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ORIGINAL ARTICLE

# Application of sulfonamide derivative of calixarene for improvement of mechanical properties and thermal stability of polyurethane composite

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**Abstract** A calixarene derivative, 5,11,17,23-tetrakis (hydroxyl ethyl sulfonamide) calix[4]arene, was synthesized through a linear reaction from parent calix[4]arene. This sulfonamide calixarene derivative was used as a precursor to produce calixarene-polyurethane composite. Structural properties of calixarene-based synthesized precursors were studied using spectroscopic techniques such as $^{1}$H-NMR, $^{13}$C-NMR, and IR. Also, mechanical properties of produced polyurethane composite such as fracture elongation, modulus, and tensile strength were studied which indicated that these properties were deeply dependent upon calixarene ratio in composite. An increase in calixarene ratio resulted in a decrease the fracture elongation. In contrast, an increase in calixarene ratio caused a considerable decrease of modulus and tensile strength. The modulus and tensile strength were increased by 16.98 and 20 % as the calixarene/polyol ratio reached 3 %. Finally, TGA and DSC studies showed that calixarene ratio considerably enhanced the thermal stability of polyurethane.

**Keywords** Calixarene derivatives · Calixarene-polyurethane composite · Mechanical properties · Tensile strength · Modulus

## Introduction

Calixarenes are cyclic oligomers made up of phenol units. It has been established that the phenolic hydroxy groups appended on the lower rim form strong intermolecular hydrogen bonds, serving as the main driving force for the stabilization of the 'cone' conformation [1–4]. They are a class of host compounds that combine a polar and an apolar molecular region, both capable of interacting with a variety of guest molecules [4–7]. The synthesis and purification of functionalized calixarenes have been optimized very successfully, which makes them a very promising class of synthetic host molecules, particularly when selective chemical transformations convert the parent compound into highly organized host molecules, e.g., calixcrowns, calix-spherands etc. Such functionalized calixarenes form complexes with metal cations, substituted ammonium ions, and even neutral molecules like acetone, toluene, etc. [4–7]. Addition of calixarene to some polymers like polyurethane can result in many significant structural changes which consequently reflect the mechanical properties.

The synthesis of calixarene derivatives and using them as a precursor to react with polyurethane in order to form calixarene-polyurethane composite and their application in ionic complexes and biomolecules have been widely investigated [7–9].

The calixarene linked to polymer substrates has spawned a considerable interest as a promising composite in calixarene chemistry [10–14]. The calix[4]arene variability of ion selectivity and ability to substitute with different molecules are due to their special structure including holes with definite size. Additionally, they are often used as host molecule to trap ions and molecules [14–21].

In this work, a sulfonamide derivative of calixarene containing hydroxyl groups on upper rim position was

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synthesized and used as a precursor to produce calixarene-polyurethane composite.

The structure and configuration of composite reflect a variety of parameters such as thermal stability, phase behavior, and also mechanical properties including modulus, tensile strength, and fracture elongation. Therefore, the effect of calixarene and its ratio, especially because of its crosslinking role, on composite configuration is the main aim of this study.

## Experimental

### Materials

All the reagents were of analytical grade and used without further purification. Para-tert-butyl Phenol was purchased from the Acros Company. Formaldehyde, sodium hydroxide, chlorosulfonic acid, monoethanol amine, sodium metal, and benzophenone were purchased from the Merck Company. Diphenyl-methane di-isocyanate (MDI) (purity: 99.9 %) was purchased from the Huntsman company.

### Measurements

$^1$H-NMR 500 MHz and $^{13}$C-NMR 125 MHz Bruker AM model were used for NMR spectroscopic analyses. FT-IR Bruker tensor27 and Perkinelmer was used for IR spectroscopy. Mechanical properties measurements were performed using HP testing machine (Inspekt 100, Hegewald & Peschke, Germany). All mechanical properties measurements were performed in triplicates and the average value and their standard deviations were reported. The RSD % ranges of measurements were reported 7.2–7.32, 4.6–14.01, and 6.94–10.49 for modulus, tensile strength, and fracture elongation, respectively.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were performed using NETZSCH DSC 200F3 model TGA-DSC simultaneous thermal analyzer, with a nitrogen flow rate of 30 mL min$^{-1}$ at heating scan rate of 5 °C min—$^{1}$ to consider the phase behavior and thermal stability of calixarene-polyurethane composite. In DSC, 10 mg of sample was placed into aluminum pans (dimensions: 8 mm diameter, 0.5 mm thick) and placed into a differential scanning calorimeter along with an empty reference pan. Also, the TGA was performed in a similar way with heating rate of 10 °C min$^{-1}$ from 200 to 600 °C.

