Chapter 6
Shape Memory Phenolic Foams

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1 Introduction

The modernization of the world seeks attention to develop smart polymeric material with tailor-made properties with high-end applications. In consonance with this shape memory foam (SMF) gains a special place in the territory of new material development and technology related to it. Shape memory foam is a unique material that can be responding to external stimuli, such as heat, light, magnetic field, solvent, water, etc., and regains its shape when the external stimuli are removed. Foam composition and morphology together with polymer processing are the main causes of the shape memory effect. As far as the polymeric foam is concerned, transition temperature plays an important role in the shape memory effect along with polymeric configurations. Below a glass transition temperature (Tg) polymer exhibits a glassy state which can be considered as an elastic state. Above Tg, polymers show a rubbery state which is deformable. The shape recovery process happens in order, fabrication consists of material of choice for shape memory effect, heating the material above Tg to deform the material into a new configuration, cooling the material below Tg to maintain the constrain, and finally removal of it.

Phenolic resins are used worldwide. Resol is the most abundant phenol–formaldehyde resin used for foam formation. The unequivocal properties of phenolic foam demand exploitation in some highly special applications like the manufacturing of space shuttles. Despite the way that both phenolic resin and the phenolic foam itself have long accounts, more up-to-date applications have gone through a moderate turn of events. They are known for their high thermal stability, thermal insulation, fire resistance with no dripping behavior, and less toxic gas production while combustion. But they show pulverization tendency and are physically brittle. These obstacles can be hurdled by either changing the base components for foam formulation or by

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reinforcing the polymeric foam with the material for tailor-made properties. Other than constantly improving the exhibition of the current materials, the advancement of new materials should suit the necessities of genuine applications to accomplish maintainability over the long haul. Stimuli-responsive foams materials have a high potential for applications in an insignificantly obtrusive medical procedure. Degradable inserts could be embedded into the human body in a compacted shape through a little cut where they acquire their shape important for the particular application in the wake of warming up to internal heat level. After a characterized timeframe the foam is degraded. In this case ensuing medical procedures to eliminate the foam isn't important. For applications in biomedicine, it is important to have customized shape memory polymers whose warm, mechanical, or debasement properties can be changed over a wide go. These are groups of polymers in which naturally visible properties can be constrained by a specific variety of sub-atomic boundaries.

2   Need and Purpose of Shape Memory Phenolic Foam

Shape memory phenolic foam shows a concatenation of switch properties. These kinds of systems improved the performance of foam material along with various property enhancements. These SMFs allow the integration of the properties of foam with stimuli responses. They have potentially changed their shape according to the way of stimuli implemented and thus impart multiple properties in the primary structure of the foam. They have the potential to impart any features such as magnetic, thermal, mechanical stress, and response to that material. The development of such switchable material enables us to prepare utterly new SMF materials that have better properties than that of conventional SMF materials.

3   Properties of Shape Memory Phenolic Foam (SMPF) and Approaches to Enhance Shape Memory Effect

The SMPF material governs shape change properties against a stimuli response. Generally, this behavior can be measured by proving heat as a stimulus, then the material is subjected to compression to form a mechanically compact shape. Again the material is heated to gain its original form followed by cooling. The SMPF material exhibits a combination of explained properties with lower flexural and compressive strength which makes this material more friable than others. The mechanical-based properties included the observance of high strength values in diverse temperature and environmental conditions. Also, it is well-known for its excellent fire-retardant properties. Their unique chemical structure offers excellent fire-retardant behavior. Once exposed to a flame, these resins release very low amounts of smoke and toxic

fumes and are well-known for their natural tendency to form a porous carbonaceous substance that provides a barrier effect. Another category of properties defines the inherent strength properties of the material with its excellent thermal stability. This class comprises those materials which have excellent thermal stability and low thermal conductivity. Low densities make it possible to manufacture light structures with rigid components. Low thermal conductivity ensures reliable and economical insulations. Low rigidity makes foams attractive for energy-absorbing applications.

3.1   Mechanical Properties

SMPF shows low values for compression and flexural modulus which increases the breakdown tendency of material under a smaller value of the load. As a consequence, many researchers have reported their work based on the improvement of these properties with an increase in compression value and flexural modulus which ultimately decreases the friability of material [1]. The two approaches that are widely used in the polymeric sectors worldwide to improve the performance of polymeric material in the specific application are as follows:

- Chemical modification in phenol–formaldehyde resin;
- Addition of filler (fibers, a particle with specific geometry as a reinforcement).

