Chapter 1

General introduction

Highlights

This chapter provides the general introduction of the present investigation. It includes brief descriptions on biobased polyurethanes and nanocomposites, different characterization techniques such as FTIR, XRD, TGA, DSC, SEM, TEM etc. as well as various properties including shape memory behaviors for them. The importance of shape memory polyurethanes and the mechanism of shape memory behaviors are presented here. The chapter describes the importance of nanomaterials in the domain of polymer nanocomposites. The testing methods such as stretching and bending for shape memory behaviors of polymers are discussed here. This chapter provides various applications of shape memory polymers. The scopes, objectives and plans of the present investigation are also included here.
1.1. Introduction

Shape memory polymers (SMP) have generated immense interest in recent times because of their potential applications in different fields such as smart actuators, aerospace engineering, textile engineering and most importantly as intelligent biomedical devices.\textsuperscript{1-15} Ni-Ti alloy (Nitinol) is the most widely used shape memory material because of its good shape memory performance, good processability, excellent mechanical properties, good biocompatibility etc. However the shape memory alloys (SMA) have some limitations such as low deformation rate, high stiffness, high cost, non biodegradability etc. SMP have some advantages such as easier processing, lighter weight, lower cost, larger recoverable strain and lower toxicity as compared to the SMA (Table 1.1). SMP are smart materials that can change their shapes when exposed to a suitable external stimulus such as heat, light, moisture, magnetic field or electric field etc.\textsuperscript{16-23} The recovery of original shape from the deliberated fixed temporary shape is known as the shape memory effect. The shape memory behaviors i.e. the shape fixity and shape recovery of polymer network are the freezing and activation of the molecular chains below and above a transition temperature ($T_{\text{trans}}$), respectively. The extent to which the switching segment is able to fix the temporary shape and to recover the original shape on exposure of stimulus is called the shape fixity and shape recovery, respectively. The shape recovery time is a shape memory property which refers to the time that SMP used to take recover the permanent shape from its fixed temporary shape. The transition temperature can be either a glass transition temperature ($T_g$) or a melting temperature ($T_m$).\textsuperscript{24-26} For the amorphous polymers, $T_g$ is considered as the transition temperature; whereas for crystalline polymers, $T_m$ is considered as the transition temperature. On the other hand for the semi-crystalline polymers, either $T_g$ or $T_m$ can be used as the transition temperature. However, $T_m$ is being considered as the preferred transition temperature because it is sharper than the $T_g$.\textsuperscript{27, 28} The molecular mechanism of thermally induced SMP through which the shape memory effect observed is shown in Fig 1.1.

Now, most of the polymers showed the shape memory behaviors because polymer chains have the tendency to form network structures. However, due to the structural disadvantages (too low or too high $T_{\text{trans}}$ or weak mechanical properties), limited numbers of SMP are used in practical applications. A few examples of thermosetting SMP are polyethylene,\textsuperscript{29} polyisoprene,\textsuperscript{30}
Table 1.1: Comparison of the properties of SMP and SMA

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>SMP</th>
<th>SMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.9-1.1</td>
<td>6-8</td>
</tr>
<tr>
<td>Extent of deformation (%)</td>
<td>250-800</td>
<td>&lt;8</td>
</tr>
<tr>
<td>Forced required for deformation (MPa)</td>
<td>1-3</td>
<td>50-200</td>
</tr>
<tr>
<td>Recovery temperature (°C)</td>
<td>25-90</td>
<td>-10-100</td>
</tr>
<tr>
<td>Recovery stress (MPa)</td>
<td>1-3</td>
<td>150-400</td>
</tr>
<tr>
<td>Processing conditions</td>
<td>&lt;200 °C, low pressure</td>
<td>&gt;1000 °C, high pressure</td>
</tr>
</tbody>
</table>

Fig. 1.1: Molecular mechanism of thermally induced SMP polynorbornene, styrene-butadiene copolymers, polyurethane etc., whereas thermoplastics are polyurethane, block copolymers of polyethylene-nylon 6 and polyethylene-poly(vinyl acetate), copolymer based ionomers etc. Among different SMP, polyurethanes are the most versatile due to their biocompatibility, wide range tunable stiffness, large deformation, large recovery, good elastic property, water vapor permeability and multi responsive shape memory effect. The segmented block polyurethanes are made up of alternating soft and hard segments. Owing to the polar character of urethane groups, the hard urethane domains are more hydrophilic in contrast to
the soft polyol domains that cause the micro-phase separation in the structure. The soft segment of the polyurethanes is usually moderately high-molecular weight long chain polyol which is flexible in nature. The hard segment is composed of diisocyanate with low-molecular weight diol or diamine chain extender and hence is rigid. The flexible soft segments are responsible for the reversible phase transformation that allows for the shape memory effect, while the hard segments are responsible for the memorizing of permanent shape. The shape memory properties as well as the performance of the polyurethanes can be tailored by the judicious variation of chemical constituents and the molar ratio of the hard and soft segments.  