### Synthesis of calix[4]arene derivatives

The synthesis procedure of calix[4]arene derivatives and spectral evidences of produced structures are discussed in following sections.

#### *5, 11, 17, 23-Tetra tertio butyl calix[4]arene*

The structure of 5,11,17,23-tetra tertio butyl calix[4]arene derivative is shown in Fig. 1. The synthesis procedure was as follows: Stoichiometric value, 100 g, of granulated *p*-tert-butylphenol was pulverized and poured into a 3-necked round bottom flask equipped with a mechanical agitator, reflux, and a thermometer. In another pot, 33.3 g of sodium hydroxide was dissolved into 100 mL formaldehyde (37 %) and added into mentioned round bottom flask and was stirred for 40 min in room temperature. The reaction pot was heated in a paraffin bath up to 130 °C for 2 h until the solution color changed from light yellow to dark yellow. A foamy substance was obtained as the reaction system was cooled to room temperature. Then, 1000 mL of diphenyl ether was added into mentioned flask and the temperature was increased up to 120 °C. Nitrogen gas was purged into the flask while one of necks was kept open to exit vapor for 2–3 h. As the solution color was changed from yellow to gray and the water evaporation was stopped, the open neck was closed and the flask reactants were refluxed at 250 °C for 4 h. The contents color was changed into brown and black. The system reached room temperature after 4 h and 1.5 L ethyl acetate was added and stirred for 30 min. After 2 days, white crystals were obtained and the precipitates were filtered. The produced crystals were washed with ethyl acetate, glacial acetic acid, distilled water, and acetone to obtain pure calix[4]arene crystals. Yield 58 %; mp > 340 °C; $^1$HNMR: (500 MHz, $CDCl_{3,}$ TMS), δ (ppm), 1.2 (36H, s, $(CH_3)_3C$) 3.5, 4.2 (8H, d, $ArCH_2Ar$), 7.0 (8H, s, ArH), 10.3 (4H, s, OH);$^{13}$C-NMR: (125 MHz, $CDCl_3$), δ (ppm), 30.5 ($ArCH_2Ar$), 32.4 $(CH_3)_3C$), 34 $(CH_3)_3C$), 126.1 (Ar), 128.2 ($ArCH_2Ar$), 144.5 ($ArC(CH_3)_3$), 146.8 (ArOH); IR (KBr): 3200 cm$^{-1}$.

#### *5, 11, 17, 23-Tetrakis (chlorosulfonyl) calix[4]arene*

The structure of 5,11,17,23-tetrakis (chlorosulfonyl) calix[4]arene derivative is shown in Fig. 2. The synthesis procedure was as follows: All experimental facilities were dried using Bunsen burner to remove humidity. A nitrogen flow was passed through the system for 5 min. In a 3-necked 500 mL balloon equipped with a reflux condenser and nitrogen purging system, 4 g of crystallite calix[4]arene synthesized in previous step was added to 160 mL of dry

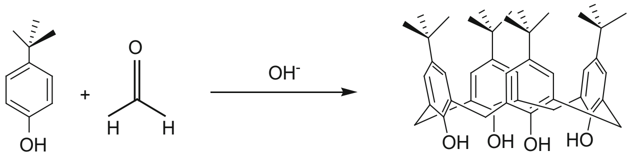


**Fig. 1** Synthesis of 5, 11, 17, 23-tetra tertio butyl calix[4]arene

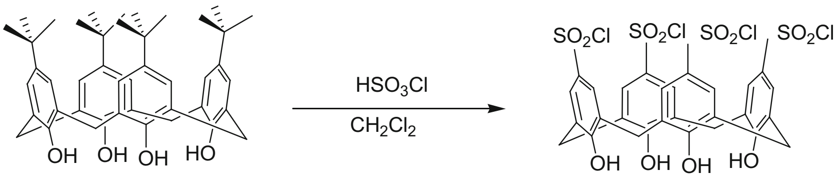


**Fig. 2** Synthesis of 5, 11, 17, 23-tetrakis (chlorosulfonyl) calix[4]arene

dichloromethane and then stirred for 20 min to obtain a homogeneous suspension. After the system cooled to −10 °C, 40 mL of chlorosulfonic acid was dropped into solution through a funnel for 2 h. The system was purged again with nitrogen before heating and was refluxed for 20 min.