As a rigid foam SMPF is anxious by the variation in compressive stress vs strain according to the density of the material. It is worth perceiving the fact that the compressive strength and Young's modulus increase with an increase in the density of the material. Regarding chemical modification, the foams are generally cured at 80 °C. There are exemptions for those that are cured at 70 °C and utilized an acid for curing. It is impossible to establish the stoichiometric relation between the OH functions of the phenolic resin and the reactive functions of the modifier because the amount of OH function is not quantified. Nevertheless, the modifier content is usually between 0 and 10 wt.%. Moreover, the filler parameters such as size, shape, geometry, surface energy, and loading percentage could change the final properties of SMPF.

3.2   Influence of Cell Size

The microstructure is often a reason for the better mechanical properties of foam material. The origin of this dependence may come from the cell density, a different distribution of the cell size, the solid fraction content, or heterogeneity across the structure. One approach for mechanical improvement includes keeping all parameters constant and produce smaller cell size foam. Moreover, various studies report the mechanical properties as a function of cell size. By changing the thickness of the polycaprolactam-based foam, the diverse size of the cell has been accomplished in

the scope of 80–170 μm. An increase in the cell wall thickness and cell wall density increases the compressive modulus of the foam [2]. A 0.5–4.2 mm thick open cell with constant density crosslinked glassy carbon foam showed the independency of cell size on Young's modulus, but it is inversely proportional to flexural and compressive strength. This happens due to the decrease in the strut strength which increases the cell size [3]. The impact of cell size on the semi-static pressure mechanical conduct and the deformation behavior of plastic shut cell aluminum foams have been inspected. The result on the compressive property is surprising. Young's modulus increases with cell size. However, the cell wall thickness increases with cell size [4]. The brittle Mg alloy foam of fixed density and uniform structure has been subjected to compression property evaluation. This foam shows better deformation stability when being tested. Also, the load has been shared with the neighboring cell structure as the cell size decreased. Strain densification remains as it is [5]. A closed-cell styrene-acrylonitrile foam of density 0.15 lb/ft^3 showed the affection of cell size enhancement, which ultimately reduces the compressive strength and Young's modulus. It has occurred that there is no relation between moduli and relative density [6]. A linear and nonlinear compression behavior of polystyrene foam with different cell sizes has been investigated. Above 18% solid fraction, the compressive strength and Young's modulus increase with cell size.

Fillers as a reinforcement play a major role in the structural designing of cells in phenolic foams. The solubility of fillers determines the properties of the final foam product. As long as the system is homogenous, numerous and regular size cells are produced. They followed three mechanisms.

- Fillers act as a nucleating agent during foam formation.
- They increase the system viscosity that limits the growth and coalescence of cells.
- They act as a stabilizer during the mixing step and before the foaming stage.

All the above mechanisms combinedly promote the formation of a small size uniform cell structure. Reinforcement can be added in the form of fiber, particle, nanoparticle, hollow glass beads, and core–shell particles.

Concerning particles, mean cell diameter decreases with an increase in particle size due to a reduction in the surface area which ultimately results in higher compressive strength. A multiwalled carbon nanotube and graphene-reinforced phenolic foam have been investigated for their controlled morphology. It was found that the curing reaction happens at low temperature as early as reinforcement act as a catalyst. The density and porosity of reinforced foam were lower than standard phenolic foam due to high cell density. Compressive strength has increased from 71 to 157% [7].

Graphene-oxide-reinforced phenolic foam shows an increase in impact toughness with an increase in graphene oxide content. It showed a drastic increase in impact toughness after 0.5% addition of reinforcement [8]. Titanium nitride (TiN) nanoparticle-reinforced phenolic foams have shown an enhancement in compressive strength and tensile strength. At the point when the dose of TiN nanoparticle was 1%, compressive and tensile strength showed a 10% increment as compared to virgin phenolic foam [9]. Glass-bead-reinforced phenolic foam composite was evaluated

for its mechanical properties. Results showed that a 10% addition of reinforcement gives higher compressive strength over nonreinforced phenolic foam [9].

Cellulose fiber-reinforced phenolic foam was fabricated and tested for its compressive strength. Results showed that there was a 13% decrease in cell size when a 2% addition of reinforcement is done. Also, reinforced phenolic foam showed the increment in compression modulus and strength by 21% and 18% at 2 wt.% loadings of cellulose fiber [10].

The activated carbon-reinforced microcellular phenolic foam was established and tested for its mechanical properties. It was found that the cell size and thickness decrease with an increase in activated charcoal content. The average compressive strength was found to be increased by 9% with only 1% addition [11]. Cloisite clay nanoparticle-infused phenolic foam was developed. The mean cell size was decreased to 50 µm when 2% of Cloisite clay was added. The reinforcement showed a 160% increase in compressive strength and 182% in compression modulus [12]. Lignin particle and wood floor-reinforced phenolic foam have been produced. At 8.5% expansion, the mean cell size was diminished by around 31%. Then again, a 1.5% expansion of the wood floor diminished the cell size less significantly just by 9% to 81 µm [13].

