Study on Development and Quality Improvement of Flexible Polyurethane Foams by Substitution of Polyol with Zeolite and/or Unrefined Oils

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Abstract— Owing to the increasing demand of production of flexible polyurethane (PU) foam, called industrial sponges, and from economical point of view to minimize the consumption of raw materials of high cost involved in the manufacture of PU foams, the present work was devoted to partially replace some quantity of polyols with unrefined vegetable oils, and to add the natural **microporous**zeolite as a filler to support the compressibility of flexible PU foam products. It can be concluded that the flexible PU foam products can be significantly developed and their quality can also be enhanced by addition of natural zeolite and/or UO which are of low cast as compared to the industrial polyol.

Index Terms— Flexible PU, Zeolite, Unrefined vegetable oil. Polyol.

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1 INTRODUCTION

POLYURETHANES (PUs) are a broad class of functional materials utilized in a wide variety of applications. Products in this family are chemically complex and may contain several different types of bonds, yet all have the PU linkage in common. This linkage is formed from the reaction between the isocyanate functionality like toluene diisocyanate (TDI) of one component with the alcohol group of another component [1].Each application of flexible PU foams has specific performance criteria so there are many components needed in a typical formulation to ensure that the product will be open- celled and still meet other requirements. For example, fillers may be added to enhance strength, or a lower potency surfactant may be used to provide more cell openness [2,3].Polyether polyols for flexible application use low functionality initiators such as di propylene of glycol or glycerin. Propylene oxide is then added to the initiator until the desired molecular weight achieved. Polyols extended with propylene oxide are terminated with secondary hydroxyl groups in order to change the compatibility, rheological properties, and reactivity of a polyol, ethylene oxide is used as a co-reactant to create random or mixed block heteropolymers[4].

Owing to the high cost of some raw materials involved in the manufacture of flexible PU foams, this work was devoted to partially replace some quantity of polyols with unrefined vegetable oils, and to add the natural microporous zeolite as a filler to support the compressibility of flexible PU foam proucts.

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2 MATERIALS & METHODS

2.1 RAW MATERIALS & CHEMICALS

The list of raw materials and chemicals used for production of PU foams are illustrated in Table 1.

TABLE 1

RAW MATERIALS & CHEMICALS USED FOR PRODUCTION OF PU FOAMS.

Raw material / Chemical	Source
Polyol	AbduljalilRadman Company for Industry of Sponge and Plastics, Taiz , Yemen.
Amine catalyst	AbduljalilRadman Company for Industry of Sponge and Plastics, Taiz , Yemen.
Diethyl amine	L0BA cheme. PVT. LTD.
Ethylene glycol	Himedia Laboratories. PVT. LTD.23,Vadhanim ind.ESt.,LBS Marg, Mumbai -400086, India
Silicon surfactant	AbduljalilRadman Company for Industry of Sponge and Plastics, Taiz, Yemen.
Zeolite	Natural
Unrefined vegetable Oil	Local market
Congo red	Our lab.
Methyl blue	Nice Chemicals. PVt. Ltd. B.no.307662.
Sudan dyes	Our lab.
TDI(Toluene diisocyanates)	AbduljalilRadman Company for Industry of Sponge and Plastics, Taiz, Yemen.
Chloroform($CHCl_3$)	SIGMA-Aldrich chemieGMBH,Riedstr 2,D-89555 steinheim,+49-7329-970
Tin dichloride($SnCl_2$)	BDH chemicals LTD., Poole, England

2.2 PREPARATIONS OF PU FOAM SAMPLES

Pure sample of PU foam was prepared by a single- batch process using a cartoon- made box as a batch reactor (BR). Firstly, two main batches; batch (1) and batch (2)were prepared by thoroughly mixing the relevant components as shown in Table 2.

TABLE 2

COMPOSITION OF BATCH (1) AND BATCH (2) FOR PURE PU FOAM FORMULATION.

Batch(1)	w/w%	Batch (2)	w/w%
Polyol	54.61	TDI	35.52
Amine catalyst	0.28	Chloroform($CHCl_3$)	1.45
Diethyl amine	0.84	Tin dichloride($SnCl_2$)	0.11
Ethylene glycol	0.9		
Silicon surfactant	0.83		
Water	5.46		
Zeolite	0		
Dye	0		

Zeolite (Z) and unrefined oil (UO) to be investigated were added into the batch (1) with varying compositions as illustrated in Table 3.