Since the precipitation process was exothermic, the reaction balloon was placed into an ice bucket to keep the room temperature condition. Then, 700 mL ether was added to mixture during an hour and slowly stirred to change the solution color from brown to pale yellow consisting the suspended white precipitates. After a day, fine precipitates were separated by sintered glass and dried with diethyl ether. Yield 93 %; mp >250 °C; $^1$HNMR; (500 MHz, DMSO-d$_6$, TMS), δ (ppm), 3.94 (8H, s, ArCH$_2$Ar), 7.39 (8H, s, ArH), 8.87 (4H,s, OH); $^{13}$C-NMR (125 MHz, DMSO-d$_6$), δ (ppm), 30.4 (ArCH$_2$Ar), 126.4 (ArH), 127.3 (ArCH$_2$Ar), 138 (Ar-SO$_2$), 151.4 (ArOH); IR (KBr): 1163, 1356 cm$^{-1}$.

### *5, 11, 17, 23-Tetrakis (hydroxyl ethyl sulfonamide) calix[4]arene*

The structure of 5,11,17,23-tetrakis(hydroxyl ethyle sulfonamide) calix[4]arene derivative is shown in Fig. 3. The synthesis procedure was as follows: All reaction steps were carried out in completely dry medium. Nitrogen gas was passed through the system for 5 min. In a double necked balloon (balloon A), 4 g of calixarene was added to 50 mL of dry THF while a nitrogen flow was passed through one of the bottle necks. The whole system was kept in ice medium. In balloon B, 0.29 mL mono ethanol amine was added to 50 mL dry THF under the nitrogen flow. Both A and B balloons were kept in ice medium for a better dissolution of contents. Then, the content of balloon A was added gradually into balloon B and was stirred for 30 min. About 20 mL of HCl 0.1 M was added to system to obtain a pale yellow precipitation which washed then with methanol after filtration using a Buchner funnel. Yield 25 %; mp = 251 °C;$^1$H-NMR (500 MHz, DMSO, TMS), δ (ppm), 2.80 (8H, s, ArCH$_2$Ar), 3.06 (8H, t, CH$_2$N), 3.22 (4H, s, R-OH), 3.39 (8H, t, CH$_2$O), 7.04 (4H, s, OH), 7.54 (8H, s, ArH), 8.87 (4H, s, NH); $^{13}$C-NMR (125 MHz, DMS), δ (ppm), 37.9 (ArCH$_2$Ar), 46.1 (CH$_2$N), 60.4 (CH$_2$O), 127.4 (ArH), 130.2 (ArH), 158.4 (ArSO$_2$), 159 (ArOH), IR: (KBr): 1144, 1331, 2900–3500 cm$^{-1}$.

### *Synthesis of calixarene-polyurethane composite*

The synthesized calixarene was kept in oven at 80 °C for an hour in order to evaporate water or any residual solvents. As the dried samples were pulverized using a mortar, stoichiometric values of calixarene weighed and added to 10 g polyol. The prepared mixture was stirred and agitated using an agitator and ultrasonic bath to obtain a homogeneous mixture. Then, 12 g diisocyanate was added to above mixture and stirred till the cream time reached. The same procedure was used to produce composites with different calixarenes/polyol ratios (0.5, 1, 1.5, 2, 2.5, and 3) in similar conditions at room temperature. The ratio of diisocyanate/polyol was 10:12 for all composites. Also, pure polyurethane foam was produced to compare with calixarene containing polyurethane composites. The structure of obtained composite and reaction scheme are shown in Fig. 4.

## Results and discussion

The spectroscopic studies including $^1$H-NMR, $^{13}$C-NMR, and IR were performed to confirm the structural details of 5,11,17,23-tetrakis (hydroxyl ethyl sulfonamide) calix[4]arene.

### $^1$H-NMR spectrum of 5, 11, 17, 23-tetrakis (hydroxyl ethyl sulfonamide) calix[4]arene

$^1$H-NMR of mentioned product, in DMSO-d$_6$ solvent, is shown in Fig. 5. Since the NMR solvent medium is a polar solvent, the bridge singlet hydrogens can be attributed to fast conversion of conformations in room temperature which is not detectable by the method. Both hydrogens were detected in 2.80 ppm. The phenolic aromatic proton was appeared in singlet at 7.54 ppm. Also, 4 hydroxyl protons of aromatic rings and NH sulfonamide protons were appeared in 7.04 and 8.87 ppm, respectively. The NH sulfonamide are unshielded since they are acidic and delocalized on nitrogen atom. 8 NCH$_2$ and CH$_2$ protons were appeared in 3.06 and 3.22 ppm, respectively. Finally, 4 hydroxyl aliphatic protons were seen at 3.22 ppm.