Another approach to enhance mechanical properties is the chemical modification of phenolic resin. Many polymeric species were found to be incorporated in phenolic resin to modify its compression and flexural strength with a decrease in friability. Most often, polyurethanes and polyethylene glycols (PEGs) have been utilized. The fusion of 3–7% castor-based polyurethane prepolymer in phenolic resin brought about an expansion in cell size by 18–59% [14]. PEG modified with boric acid to form a PEG borate was used as a toughening agent in phenolic foam. The mean cell size was decreased by 56%, 17%, and 17% on the addition of 4.5% of boron-modified PEG 200, 400, and 600 [15].

Regarding SMPF many approaches could be compared to enhance its mechanical properties. Various techniques that improve mechanical execution by modifying cell size are as per the following:

1. Surface stabilization of phenolic resin during mixing step through the surfactants adsorbs at phenolic–droplet resin interface and reduce coalescence of droplets.
2. Filler with surface modification may act as a stabilizer in emulsion by the Pickering phenomenon.
3. Utilization of a high boiling point foaming agent increases the cell diameter.
4. Process parameters such as time and speed of mixing influence the size and number of cells.

3.3 Compressive Strength

Compressive strength is the limit of a material or structure to withstand loads tending to decrease the size, rather than which withstands loads tending to extend. Ultimately, compressive quality restricts a material from being pushed together. It is one of

the prominent properties in the application of shock absorption. The compressive strength of foam relies on the foam density as well as the toughness of the cell wall. There are three main categories to improve the compressive strength of phenolic foam by modifying the density.

1. Fiber reinforcement;
2. Addition of inert particle;
3. Chemical modification of the phenolic resin.

The first challenge to improve the compressive strength is the uniform dispersion of reinforcement in the phenolic resin matrix during foam production. The addition of reinforcement increases the density of the foam. As the external phase is included, it expands the thickness of the phenolic pitch and brings about issues during the foaming process. The enhancement in compressive strength by fiber reinforcement is based on the properties of fiber, such as stiffness, loading percentage, orientation in foam, and compatibility with phenolic resin. Fiber stiffness plays an important role in foam reinforcement. The compressive strength of phenolic foam was increased by 275% after adding 5% of glass fiber and by 36% after the addition of the same amount of aramid fiber [16]. Fiber orientation in the direction of foaming significantly enhances the compressive strength due to the isotropic nature of the foam.

Another significant factor of support liable for compressive property upgrades is the similarity between the phenolic resin and fortified strands. Alkali-treated aramid fiber increases the polar function of the surface and interacts more vigorously with phenolic resin. This improved the interfacial adhesion between the fiber and phenolic resin matrix. After the addition of 6 wt.% in phenolic resin, the compressive strength was increased by 67% as compared with unmodified fibers [17]. Besides this, an appropriate amount of fiber reinforcement into the phenolic resin needs to be promised for better mechanical properties. The addition of 2 wt.% of cellulose fibers in phenolic foam increases the compressive strength by 18%, while at 8 wt.% the loading is reduced by 19%. Bamboo strands of various lengths (<1 mm, 1–3 mm) have been fused into the phenolic foam to improve their mechanical properties. The strands with 1–3 mm length at 2.5 wt.% upgrade the compressive quality from 0.103 MPa to 0.130 MPa by 26.21% [18]. Among fibers, glass fibers are the best material to enhance the compressive property of foam due to inherent stiffness [10].

Numerous types of nano/micro/macroparticles are also used as reinforcement to improve the mechanical properties of phenolic foams. Particle reinforcement is based on the same mechanism as for fibers, i.e., their stiffness, loading percentage, and orientation in foam. While foam formation particle also acts as a nucleating agent by providing a heterogenous surface for growth which increases foam density, clay as reinforcement has gained so much attention related to the enhancement in mechanical properties. A 17% increase in compressive strength after the addition of attapulgite modified with hexadecyl trimethyl ammonium bromide (HTAB-ATP) has been reported [19]. Fortification of 0.8 wt.% of expandable graphene oxide with silica nanosphere has indicated the improvement in compressive quality by 70–80%[20]. Another fruitful endeavor has been made by the utilization of zirconium phosphate-graphene oxide hybrid to improve compressive quality. Results indicated
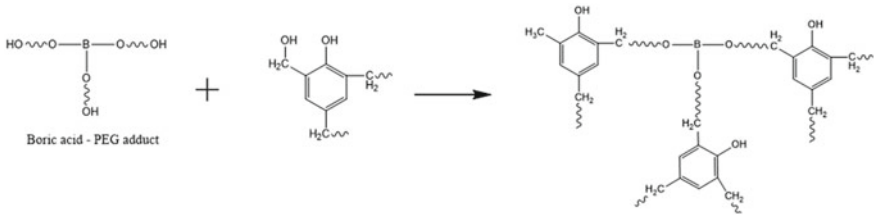
Fig. 1 The reaction of PEG–boric acid while curing of phenolic foam [15]

that compressive strength has been increased by 38% when the blended hybrid was used [21].

