widely in all the sectors. The present study involves the preparation of PUF_F at laboratory scale level with the addition of different % of non-silica (NS). To optimize the best operating condition, the composition of NS was varied from 0.5 % to 2 %. The important characteristic of the prepared sample was assayed. Flammability test was conducted by UL 94 HB (Horizontal Burning) method. Thermal stability of the prepared PUF_F was evaluated by thermo gravimetric analysis (TGA). The improvement in thermal stability was observed more in NS sample (1.5 %). Weight loss of about 5 % and 50 % was observed at 257 ˚C and 337 ˚C in NS (1.5 %) sample, respectively. Additionally the presence of different functional groups was studied by Fourier Transform Infrared (FTIR) Spectroscopy. FTIR results reveal the complete conversion of precursor (isocyanate) into final product PUF_F. The measure of elasticity was carried out by rebound resilience (RR) test. Significant increase in % of RR was observed. The structure and the form of the prepared PUF_F samples were investigated by optical microscopy (OM). OM shows the presence of open cell structure with strut, strut joint and cell window. The characterization tests reveal the fact of change in property of NS filled PUF_F especially in terms of thermal stability and flame retardancy.

Keywords: Nano filler, Flexible Foam, nano-silica, Polyurethane and PU foam.

I. INTRODUCTION

Polyurethanes (PU) are made by addition of polyol with diisocyanate and this comes under the class of a polymeric material. Diisocyanate and polyol are available in wide ranges. With respect to the specific need these two can be mixed together along with the catalysts and additives in order to get finished product. Comfort, durability, energy absorption, firm support and resiliency are the main characteristics of PUF_F which leads to the necessity and demand of PUF_F in the current market situation. PUF_F has remarkable applications in various fields like bedding, furniture, packaging, safety cushions and transportation etc [1]. In transportation especially, it simultaneously helps in sound/vibration absorption, fuel efficiency and reduction in weight etc [2].

The requirement of PUF_F has been increasing and the market survey statistics shows that the demand of PUF_F may attain to $ 72.2 billion by 2020. Increase in consumption is a positive note, but on the other hand the negative side is like its inherent quality of flammability. PUF_F burns immediately. The most dangerous thing is that it catches fire to the materials closer to it. This loss of material leads the property damage. At least property damage can be repairable, but if there is human loss due to the fire hazards it is questionable. Stringent monitoring bodies stipulate the regulations concerning these damages.

Open cell structure, large surface area, less density and permeation to air are the main physical conditions of the PUF_F. These characteristics will result in the quick combustion of the material when it is subjected to fire. Flame retardants (FRs) if added in foams will reduce the flammability. The choice of selection of flame retardant (FR) should be in such a way that the property of the finished material should not be affected, generate less smoke and no toxic fume emissions.

The necessity of safety has been pressurized a technology where the study of incorporation of FR in PUF_F has been investigated by many researchers [3-7]. FRs are the one, which will subside the flammability nature of PU foam. The selection of FR plays a vital role. Stringent standards at current situations do not permit the emission of toxic gases.

Researchers conducted investigations in many types of FRs liken boron, halogen, nitrogen phosphorous, sulphur and silicon based etc [8-12]. Of these, halogen free FRs

finds its way a welcoming one when compared to the other FRs. Halogen free nano FRs are the most preferable because over a small % of addition may enhance the FR characteristics of foam and also environmentally benign with zero level toxic gas emission.

Studies have been conducted in improving the properties of PUF_F. Fillers are added in PUF_F to improve or modify its mechanical, thermal stability and flammability characteristics. These fillers lead to the reinforcement of polymer matrix because of adsorption, chemical bonding and mechanical adhesion [13]. Fillers may be of any type like organic and inorganic. Organic fillers used are organically modified montmorillonite (OMMT), natural fibers and carbon black etc. Inorganic fillers are like barium sulfate, calcium carbonates, glass fibers, hydrated alumina, silica, silicate, talc and titanium dioxide etc. Fillers when added may increase the density and decrease the resiliency. It may be available in macro, micro and nano particle size. The sizes of the fillers are really important, when added should easily disperse in the finished product [14]. The influence of fillers depends mostly on the aspect ratio, dispersion and hybrid morphology [15-16]. The addition of filler in any polymeric material may result in the generation of three types of polymer nano composites microstructure based on interactions. There are exfoliated, intercalated and unintercalated composites [17]. Chemical modification of PUF_F was also carried out to enhance the efficiency in specific application of PUF_F [18-19].