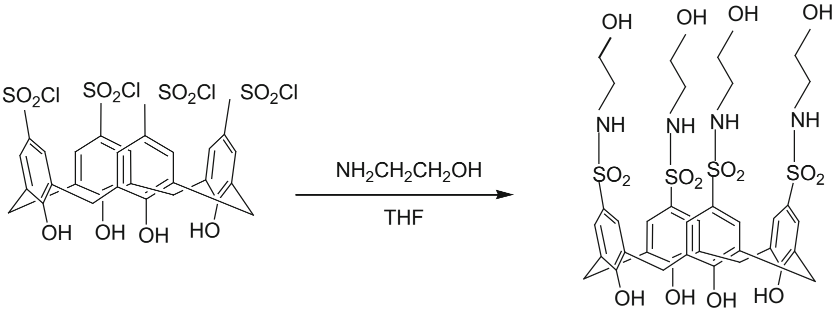


**Fig. 3** Synthesis of 5, 11, 17, 23-tetrakis (hydroxyl ethyl sulfonamide) calix[4]arene

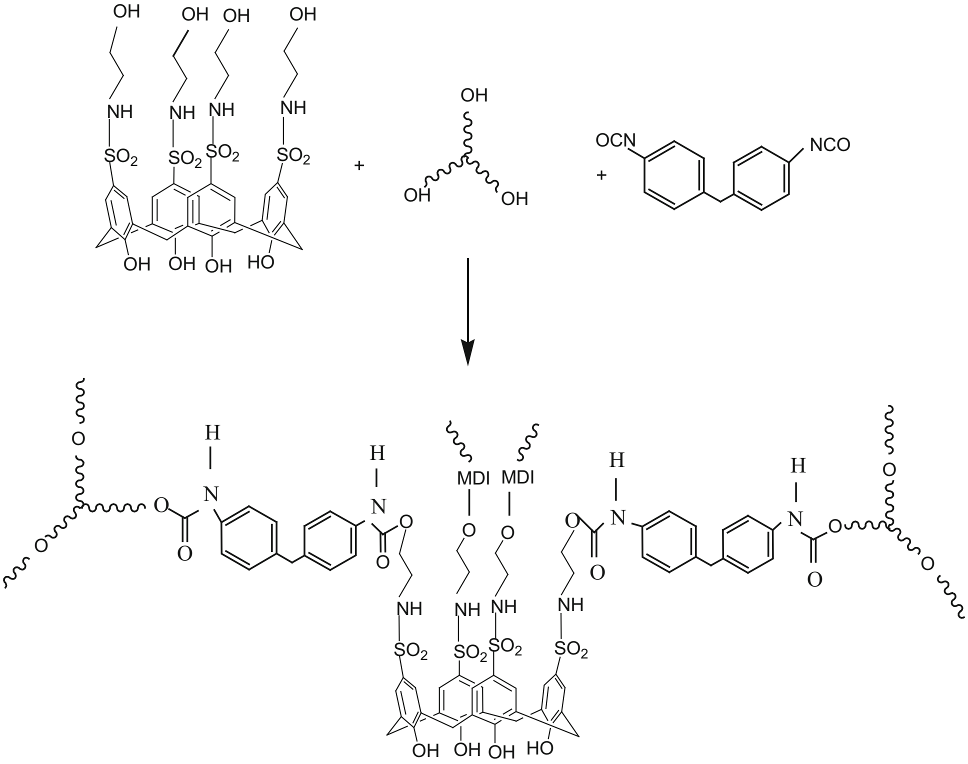


**Fig. 4** Synthesis of calixarene-polyurethane composite

## $^{13}$C-NMR spectrum of 5, 11, 17, 23-tetrakis (hydroxyl ethyl sulfonamide) calix[4]arene

$^{13}$C-NMR spectrum of this calixarene in the same medium (DMSO-$d_6$ δc 40.0 ppm) is shown in Fig. 6. The mentioned spectrum shows 8 carbon types. The aliphatic bridge methylenes, O-linked aliphatic carbons, and N-linked aliphatic carbons were appeared in 37.93, 60.44, and 46.13 ppm, respectively. Also, 4 aromatic carbons were detected in lower fields since they are linked to hydrogen.