Chemical modification has been gaining attention since long back. It is typically based on the introduction of a flexible chain segment in the rigid phenolic backbone which decreases the crosslinking density of the phenolic foam and yield high strength. Mostly polyurethane, PEG urethane ether, dicyanamide, and epoxy long-chain components are used to modify phenolic resin.

A reaction of modified boric acid and PEG was performed to obtain a moiety with three functionalities which later crosslinked with methylol groups of phenolic resin, as shown in Fig. 1. Virgin PEG and boric acid-modified PEG were added in phenolic resin at a measure of 4 wt.%. Compared to pure PF foam, the compression strength of PEG400-toughened PF foam increases by 30.0%, whereas the compression strength of boric acid-modified PEG toughened foam increases by 80%, respectively. In both cases, compressive strength was found to increase, whereas in PEG-modified boric acid efficiency of improvement is higher. The reason for this is an increase in flexible chain length to a certain extent decreases crosslinking density, and the material can achieve high strength [15].

A new approach to introduce phosphorus and nitrogen-containing polyurethane backbone in phenolic resin has been studied as shown in Fig. 2. A 3% addition of polyurethane block improves the compression strength by 19%, whereas the advantage of polyurethane in phenolic resin lies in the chain length of the polyurethane segment [22].

A novel phosphorous and silicon base polyurethane prepolymer was used in phenolic resin to enhance compressive strength, as shown in Fig. 3. At 3% loading, the compressive strength was increased by 136%. It was also noticed that the density of the prepolymer-modified phenolic foam is higher than the unmodified phenolic foam [23].

Another endeavor has been to use dicyanamide to adjust the phenolic foam properties. The adjustment improves the compressive quality by 180% with the expansion of 8% dicyanamide to the phenolic resin [24].

An epoxy-modified phenol–formaldehyde resin is shown in Fig. 4. An improvement in the compressive strength of phenol–formaldehyde resin from 0.57 MPa to 108.20 MPa corresponds to the increase in the foam density. It is surprising that the increase in compressive strength is around 19,000%. Hence the results seem to be incongruous [25].
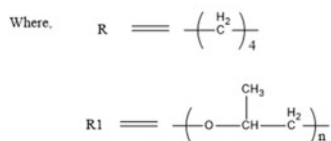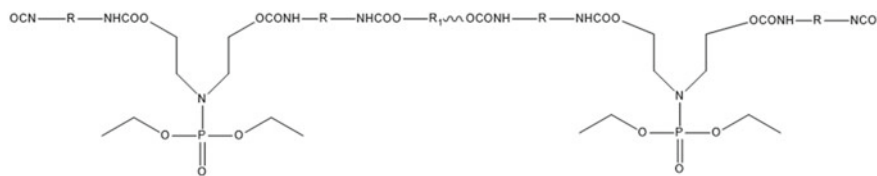
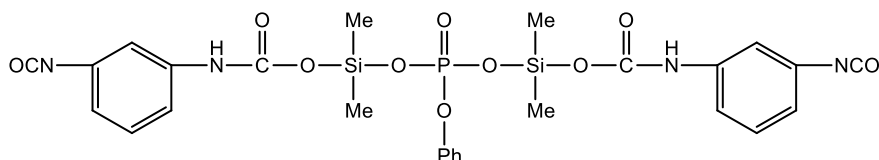Fig. 2 Phosphorous and nitrogen-containing polyurethane segment [22]

Fig. 3 Phosphorous and silicon-based polyurethane prepolymer [23]
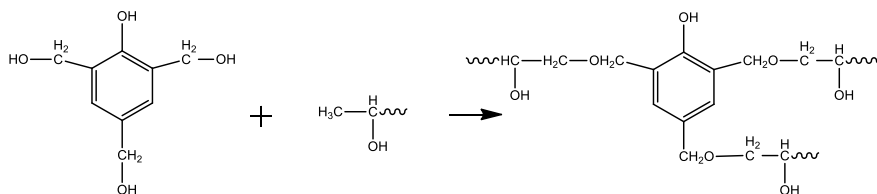

Fig. 4 Epoxy-modified resol resin synthesis process [25]

A phosphorus-containing tung oil-based siloxane-hardened phenolic foam has been set up to improve its mechanical properties. It was discovered that the compressive quality of the bio-based phenolic foam has expanded from 0.20 MPa to 0.31 MPa by 79.6% where the density of the material is unaffected [26]. As of late, another detailing has been created by utilizing kraft lignin as a greener feedstock for bio-based phenol–formaldehyde sap for foam creation. At 20% phenol replacement proportion, the compressive quality was discovered to be 1.012 MPa [27]. A novel solid acid catalytic phenolation measure has been embraced for hydrolysis of lignin, and thus the modified lignin has been utilized in lightweight phenolic foam fabrication. The compressive strength was found to decrease from 0.37 MPa to 0.27 MPa at 50% phenol substitution [28].