PUF_F samples was prepared with different % of NS and the effect of different properties like physical, thermal and flammability was discussed in the present investigation. The test results were compared with the control PUF_F in order to confirm the improvement of different characteristics imparted in the prepared PUF_F with NS.

II. MATERIALS AND METHODS

2.1 Materials
The raw materials used were polyether polyol, isocyanate (toluene diisocyanate). The filler material used was NS.

2.2 Method of Foam Preparation
Using mechanical stirrer, polyol and NS was stirred thoroughly aiming for the complete dispersion of NS. Isocyanate was added to this mixture after stirring, which lead to the formation of PUF_F. The required size of mould was made.

The release agent was applied on the mould before pouring the mixture (polyol, NS and isocyanate) into it. Then the mixture was poured into the mould and was allowed to cure. After 24 h of curing period, the testings were done using the standards. Samples were prepared by changing the composition of NS in polyol.

The percentage of NS varied for the present investigation was 0.5 % (NS_{FRA}), 1 % (NS_{FRB}), 1.25 % (NS_{FRC}), 1.5 % (NS_{FRD}), 1.75 % (NS_{FRE}) and 2% (NS_{FRF}).

2.3 Morphological and Physical Properties
2.3.1 Optical Microscope
Optical microscope was utilized to study the cell structure of the prepared PUF_F. The indigenously developed PUF_F cell structure was measured with 5 X magnification using the optical microscope CARLL ZEISS (AX10 ERC5s), Germany with the help of Axiovision Rel.4.8 software.

2.3.2 Fourier Transform Infrared Spectroscopy
The PUF_F sample was characterized by using JASCO 6300 model (Japan). They were analyzed in the range of 4000-400 cm^{-1}. The samples were conditioned by washing it with distilled water and dried in oven prior to testing. The presence of functional groups was confirmed using this technique.

2.3.3 Rebound Resilience
Rebound resilience of the prepared PUF_F was analyzed by using resilience tester, Blue Steel Engineers Pvt. Ltd., India, according to standard [20]. RR was tested by placing the PUF_F on a flat surface and then a load of known weight and geometry was dropped from a specified height (based on the weight and geometry of the plunger) on the surface of the PUF_F. The plunger rebounds after contact and the distance was noted. This was repeated three times and an average was taken.

2.4. Thermal property-Thermogravimetric Analysis
The thermal stability, physical and chemical changes of the developed PUF_F was analyzed using EXSTAR6000 (TG/DTA), Japan with respect to increase in temperature. A known weight of the sample was taken and heated up to 800 ^oC at a heating rate of 20 ^oC/min in an inert N_2 atmosphere (nitrogen flow rate 140 mL/min).

2.5. Flammability – UL 94 test
UL 94 flammability test is categorized as vertical burning (VB) and horizontal burning (HB) test. VB test is usually carried out for rigid materials such as thermoplastics and thermoset. HB test is meant for flexible materials such as foams and films.

The flammability feature of the developed PUF_F was measured using UL 94 HB test. According to the standard, sample size was used [21]. The UL 94 HB test was performed on a horizontal burner and the blue flame height was maintained between 2 to 2.5 cm.

III. RESULTS AND DISCUSSIONS

3.1 PUF_F Structure-Cell Morphology
The structure, form, dimensions of foam is really important in analyzing its properties. Optical microscopy presents the option of decoding the structure of cellular PUF_F.

The optical micrograph with and without NS is shown in the Figure 3.1.1 to 3.1.4. Cell window, strut and strut joint comprise the foam structure. In all the micrograph, these are found which states that the addition of NS did not collapse the cell structure.