TABLE 3

VARYING COMPOSITIONS OF ZEOLITE (Z) AND UNREFINED OIL (UO)ADDED INTO BATCH (1) FOR MODIFIED PU FOAM FORMULATIONS.

S.No.	Z (w/w %)	UO (w/w %)
1-	2.66	0.0
2-	5.18	0.0
3-	7.57	0.0
4-	9.85	0.0
5-	7.57	2.53
6-	7.57	5.05
7-	7.57	7.54
8-	7.57	10.09

The two homogeneous batches were then thoroughly mixed together in BR using an axial stirrer for about 10 – 15 sec till a foam is grown up. The reaction content was thereafter left for 24 hrs in air for completion of gelation reaction till foam becomes solidified and cold. The final solid foams produced were cut to different pieces of well- known dimensions.

2.3 PHYSICAL CHARACTERIZATION

2.3.1 BULK DENSITY OF PU FOAMS

Bulk densities expressed in kg/m³ of PU forms were obtained by measuring the ratio of the weight to bulk volume for approximately equal foam pieces (13 cm × 6 cm × 4cm).

$$d_{bulk} = \frac{Wt(kg)}{V_f(m^3)} \tag{1}$$

2.3.2 COMPRESSIBILITY OF PU FOAMS

Compressibility of PU foam sample was expressed as the ratio of change in the foam volume (ΔV_f), to the axial dynamic pressure applied (P_{ax}),

$$Compressibility \ (m^3 Pa^{-1}) = \frac{\Delta V_f(m^3)}{P_{ax}(Pa)} \tag{2}$$

Accurately weight metal plate is placed on the surface of a foam piece of known dimensional, so that the place corers the whole surface. A constant mass of a weight ranging from 3 to 5 kg is then placed on the center of plate and the change in the thickness of the foam piece (ΔTh) is measured precisely using the following relation:

$$\Delta V_f(m) = \Delta Th(cm) \times A(cm^2) \times 10^{-6} \tag{3}$$

where A (cm²) is the surface area of a PU foam sample.

$$P_{ax}(Pa) = \frac{Force\ applied}{A(m^2)} = \frac{m_t(hg) \times g(m\ s^{-2})}{A(cm^2) \times 10^{-4}} \tag{4}$$

where m_t is the total mass applied (i.e., the weight of constant mass and metal plate applied), and g is the gravitational acceleration in m/s².

2.3.3 WATER ABSORPTION CAPACITY (WAC) OF PU FOAMS

WAC was expressed as the ratio of the volume of water absorbed by a foam sample, V_w (ml) to that of the bulk foam piece, V_f(cm³):

$$WAC = \frac{V_w(ml)}{V_f(cm^3)} \tag{5}$$

A definite volume foam piece is completely immersed into a sufficient quantity of tap water for 15-20 min. Thereafter, it was transferred so rapidly into a funnel on the top of a clean graduated cylinder for measuring the entire volume of water removed from the foam piece by squeezing hardly till no residual water remains.

2.3.4 OPTICAL MICROSCOPIC (OM) IMAGING

OM images of foam surfaces were taken using an optical microscope (Model:6331 nauborn-wetzlar) equipped with a 10 X-magnification object lens.

3 RESULTS & DISCUSSION

3.1 EFFECTS OF ADDITION OF ZEOLITE ON THE PHYSICAL PROPERTIES OF PU FOAM PRODUCTS

The variation of bulk densities for prepared PU foams with varying compositions of zeolite are shown in Figure 1,and also listed in Table 4. The highest d_{bulk} values (28.53 kg/m³) is observed for PU foam with a zeolite content of Z= 9.85 w/w % .

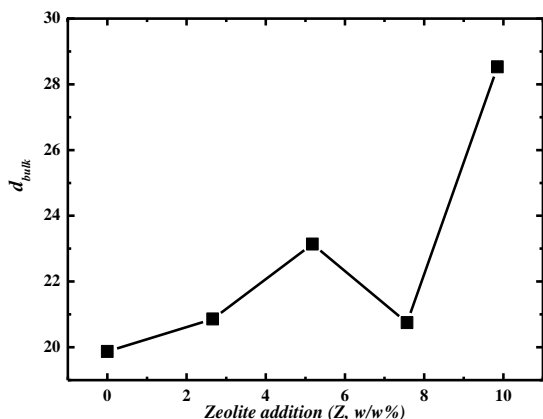However, a local minimum value of d_{bulk} is observed with Z = 7.57 w/w %.