## IR spectrum of 5, 11, 17, 23-tetrakis (hydroxyl ethyl sulfonamide) calix[4]arene

The IR spectrum is shown in Fig. 7. A wide peak in 2900–3500 $cm^{-1}$ is attributed to phenol and also NH groups. Two strong peaks of sulfonamide were detected in 1144 and 1331 $cm^{-1}$ which are associated with $–SO_2–NH–$. The mentioned IR evidences verify the functional groups of this calixarene derivative and the substitution of chlorine by $–NH(CH_2)_2OH$ according to reaction scheme depicted in Fig. 3.

## Mechanical properties of composite

The hard foam of polyurethane is formed of an exothermic reaction between diisocyanate, polyol, and calixarene derivatives releasing carbon dioxide. Calixarene was used as cross linking agent since it has 4 hydroxyl groups in upper rim position. When calixarene was used as cross linking agent in polyurethane chains, the resulted composites showed better mechanical properties including modulus, tensile strength, and fracture elongation.

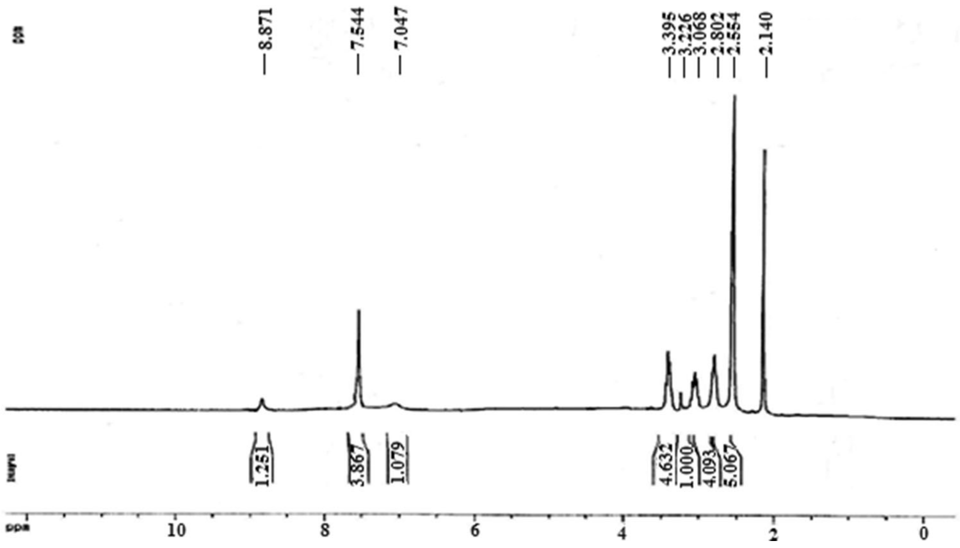


**Fig. 5** $^{1}$H-NMR spectrum of 5, 11, 17, 23-tetrakis (hydroxyl ethyl sulfonamide) calix[4]arene

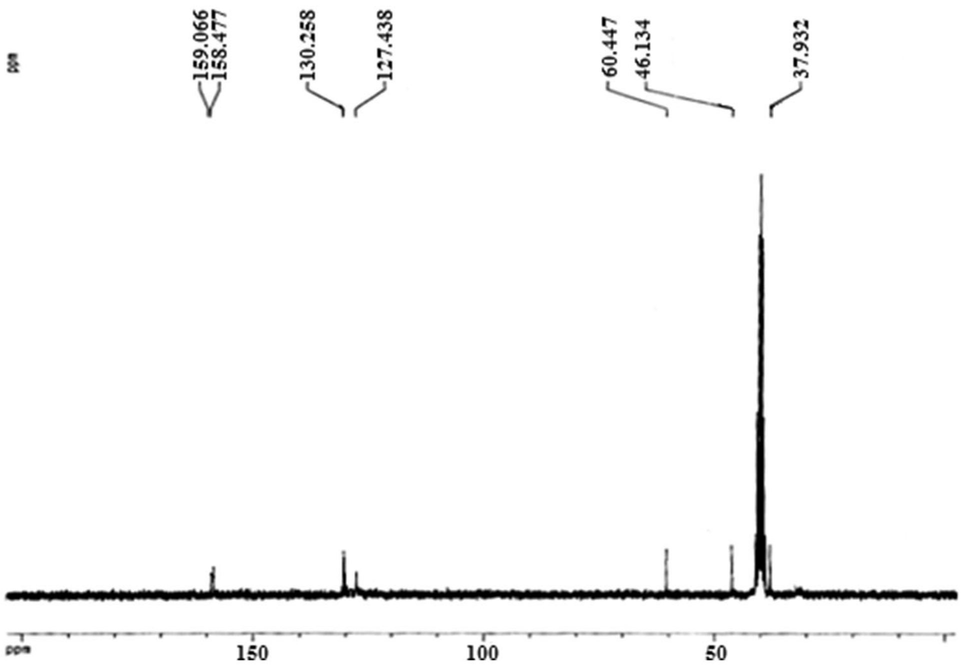


**Fig. 6** $^{13}$C-NMR spectrum of 5, 11, 17, 23-tetrakis (hydroxyl ethyl sulfonamide) calix[4]arene

Tensile strength is defined as the threshold resistance against stretching or maximum stress that a material can endure while being stretched or pulled before failing or breaking.