Among the entirety of the above which drew closer examination, fiber fortification gives the best improvement in compressive quality because of the characteristic properties like fiber solidness and direction propensity toward foaming. Also, it hampers the isotopic nature of the foam. Enhancement can be increased further by modifying the fiber surface to get better fiber–resin compatibility. Like fiber, particle–resin interaction also can play an important role in the enhancement of compressive strength. A bonding between the particle and the resin allows decreasing the density of the foam and also allows the dissipation of stress-generated dusting compression of foam. The chemical modification allows covalent bonding between added species and the phenolic resin. The chain length and flexibility of the chain contribute to increase in the ability of the foam to be compact.

3.4   Flexural Strength

The resistance to flexion or bending is called the flexural strength of the material. It represents the stress-bearing capacity of the material before yields in the flexion test. Flexural strength is mainly improved by using particles. It is based on the stiffness of the filler, their aspect ratio (Area/thickness), covalent bonding with a phenolic resin matrix, and the uniformity in structure. Flexural strength can be improved by using poly (butyl acrylate)-silica core–shell particle incorporation in phenolic resin, as shown in Fig. 5. It was found that 35% of flexural strength was increased due to the covalent bond formation between the hydroxymethyl group of phenolic resin and the silanol group of particles [29]. Likewise, the function of delicate particles is more mind-boggling brought by altering the foam lattice structure and improves cell size consistently.

The use of clay instead of pentane as a blowing agent was found to increase flexural strength. A 6 phr of clay into foam was found to increase the flexural strength by 61%.

The pathways for improvement in flexural strength are similar to those which are explained in compressive strength. Moreover, the interaction between the particle and phenolic resin interaction is the defining factor to improve flexural strength.
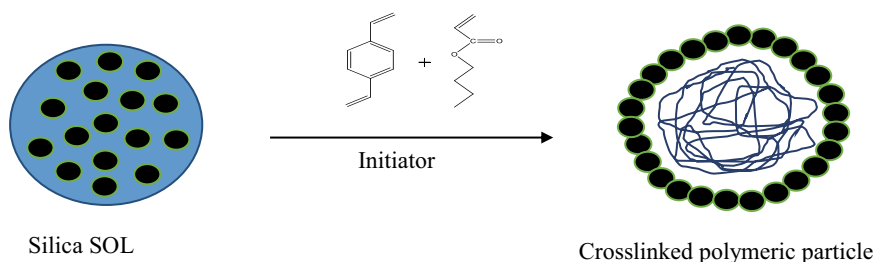

Silica SOL   Crosslinked polymeric particle

Fig. 5 Synthesis of poly (butyl acrylate)-silica core–shell particle by emulsion polymerization [29]

4   Fire-Resistant (FR) Properties

Phenolic foams are well known for their FR properties, such as low smoke density, low flammability, and lesser generation of toxic gases during the burning process. They are considered an excellent nondripping material. These properties of phenolic foams are governed by a structural component such as a benzene ring. It is well known that the molecular structure containing benzene ring and halogen atom shows superior fire resistance behavior over the others. The foam density plays a major role in flame resistance. Increasing the density may increase the number of closed cells which modify the surface in contact with flame. This results in a decrease in oxygen ratio for combustion and ultimately reduces the flammability of phenolic foam. Fire behavior can be described by three parameters, ignition source, a contributor to flame spread, and heat release. Two main tests are used to evaluate the flame-retardant behavior of foam material.

1.   Limiting oxygen index (LOI);
2.   Cone calorimeter test.

Limiting oxygen index is defined as the minimum concentration of oxygen in the mixture of oxygen and nitrogen that supports the ignition of the material. Hence a higher value of LOI denotes higher flame retardancy. Phenolic foam shows excellent flame retardancy with LOI ranging from 27 to 58%. It is very challenging to improve the initial value without hampering the mechanical properties of the foam. Flame retardancy in the phenolic foam is imparted by three routes:

• Introduction of nonflammable particles;
• Making the system fire retardant;
• Chemical modification in structure by introducing phosphorous, boron, or nitrogen.