Figure 1. Effect of zeolite addition on bulk densities of PU foam products.

Compressibility measurement was also carried out to investigate the effect of addition of zeolite on the persistence of PU foams to elastic – plastic deformation. The lower the degree of compressibility of PU foams, the higher will be the persistence to the deformation[5]. The variation of the degree of compressibility with addition of zeolite is shown in Figure 2 under applied force of 29.9 N. The compressibility is sharply increased with increased zeolite content up to Z = 2.66 w/w% and is thereafter slightly decreased by further addition till Z = 7.57 w/w%. Behind this point of zeolite addition, it remarkably drops down to 1.50 m³ Pa⁻¹ (Table 4).
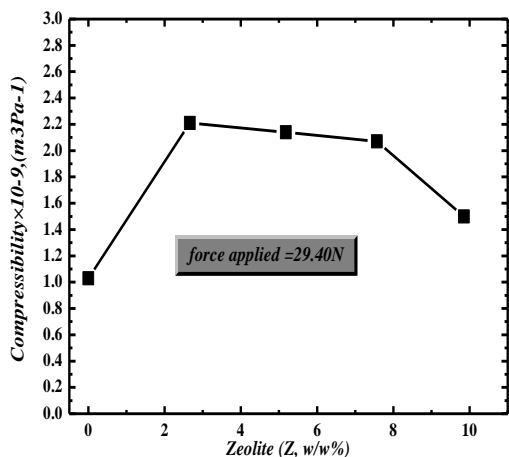

Figure 2. Effect of zeolite addition on the compressibility of PU foam products.

TABLE 4
THE VARIATION OF BULK DENSITY, COMPRESSIBILITY, WAC OF PU FOAMS WITH ADDITION OF ZEOLITE.

Z (w/w %)	Bulk density d_{bulk} (kgm⁻³)	Compressibility (×10⁻⁹ m³ Pa⁻¹)	WAC
0	19.87	1.03	0.308
2.66	20.86	2.21	0.185
5.18	23.140	2.14	0.212
7.57	20.75	2.07	0.308
9.85	28.53	1.50	0.189

Water absorption capacity (WAC) measurement can also be employed as and indicative assessment for a relative quality of PU foam products. The higher the value of WAC ofa PU foam, the greater will be the expected number of air bubbles incorporated into a bulk block of PU foams during a manufacturing process[6,7].

The variation of WAC of as-synthesized PU foams as a function of zeolite content is listed in Table 4 and is also presented in Figure 3. WAC first decreases as zeolite content increases up to Z= 2.66 w/w% and it then show maximum (0.185) with the addition content (Z=7.57 w/w%). However, the maximum value of WAC of PU foam sample with the formulation Z=7.57 w/w% may be attributed to absorption of some quantity of water in to the crystal structure of zeolite. While the decrease of WAC beyond this point of zeolite addition may be due to the increase in cell openings.
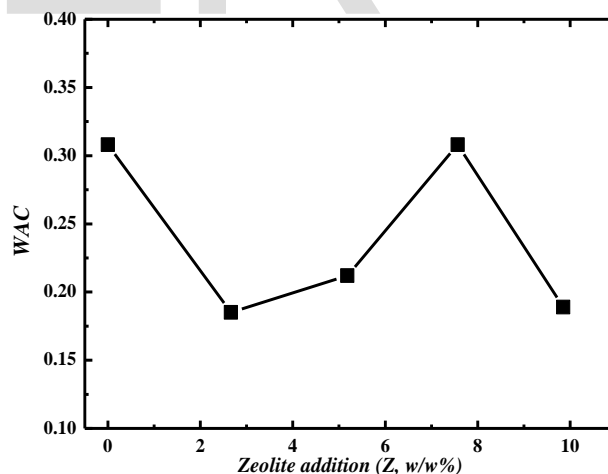

Figure 3. Effect of zeolite addition on WAC of PU foam products.