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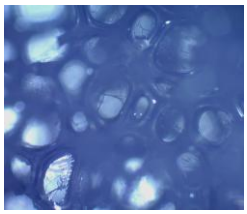

Figure : 3.1.1 PUF_F-Control

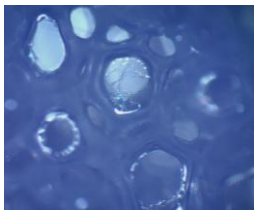

Figure : 3.1.2 PUF_F -NS_{FRA}

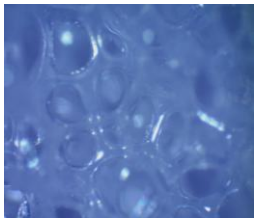

Figure : 3.1.3 PUF_F -NS_{FRD}

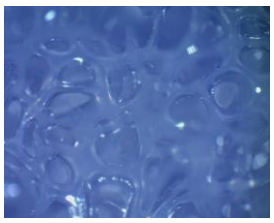

Figure : 3.1.4 PUF_F -NS_{FRE}

There are two types of cell structures namely open cell and closed cell structure. While analysis the open cell structure mainly comes und the category of PUF_F. If only each cell has the presence of two pores, face broken, open cell structure will be obtained [22-23]. These conditions were seemed to be satisfied and this has been shown in the Figure 3.1.1 to 3.1.4.

3. 2 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy is an analytical testing method where chemical compounds present in a material can be easily identified. The FTIR spectrum of the prepared PUF_F samples with different percentage of NS is shown in Figure 3.2.

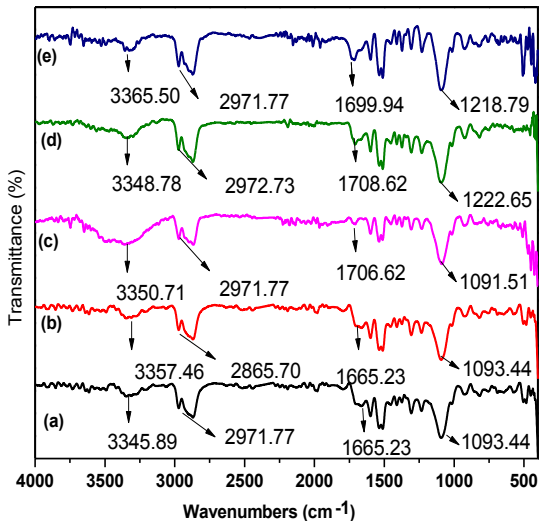

Figure : 3.2 FTIR Spectrum of PUF_F samples
(a) NS_{FRA}, (b) NS_{FRB}, (c) NS_{FRC}, (d) NS_{FRD} and (e) NS_{FRF}

In the present investigation, the effect of addition of NS on the characteristics of the structure has been studied. The spectrum of the PUF_F with NS was found to follow the same bands with respect to control. The peak at 3345.89 cm^{-1}, 3357.46 cm^{-1}, 3350.71 cm^{-1}, 3348.78 cm^{-1} and 3365.50 cm^{-1} are stretching vibrations of N-H band for the PUF_F samples with NS. The bands found at 2971.77 cm^{-1}, 2865.70 cm^{-1}, 2971.77 cm^{-1}, 2972.73 cm^{-1} and 2971.77 cm^{-1} illustrates the presence of -CH stretching vibrations for the PUF_F samples with NS. NS_{FRA} had three vibrations peak of -CH at 2893.66 cm^{-1}, 2959.23 cm^{-1} and 2982.37 cm^{-1}. NCO (isocyanate chemical group) peak of isocyanate lies in the range between 2270-2250 cm^{-1}. The absence of peak near 2250 cm^{-1} specifies short of isocyanate groups. This means that isocyanate has been completely transformed to PUF_F during the experiments of preparation of PUF_F along with the NS [24]. FTIR of NS_{FRD} sample shows presence of carbonyl absorption band at 1708.62 cm^{-1}. C-N stretch was found in all samples (NS_{FRA} to NS_{FRF}) within the range 1250 cm^{-1} to 1020 cm^{-1}.

3.3. UL 94 (HB) rating and Thermal Stability of PUF_F

The flammability of any polymeric material can be assessed by UL 94 rating. This is the Standard for Safety of Flammability of Plastic Materials for Parts in Devices and Appliance testing. The standards are meant for polymeric materials and decode clearly the classification based on the minimum to maximum flammability.

The best conditions for UL 94 (HB) rating have been reported [25]. Best condition with the maximum flame retardancy was found in the sample NS_{FRD}. It was found that 25 s was required to extinguish 28 mm length sample and this was tested according to the standards.

NS addition may enhance the char formation in the prepared PUF_F samples. Similar results have been reported [26]. The heat release rate may be slow down because the char formation controls the combustion gases and arrests the rates (heat and mass) which usually happen between the condensed and gaseous phase.