Improvement in FR properties of phenolic foam depends on the reduction in oxygen permeability after the addition of filler and reduction in barrier properties due to the formation of a compact charred layer on the surface. Modified montmorillonite clay is used in the fabrication of phenolic foam. This clay exfoliates and disperses well in the phenolic matrix due to the hydrogen bonding which prevents oxygen permeability and improves the fire resistance [30]. A synergistic effect of zinc oxide, pentaerythritol, and ammonium polyphosphate to impart FR properties in phenolic foam was evaluated. Results were unbelievable on the addition of 1 wt.% of zinc oxide, which improves the LOI value by 80%. But its flexural and compressive strength was found to decrease by 27% [31]. Another attempt has been made by the use of silica-graphene oxide and alpha zirconium-graphene oxide hybrid system to improve FR properties. A slight increase in LOI of phenolic foam from 1 to 5% with an increase in graphene oxide content was observed. The LOI value further increased by increasing the amount of hybrid content [20].

The most common class of flame retardant is compounds containing phosphorous. When heat is applied, they act by generating phosphorous acid which captures
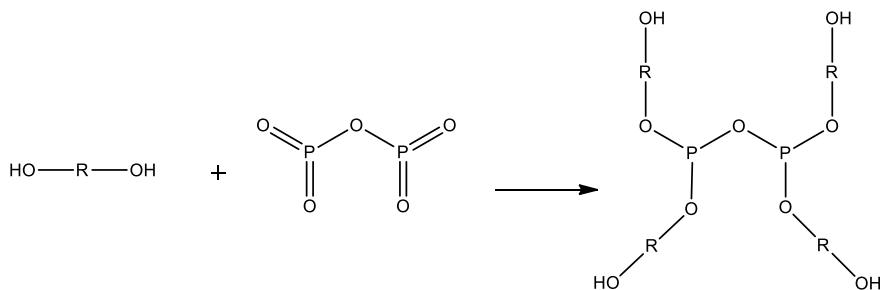
Fig. 6 Scheme for phosphorous containing PEG synthesis [32]

radicles while burning and accelerates the charring process. Along with phosphorous, Si and N are need to be added to compensate for the mechanical properties of phenolic foams. Most commonly, they are added by the reaction of modified PEG or polyurethane with phenolic resin. PEG is a flammable material due to long-chain molecules. Two different phosphorous-containing PEGs were synthesized. It was found that the LOI was reduced to 21% and 12% by adding 10 wt.% of synthesized compounds [22]. The introduction of phosphate-modified PEG (200, 400, and 600) led to an increase in the LOI by 36%, 28%, and 14%, respectively. The chain length of PEG 200 is smaller as well because the amount of phosphorous bearing is higher in PEG 200, which is the main cause of LOI increment [32]. The reaction scheme for the synthesis of modified PEG is shown in Fig. 6.

A novel phosphorous-based compound methyl-DOPO(9,10-dihydro-9-oxa-methylphosphaphenthrene-10-oxide) was synthesized to enhance the FR properties of phenolic foam. The resultant product acts as a scavenger by diluting the burnable gas in the vapor phase. When burned it forms PO, PO_2, and CH_3PO, which act as a radical scavenger [33]. A phosphorous and nitrogen-containing polyurethane framework was created. A noteworthiness improvement in LOI by 21% has been seen when 10 wt.% of the polyurethane system is added to the phenolic resin. This synergistic enhancement is attributed to the nature of nitrogen that acts as a gas source and produces nonflammable gas. These gases dilute the concentration of flammable gases and retard the decomposition of phenolic foam [34]. Recently, a magnesium amino tris-reduced graphene oxide half breed material has been arranged and used in phenolic foams for fire-resistant conduct. The LOI of the foam was expanded to 41.5% at 4 phr when contrasted with the unmodified one. It likewise diminished all-out-smoke discharge by 52.5% [35].

Besides their enhancement in mechanical properties, polyurethane and PEG system are not suitable to enhance the FR properties of phenolic foams. Phosphorous-based compounds are the most efficient way to enhance the FR properties of phenolic foams, especially in combination with nitrogen.

5 Shape Memory Properties

The shape memory behavior of foam has been broadly explored in the last decade. The core of their research relied on the fabrication, characterization, and possible application of shape memory foam. The shape memory behavior of phenolic foam can be augmented due to the higher compression even if the stiffness and strength values are reduced. Additional advantages of foam materials are lighter in weight and high recovery force.

The fundamental mechanism of shape memory behavior lies in the dual segment of the polymer. One segment serves as the elastic domain and the other is the transitional domain. At room temperature or even at low temperature both the domains are hard and the polymeric material is stiff. Upon heating, the polymer above Tg makes the transitional domain soft and deformable. The versatile area likewise goes through distortion by retaining the vitality and put away it as flexible vitality. As we chill off, the material progress area goes through the freezing of chain development and solidified the momentary space. If the deformed shape is held during cooling (a compressed form of the foam), it will stay in the same shape even after the removal of compressive force. This happens because the transition domain gets harden below Tg which prevents the recovery of the elastic domain. After heating above Tg, the transitional domain loses its ability to hold the elastic domain due to the absorption of energy in chain movement and the polymer regains its original form due to the release of elastic energy.