The optical microscopic (OM) images can also be used as a tool for a comparative investigation of relative Structural morphologies of PUfoam products. Figures 4(a-d) exhibit OM images of PU foam surfaces with varying zeolite content at the same object lenses magnification of (10X). The cell openings for PU foam free from zeolite (Figure 4(a)) seem to be uniform

and of approximately equal sizes. The increased darkness of cell edges observe with increasing zeolite contents is indicative of incorporation of zeolite molecular structure within PU polymeric network. Moreover, in all OM images of zeolite based PU foam products except for Z= 7.57 w/w% Figure 4(c), no zeolite aggregations can be distinguished within cell openings.

3.2 EFFECTS OF ADDITION OF BOTH ZEOLITE AND UNREFINED OIL ON PHYSICAL PROPERTIES OF PU FOAM PRODUCTS

The investigation of changes in the bulk density of PU foams with the variation of unrefined oil content was performed for foam formulation, where local minimum d_{bulk} value is obtained, i.e., the zeolite content form all formulations was fixed at Z=7.57 w/w % in order to explore whether the bulk density

This can also be clearly seen in variation of d_{bulk} with UO content (Figure 5).

TABLE 5
THE VARIATION OF BULK DENSITY, COMPRESSIBILITY, WAC OF PU FOAMS WITH ADDITION OF UNREFINED OIL (UO) IN THE PRESENCE OF ZEOLITE WITH Z = 7.57 W/W%.

UO (w/w %)	Bulk density d_{bulk} (kg/m³)	Compressibility (×10⁻⁹ m³ Pa⁻¹)	WAC
0	19.87	2.07	0.308
2.53	20.86	11.90	0.285
5.05	23.140	8.07	0.265
7.54	20.75	8.39	0.477
10.09	28.53	3.90	0.343

Figure 5. Effect of unrefined oil addition on bulk densities of PU foam products at fixed zeolite (Z = 7.57w/w %).

Influence of partial substitution of unrefined oil for polyol in the PU production (Z=7.57 w/w %) on the degree of compressibility at 29.40 N is illustrated in Figure 6, and Table 5. It is interesting to note that a maximum compressibility of PU foam (11.90 × 10⁻⁹ m³ Pa⁻¹) is observed at initial addition of unrefined oil (i.e., UO = 2.53 w/w%). Thereafter, the compressibility levels out over UO range of 5.05 to 7.54 w/w %. It is then reduced with increasing UO content. The variation of compressibility with addition of unrefined oil is in a good agreement with the change of corresponding bulk density of PU foam. This suggests that the quality of PU foams with Z = 7.57 w/w% can also be enhanced by further addition of unrefined oil in composition range from 5.05 to 10.09 w/w% UO. The effects of vegetable oils on the improvement of PU foam quality have been investigated elsewhere earlier [11-13].
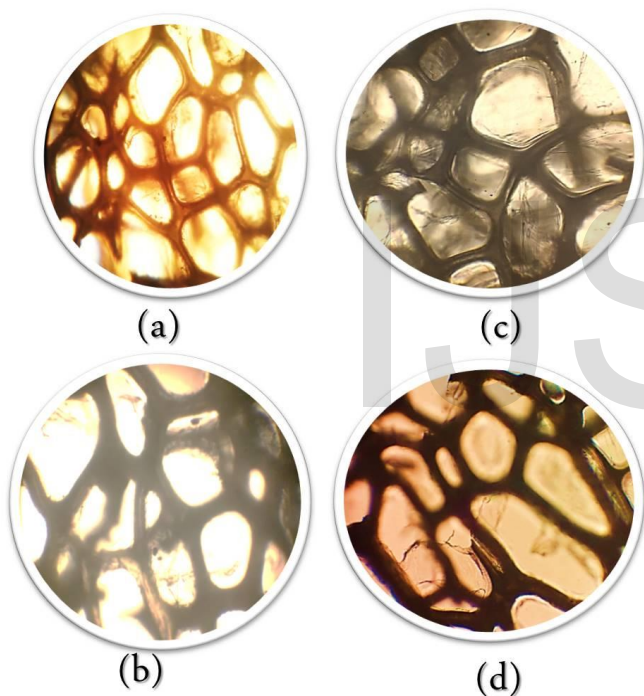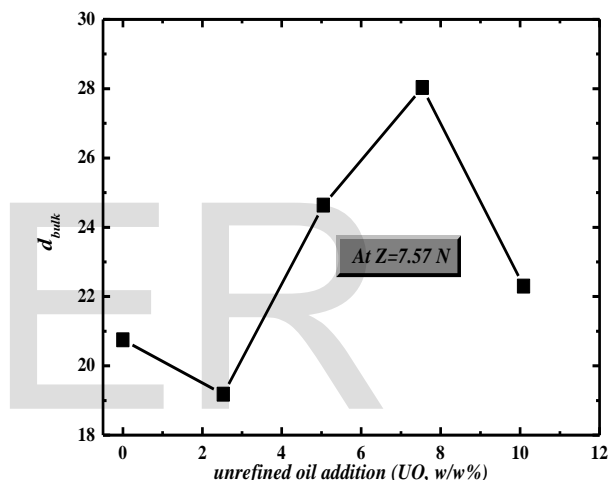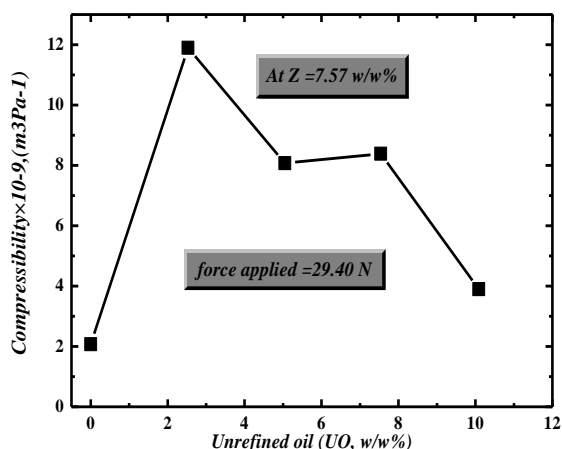
Figure 4. OM images of PU foam surfaces: (a) Z= 0 w/w% &UO = 0 w/w%; (b) Z= 5.18 w/w% & UO= 0 w/w%; (c) Z= 7.57 w/w% & UO= 0 w/w%; (e) Z= 9.85 w/w% & UO= 0 w/w%.