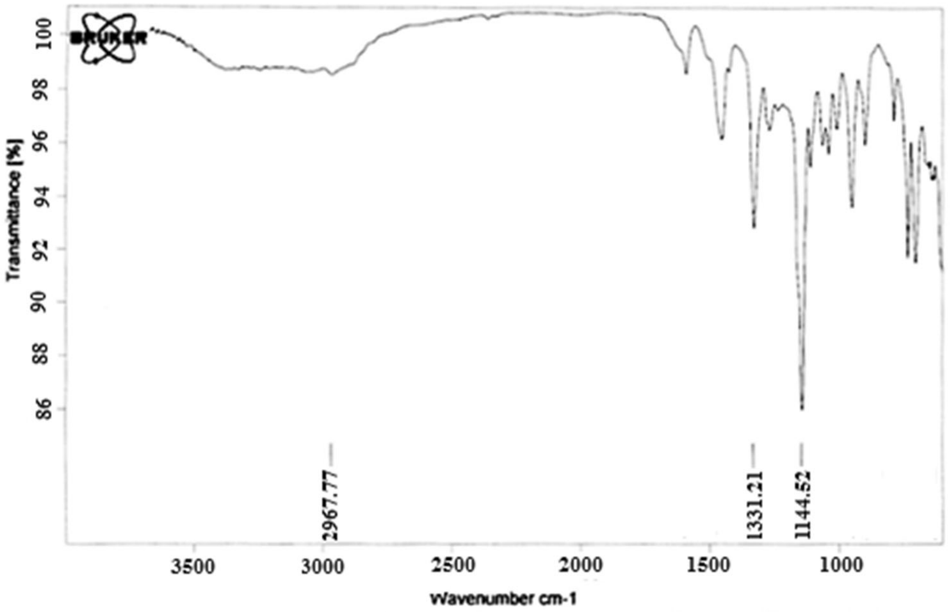
Since the aromatic parts of calixarene often increase the tensile strength, it's expected that calixarene having phenolic and aromatic parts increases the tensile strength which is in agreement with the findings observed in present work according to Fig. 8. As can be seen, the tensile strength of polyurethane composite was increased as the calixarene ratio increased.

The elasticity or modulus is defined as the stress/strain ratio. As can be seen, an increase in calixarene ratio resulted in modulus increase. The calixarenes interact with polyurethane chains through many active sites. For example, sulfonamide derivative of calixarene acts through 4 hydroxyl sites as shown in Fig. 3. According to Fig. 9 diagram, the modulus was increased by 16.98 % as the calixarene ratio increased from 0 to about 3 % (w/w).

According to obtained data, the modulus of polyurethane composites is deeply dependent upon the calixarene ratio which indicated that the calixarene presence results in higher hardness of the polyurethane foam product.

Finally, the fracture elongation or fracture strain was studied as an index of elastic property of the polymer. In