Two factors are the basis for the shape memory effect in SMPF. Glass modulus of foam material is responsible for shape fixity and the rubbery modulus for shape recovery. These factors decide the shape memory properties of phenolic foams. The glass transition temperature of phenolic resin plays an important role in the shape memory effect. Phenolic foam has a high crosslinking density; their Tg would be on the higher side. As far as the mechanical properties are concerned, higher thickness material has higher rigidity. As the molecular weight increases with an increase in crosslinking density, glass modulus would be shifted to the higher side, which ultimately increases the Tg. The shape memory effect in phenolic foams can be implemented by the use of

- long-chain phenol substitute;
- polyurethane pre-polymer in phenolic foam fabrication;
- long-chain epoxy polymeric backbone for phenolic foam formation.

A 20% relative density epoxy shape memory foam was synthesized and evaluated for their shape memory behavior. These foams were subjected to different conditions of stress, strain, and temperature to measure the change in properties. Tensile strain to a material failure is generally associated with the maximum recovery limit of the foam. These foams were compressed to 80% of their original volume, and multiple recovery cycles were performed. It was found that the packing temperature doesn't affect the overall recovery strain level. Also, the temperature and maximum strain levels have a significant effect on the reversibility of foam shape [36]. The effect

of long storage shape-holding capacity was investigated in polyurethane foam. The foam was strained at 80–90% strained above their glass transition temperature and then cooled to room temperature. After two months, it is reheated to gain its original length under different constant loads. It was found that the maximum stress wields at a fixed length depending on the amount of pre-strain. An expansion rate from 380 to 1273% has been accomplished from the hibernating size of grains against 1 N load [37]. This is a very important characteristic of a material used in space applications.

A magnetic susceptor filler particle was incorporated in the thermoset foam matrix to thermally activate the shape memory behavior. Results demonstrated that as the number of filler particles increased to 10 wt.%, the heating performance of foam increased without any deterioration of thermomechanical properties [39]. A net set of thermosetting foams were produced by solid-state foaming. This technique involves the direct overheating of a solid tablet of uncured resin. Composite foam can be produced from compression of fillers with uncured resin powder. Montmorillonite clay incorporated epoxy foam showed improvement in shape memory behavior. At 5 wt.% of filler content, the shape recovery property of foam is optimum without any damage. It was worth noting that the height of recovery of these foams was never lower than 97% [38].

A new ortho grid structure-based shape memory syntactic foam was designed and tested for healing impact damage repeatedly. The results implicated that the healing efficiency was 100% for all impact healing cycles. However, three-dimensional geometry recovery is confined to higher residual strength than two-dimensional recovery, and as the impact energy increases, healing efficiency slightly goes down [39]. An integral model based on the thermodynamics of foam formation has been investigated for its thermomechanical behavior. This study involves the insertion of a glass micro balloon into the shape memory polymeric matrix while fabrication of foam. Owing to the high-volume fraction of the glass balloon and the stiffness, it provides strength to the foam and increases the recovery stress. Also, it dictates that as the external confinement stress increases, the external recovered strain is reduced but the internal deformation increases. This led to better self-healing and shape recovery of the material [42].

Recent studies have focused on the applications of shape memory foams in biomedical devices. In particular, they are used to treat intracranial aneurysms. This condition is also known as a brain aneurysm. It involves weakness in the blood vessels, which results in balloon formation. To treat this condition shape memory foam may be a better material to fill that balloon with less stress generation in blood vessels. An attempt has been made by using hexamethylene diisocyanate-based polyurethane shape memory foam to treat an aneurysm. It has been predicted that 1.5 times oversized foam can be deployed bearing the capacity of 65 kPa circumferential stress, which is lesser than the minimum blood vessel wall breaking stress (700 kPa) [40]. The radio-opacity of a network polyurethane shape memory foam is enhanced by adding a small amount of tungsten. At 4 wt.% loading opacity has been found to increase without affecting its mechanical properties [41]. A novel sterilization method was implemented to determine the effect of sterilization on both thermochemical and shape recovery behavior. Both morphology and chemical

structure have been affected by sterilization methods which will have an impact on shape memory behavior. The shape recovery test showed that 98% of the shape has been regained after the sterilization [42]. A polyurethane hydroxyapatite-based shape memory foam had been engineered to use as a scaffold to expedite tissue regeneration. Results were satisfying as the self-fitting performance in rabbits passes all the in vitro studies. Shape memory foam could expand in 60 s and fill the bone defect by the heat-triggered mechanism [43].