3.3.1. Thermal Stability-Thermogravimetric analysis

TGA is one of the method in which the change in weight of the material was recorded with the increase in temperature using inert gas medium (N_2).

The weight of the sample may range from 1 mg to 100 mg. Testings were carried out with the small pieces of samples of about 5 mg-7mg.

The onset (procedural) thermal decomposition (TD) of all the samples was found to be approximately 250 ˚C. This is the lowest temperature where the weight of the samples starts to vary. Figure 3.3 shows single stage decomposition thermo gram of PUF_F samples.

Weight loss of 5 % and 50 % was confirmed at the temperature 257 ˚C and 337 ˚C for NS_{FRD} sample, respectively. Weight loss of 50 % was found at 324 ^oC to 337 ˚C for PUF_F samples NS_{FRA} to NS_{FRF}.

The samples with the addition of NS decipher the increase in thermal stability. Maximum 5 % increase in thermal stability was observed for the sample NS_{FRD} at 50 % weight loss.

This confirms the improvement in thermal stability when compared to the control.

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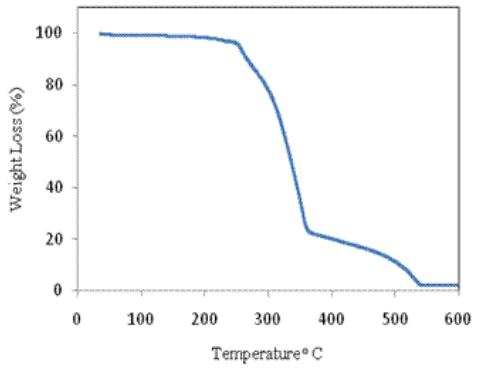

Figure 3.3 : Thermogram of PUF_F - NS_{FRD} sample

The thermal stability could be correlated with the UL 94 rating. The NS_{FRD} samples show the best rating and 50 % weight loss was observed at maximum temperature of 337˚C for the same. The similar results have been reported [25].

3.4 Rebound Resilience

Rebound Resilience which gives an idea about the surface elasticity and this can be related to comfort. With respect to the resilience % the application of foam can be decided. In this present study, resilience values were obtained in the range from 28 % to 35 %. RR effect with different % of NS is shown in Figure 3.4. Significant increase effect was found with the increase in % content of NS. The similar results have been observed [27]. Low resilience value of below 10 % has also been reported [28]. The low RR value is suitable for specific applications which are termed as viscoelastic foams.

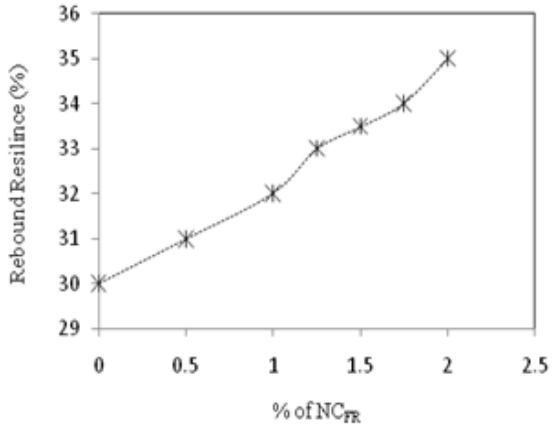

Figure 3.4 : Rebound Resilience (%) of PUF_F – NS_{FR} samples

CONCLUSION

The present study evaluated the impact of NS in PUF_F samples. PUF_F samples were prepared by varying different % of NS. The percentages of NS varied are 0.5 % (NS_{FRA}), 1 % (NS_{FRB}), 1.25 % (NS_{FRC}), 1.5 % (NS_{FRD}), 1.75 % (NS_{FRE}) and 2 % (NS_{FRF}). The samples were subjected to optical microscopy in order to study the structure of the prepared foam. In all the micrograph, it was found that the addition of NS did not collapse the cell structure. FTIR analysis shows that the absence of peak near 2250 cm^{-1} specifies short of isocyanate groups which mean the complete transformation of isocyanate into PUF_F. In flammability test, NS_{FRD} samples shows the best rating with requirement of 25 s to extinguish 28 mm length sample. In thermogram analysis of NS_{FRD} sample, 50% weight loss was observed at the temperature of 337 ˚C. Resilience values were found to be obtained in the range from 28 % to 35 %. The investigation shows the successful improvement of thermal stability and flammability property of developed PUF_F at the laboratory level.

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