**Fig. 7** FT-IR spectrum of 5, 11, 17, 23-tetrakis (hydroxyl ethyl sulfonamide) calix[4]arene



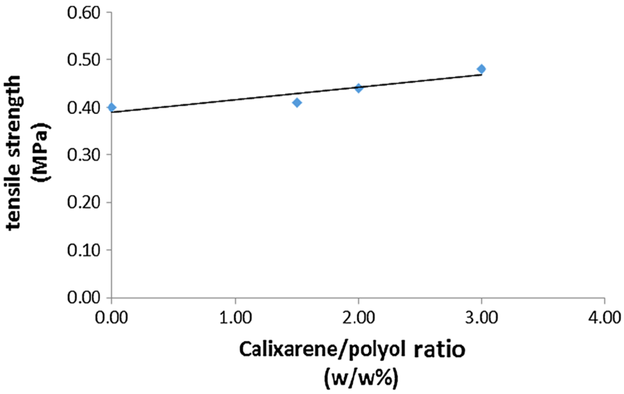


**Fig. 8** Tensile strength of calixarene-polyurethane composite versus calixarene/polyol ratio

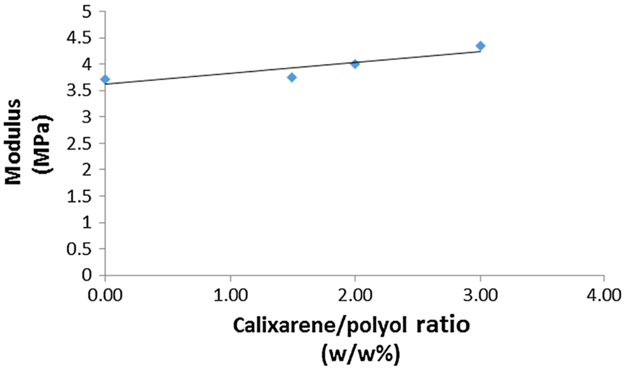


**Fig. 9** Modulus of calixarene-polyurethane composite versus the calixarene/polyol ratio

contrast to two afore-mentioned mechanical parameters, the fracture elongation was decreased as the calixarene ratio increased according to Fig. 10.

As can be seen, the fracture strain was not significantly changed in calixarene ratio lower than 1.5 %(w/w) while it was noticeably dramatically decreased in higher ratios of calixarene in such a way that it was decreased by 12.52 % as the calixarene increased from 1.5 to 3 %(w/w).The nature of fracture elongation differs from that of two other mechanical properties since the cross linking of calixarene and hard parts of diisocianate form a hard lattice and prevent the composite structure to have a considerable elongation. The overall mechanical properties results are summarized in Table 1.

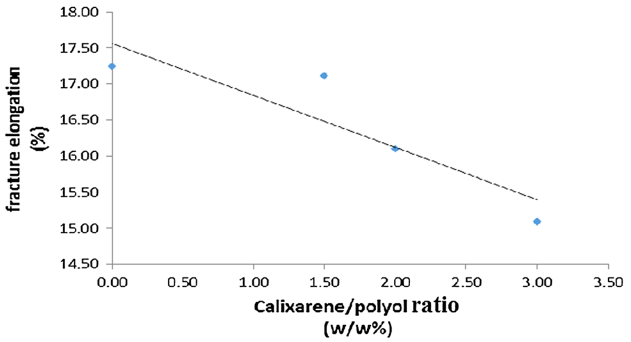


**Fig. 10** Fracture elongation of calixarene-polyurethane composite versus calixarene/polyol ratio

**Table 1** Average mechanical properties of polyurethane and calixarene-polyurethane composite containing different ratios of calixarene

| Calixarene/polyol percentage (w/w%) | Modulus (MPa) | Tensile strength (MPa) | Fracture elongation (%) |
|---|---|---|---|
| 0 | 3.71 | 0.40 | 17.25 |
| 1.5 | 3.75 | 0.41 | 17.12 |
| 2 | 4.01 | 0.44 | 16.10 |
| 3 | 4.34 | 0.48 | 15.09 |

The calixarene-polyurethane composite is crystalized when it is stretched meaning that the amorphous parts are crystalized as a results of stretching due to H and O atoms in urethane which allows the formation of hydrogen bonds in polymer chain preventing the motion of polyurethane chains and remaining in the lattice. The crystallization resulted from stretching can be observed on the tensometery and the polymer gets white because of stretching. Stretching and releasing polyurethane may result in reorientation of molecules in primary structure. In this work, calixarenes were used as cross linking agents. Using tetraols in polymer structure, the polymer became harder and its modulus was increased while its fracture elongation decreased. The hard parts may have the crystalline state playing the role of physical bonds in polymer. Strength and resistance against tension are often increased when the hard parts are longer, symmetric, and proportionate which are the main cause of attractive intermolecular forces. Since the aromatic parts increase the tensile strength and decrease the stress, calixarene presence results in an increase in modulus.

FT-IR spectra of the synthesized calixarene-polyurethane composite is shown in Fig. 11. As can be seen, the broad band observed at 2800–3215 $\mathrm{cm}^{-1}$ is attributed to the presence of a –NH and –OH stretching vibration. The absorption peak around 1720 $\mathrm{cm}^{-1}$ corresponds to –NHC=OO in the ester while the peak around 1525–1595 $\mathrm{cm}^{-1}$ is attributed to –N–H bending.