Various SMP foam from organic to inorganic material comprising inorganic poly dimethoxy silane (PDMS) and polycaprolactone (PCL) had been investigated for their shape memory effect. PCL block serves as a switching segment in foam whereas the compressive properties are based on the PDMS segment. Shape recovery was found to be decreased as the PDMS chain length increases. PDMS segment has low Tg which is caused by a decrease in compression modulus accompanied by a decrease in PCL crystalline domain [44].

6 New Trends in Shape Memory Phenolic Foam

Nowadays, increasing cost, the anticipated future need for petrochemical, and viable developmental concerns brace for an eco-friendly and renewable bio-based material. The probable replacement of petroleum-based phenol and formaldehyde is reported in regards to their application. The lignocellulosic biomasses such as bark and wood are being considered as capable alternatives. Lignin is the most richly found material on the earth and stands second in the rundown of biopolymers. Lignin contains some phenolic functionality that could be used as reinstatement for phenol in the synthesis of SMPF. Another promising way is to modify resol resin by oxidative degradation of lignosulfonate. However, phenolated lignosulfonate-based resin bids a better perspective than oxidative degraded lignosulfonate-based resin. Among the chemical and thermal techniques established in the past few decades, liquefication of biomass use of water or organic solvents like alcohol or supercritical extraction has been advised for high biomass conversion into a phenolic resin. Many attempts have been made to modify the phenolic resin with bio-based materials such as bamboo and walnut shell. It is easier to liquify walnut shells than wood at low temperatures. Cardanol, a versatile and renewable source of meta substituted phenol, would be a partial substitute for phenol. The development of bio-based phenol PF requires the investigation of green routes and techniques while keeping global environment protection of prime importance. The exploration concerning shape memory foam proceeds with its quick development, with present endeavors, separated between empowering innovations (materials, cycles, and methods) and application and prototyping. On the empowering front, there is an expanding number of reports finding novel recuperation trigger mechanisms other than outside warming, which includes photoresponsive, magnetic responsive, and humidity responsive foams. Aside from alternative triggering mechanisms, there is also an emerging interest in shape memory

polymers capable of memorizing two or more temporary shapes. At different temperature stages, this kind of polymers can recover in a tandem manner from one shape to another and finally to its original shape. The interest for flower foam is expanding step by step in the floristry business, dinners, wreaths, in containers, and tabletop courses of action. The shape memory effect in those foams can preserve the space in the field of use. Additionally, a shape memory cushion that we can convey in our pocket expands into a pillow after warming which will be a superior alternative to moving explorers or in public transport.

7 Conclusion

This chapter is essentially devoted to a review of the improvement of shape memory properties, mechanical properties, and the fire-resistant properties of phenolic foams. The mechanical properties are frequently identified with the cell morphology. In reality, strands and particles have been demonstrated to lessen the cell size, to expand the cell thickness, and lastly to improve the cell homogeneity. The MWCNT and graphene oxide hybrid particles appear to be acceptable possibilities to accomplish this support for compressive quality and modulus properties. Concerning support, the presentation of adaptable chains into the inflexible spine of the phenolic pitch that is covalently connected is by all accounts extremely encouraging if the crosslinking thickness decrease isn't critical. Polyurethane and polyethylene glycol family is the most utilized item, yet dicyandiamide is by all accounts the most productive.

The shape memory properties depend on the dual segment of the polymer. The Tg of polymer assumes a significant function that fits as a shape memory impact. A long-chain polyurethane section appears to be encouraging to bestow shape memory impact in phenolic foam. Likewise, PDMS fills in as another substitute for polyurethane for development fit as a shape memory impact in phenolic foams. All things considered, little work has been completed in the territory of shape memory properties of phenolic foams.

Concerning flame retardancy properties, phenolic foams have much preferable fire properties over all other polymer foams. The improvement was credited to the homogeneous scattering of the particles that assist in diminishing the oxygen penetrability and offer a superior division of phenolic framework from the air and the warmth. Concoction adjustment containing explicit components is the most mainstream course for improving fire-retardant conduct. To begin with, components, for example, nitrogen go about as noncombustible gases sources that decline the combustible gas fixation, subsequently hindering the deterioration of the basic material. Second, phosphorous mixes, while decaying, produce phosphorous acids that quicken the singing cycle of the foams, permitting lower warmth and mass exchanges. The acquired scorch assumes the function of a defensive hindrance. Specialists attempt to substitute, at any rate mostly, the phenol with sustainable biomass assets. Biomass-based resol gums from pecan shells, wood, or bamboo powder showed the chance of substitution of traditional phenolic resol tars by creating foams with

fulfilling or comparable mechanical properties. Lignin is by and large profoundly examined and gives the most intriguing outcomes. Phenolated lignin exhibited a high potential as it expanded the compressive quality and diminished the friability. Subsequently, biomass-based phenolic resol saps appear to offer intriguing viewpoints for the advancement of phenolic tar with higher mechanical properties. By and by, the durability of these bio-based materials must be considered.

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