of PU foam products is further enhanced by the addition of UO or not. Another aim of this selection of constant zeolite — limit formulation is to predict any interaction between UO and zeolite that may positively contribute to the enhancement of PU foam products. Table 5 summarizes the values of d bulk varying with UO content ranging from 0 w/w% to 10.09 w/w%. Except for 2.53 w/w% UO, a general increase of bulk density measured is observed over whole UO addition range.

Figure 6. Effect of unrefined oil addition on compressibility of PU foam products at fixed zeolite (Z = 7.57 w/w%).

Effect of unrefined oil addition on WAC can be seen in Table 5 and Figure 7. Here WAC profile shows similar behavior as that with the effect of zeolite addition (Figure 3) with a slight difference. The similarity between dependences of WAC on zeolite.
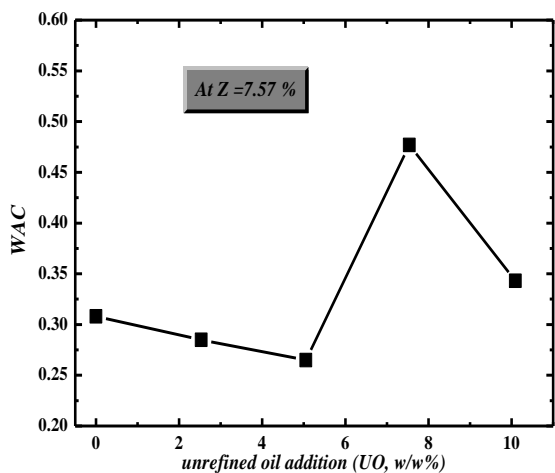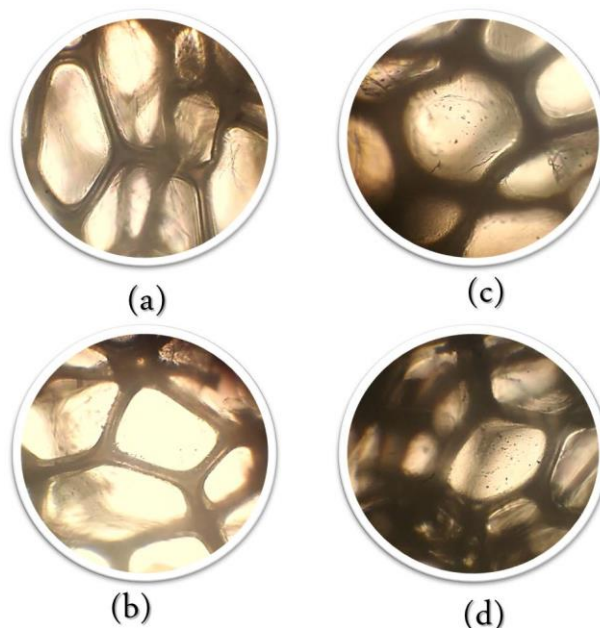