## Thermal stability of composite

The thermal stability of composite was analyzed using TGA and DSC techniques according to Figs. 12 and 13. The polyurethane is usually stable up to 215 °C [22]. However, the produced composite in this work showed thermal stability up to 300 °C due to the presence of calix[4]arene. The cross linking role of calixarene enhances the hardness of composite resulting in a higher thermal stability. Also, addition of a hard segment like diisocyanate often increases the hardness of product. Strictly speaking, both hard segments of diisocyanate and soft segments of polyol increase the hardness and consequently enhance the thermal stability because of hardness and cross linking role, respectively. According to Fig. 12, the system undergoes a significant degradation of higher rate compared to the composite degradation as the temperature exceeds 360 °C which is mainly attributed to the degradation of calixarene derivative component.

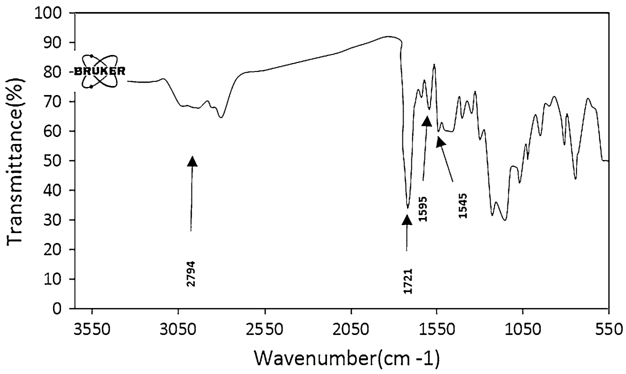


**Fig. 11** FT-IR spectra of calixarene-polyurethane composite

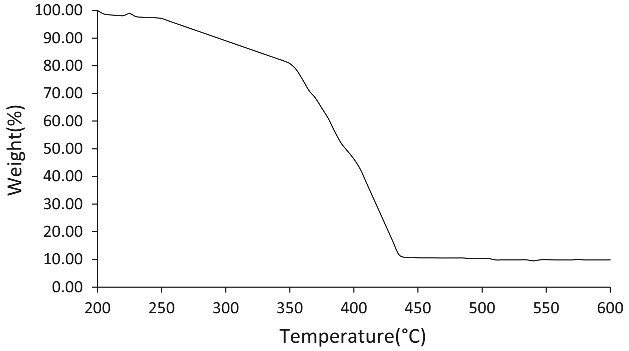


**Fig. 12** TGA diagram of calixarene-polyurethane composite at the temperature range 200–600 °C with heating rate of 10 °C $\mathrm{min}^{-1}$

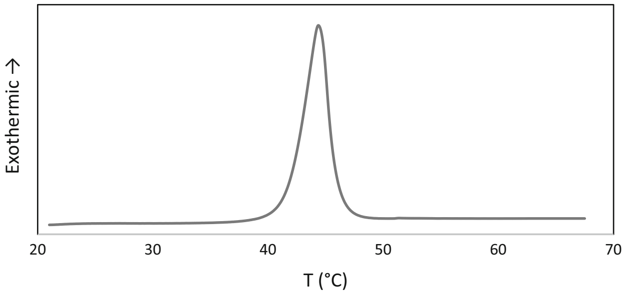


**Fig. 13** DSC heating thermograms of calixarene-polyurethane composite at the 5 °C $\mathrm{min}^{-1}$ scan rate

Additionally, the phase behavior of calixarene-polyurethane composite was investigated using the DSC technique. As can be seen in Fig. 13, the DSC thermogram shows an exothermic peak in temperature range 40–50 °C which is associated with a phase transition while no phase transition was observed in higher temperatures indicating the thermal stability of existing phase. It's noteworthy that the type of phases was not clearly analyzed and only the phase transition was considered in this work.

## Conclusion

Calixarene derivatives were used to form a composite with polyurethane in order to improve the mechanical properties of obtained products such as modulus, tensile strength, and fracture elongation. Straightforward procedures were applied to produce derivatives and the structure of products were verified using IR, $^1$HNMR, and $^{13}$CNMR spectroscopy. The measurements of mechanical properties showed that the modulus and tensile strength were increased by 16.98 and 20 %, respectively, as the calixarene ratio increased from 0 to 3 % (w/w) which was attributed to the cross linking role of calixarene. Contrarily, the fracture elongation parameter was decreased by 12.52 % as the calixarene ratio increased from 0 to 3 % (w/w). Finally, the TGA and DSC studies indicated that the calixarene considerably enhances the thermal stability of polyurethane which was attributed to cross linking role of hydroxyl groups of calixarene and also the hard segments of diisocyanate.

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