Figure 8. OM images of PU foam surfaces: (a) Z= 7.57 w/w% & UO= 2.53 w/w%;(b) Z= 7.57 w/w% & UO= 5.05 w/w%; (c) Z= 7.57 w/w% & UO= 7.54 w/w%; (d) Z= 7.57 w/w% & UO= 10.09 w/w%.

and UO is clearly exhibited by minima and maxima of WAC at lower and higher addition regions, but the difference is in the values of addition at which these minima and maxima are located. However, the maximum value of WAC with UO addition (7.54 w/w % UO, WAC = 0.477) may be attributed to the interaction between the zeolite particles and unrefined oil molecules that negatively contribute to the building up more bubbles throughout the foam products which cause a collapse of foam conformation [14,15]. This is well agreed with results obtained from bulk density and compressibility measurements.

The variation in the cell opening morphology of PU foam surface as a function of UO content at fixed zeolite formulation (Z= 5.57 w/w%) can be shown in Figure 8(a) to (c).The interesting point to be emphasized here is that the uniformity of cell openings and relative opening size for nearly all PU foam produced by the practically substitution of polyol by UO are relatively better than that for only zeolite based foams.

4 CONCLUSION

Nowdays increasing attention in industrial field is paid to producing flexible and/or hard polyurethane foams from renewable resources. In this research work an attempt was made

Figure 7. Effect of unrefined oil addition on WAC of PU foam products at fixed zeolite (Z = 7.57 w/w%).

for development and improvement of flexible polyurethane foam products by the partial substitution of zeolite and unrefined vegetable oil for polyol in the foam formulation. It's interesting to state here that the work presented in this research is a novel investigation made by our research group as a contribution to industrial fields concerned with the production of PU foam products.

PU foams were prepared by a single batch process technique with varying the zeolite content (i.e., up to 9.85w/w %) as well as varying the unrefined oil content (i.e., up to 10.09w/w %) at a constant zeolite percent (Z=7.57w/w %).

The influence of addition of zeolite and unrefined oil on the quality of PU foam products were conducted by means of physical techniques; bulk density, compressibility, absorption capacity and optical microscopic imaging .

The addition of only zeolite showed a general increase of bulk density except for Z=7.57w/w %. This point of zeolite addition was considered to be a new starting formulation of PU foams for which the effect of UO is to be investigated. It has been found that the bulk density of this foam sample is further enhanced by the addition of UO partially substituted for the polyol in the starting formulation .The results of compressibility measureed at 29.40 and 49 N are well agreed with those obtained from the bulk density measurements. Regardless of forced applied, the quality of PU foams is expectedly enhanced by the addition of only zeolite at Z ≥ 5.18 w/w % and the addition of UO at a constant zeolite content at UO ≥ 5.05 w/w %.

WAC measurement of both only zeolite and combined zeolite and UO typically showed similar variation which might resulted from the incorruption of water molecules into the crystal structure of zeolite bound to a polymeric PU foam.

Optical microscopic (OM) images gave appreciable view about the morphology of foam cell opening that also evidenced the other physical measurement. Finally, it can be concluded that the flexible PU foam products can be significantly developed and their quality can also be enhanced by addition of zeolite and/or UO which are of low cast as compared to the polyol. This is our recommendation to the national companies concerned with industries of sponges (fixable PU foams). While our recommendation to researchers who are interested in the subject of industrial chemistry of PU foams and to us in the future as well is to make possible attempts for developing new replacements for TDI in manufacture of PU foam products.

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