Recently the hyperbranched polymers have taken tremendous attentions in the development of advanced polymeric materials because of their unique characters. The hyperbranched polymers are highly branched macromolecules with significantly less regular structural architecture and contain a number of surface defects and missing branches. Hyperbranched polymer was first coined by Kim and Webster in 1988 when the authors synthesized soluble hyperbranched polyphenylene. Hyperbranched polymers exhibited some special properties like low melt and solution viscosity, high solubility and chemical reactivity, enhanced compatibility, compact three dimensional non-entangled globular structures etc. Generally, two synthetic techniques are being used for the synthesis of such hyperbranched polymers. These are single-monomer methodology and double-monomer methodology. Among different approaches, step-growth polycondensation method of AB monomers is widely used to prepare a broad range of hyperbranched polymers. Again, A2 + B3 approach is preferred to use largely now-a-days, because of its several advantages. These include easy availability of the reactants, tuning of property particularly mechanical property by using long segmented reactant etc. Thus the use of A2 + B3 approach may offer a unique route and the resulted polymer exhibits the unique architectural features.

Furthermore, realization of finite petroleum resources, growing environmental concerns and waste disposal problems encourage utilization of bio resources like vegetable oils as raw materials for the preparation of polymeric materials. This is due to the fact that such oils have numerous advantages such as easy availability, relatively inexpensive, versatility in structure and property, inherent biodegradability and environmentally benign. Again, hydroxylation of vegetable oils is one of the good approaches to obtain the required polyols to be
used as diol chain extenders in polyurethane syntheses. Properties of the vegetable oil based polyurethane depend on the characteristics like physical and chemical structures, which include the number of hydroxyl groups in the polyols, degree of unsaturation, length of the fatty acid chains and position of hydroxyl groups in the fatty acid chain. The vast forest resources and farm lands of India, particularly the North-Eastern region yields a large variety of oil bearing seeds. *Mesua ferrea* L. (Nahar) is such a plant, which has remarkable potential and its seeds surprisingly contain high amount (70%) of oil. This oil possesses mainly triglycerides of oleic (52.3%), linoleic (22.3%), palmitic (15.9%) and stearic (9.5%) acids.\(^{54,55}\)

The demands of the advanced applications required high performance polymeric materials. Recently polymer nanocomposites have taken commendable role in the domain of materials due to the significant improvement of many desired properties like mechanical strength, thermal, gas barrier, solvent resistance, flame retardant, shape memory and biodegradability of the neat polymers.\(^{56-62}\) Polymer nanocomposites are the combination of two or more phases in which the domain of one phase must be in nano range (1-100 nm). This represents a better alternative to the conventional filled polymers or composites systems. The properties of nanocomposites depend on the various factors such as size and nature of the nanomaterial, aspect ratio, surface functionality, distribution of nanomaterial and interaction of nanomaterial in the polymer matrix.

Studies on vegetable oil based hyperbranched polyurethane nanocomposites with different nanomaterials, thus, will be a good proposition in recent times in the niche of advanced polymeric materials.

### 1.2. Background

Polyurethanes are versatile polymeric materials with a wide range of physical and chemical properties. This polymer is first synthesized by Otto Bayer in the I.G. Farben laboratories way back in 1937.\(^{63}\) In 1950’s, polyurethane chemistry started to develop rapidly with toluene diisocyanate (TDI) and the first polyether polyl was reported from Dow Chemical. Again, the origin of shape memory effect can be traced back to 1932, though after the discovery of nickel–titanium alloy as shape memory material in 1963 led to real interest on the subject.\(^{64,65}\) The shape memory polyurethane was discovered by the Mitsubishi in 1988. A large number of
reports are available in the literature on the effect of different hard segments content on the mechanical, thermal and shape memory properties of polyurethane. Yang et al. studied the effect of different diisocyanates on the shape memory behaviors of polyurethanes.66

The term nanocomposite was first proposed by Theng in 1970.67 Among different types of nanomaterials carbon nanotubes (CNT), which was discovered by Iijima in 1991,68 opened the door to augment the performance and shape memory behaviors of polymer by incorporating small amount of it into the polymer matrix. Ajayan et al. reported the first polymer nanocomposites using CNT as a filler.69 Koerner et al. reported that incorporation of 0.5–10 vol% of multiwall carbon nanotubes (MWCNT) into polyurethane matrix to fabricate thermoplastic polymer nanocomposites with high electrical conductivity (1–10 S/cm) and enhancement of mechanical properties including increased modulus and yield stress.70 Deka et al. reported the enhancement of mechanical, thermal and shape memory behaviors of vegetable oil based polyurethane by incorporation of small amount of MWCNT into the hyperbranched matrix.71 Lendlein et al. have great contribution to the SMP nanocomposites for the synthesis, functionalization and biological applications of polyurethanes.14, 72, 73 Mather et al. have reported the modification of SMP (polyurethane, cross-linked polycyclooctene etc.) and their nanocomposites.74-77 Tobushi et al. reported the structure property relationship of shape memory polymers.78-80 Again by incorporation of suitable nanomaterials into the shape memory polymer, the actuation method can be tuned. Lee et al. studied the electro-active shape memory behavior of polyurethane-CNT hybrids.23 Cai et al. reported the magnetic field responsive shape memory behaviors of $\text{Fe}_3\text{O}_4$/poly($\varepsilon$-caprolactone)-polyurethane nanocomposites.81 Leng et al. reported the infrared light-active shape memory behaviors of nanocarbon particles filled styrene based polymer nanocomposites.82 Thus research on polyurethane nanocomposites including vegetable oil modified hyperbranched polyurethane with different nanomaterials based nanocomposites as contact and noncontact shape memory materials has strong background to be delved into.

1.3. Classification of SMP

The classification of SMP is based on the nature of their molecular structures such as amorphous or crystalline and covalently cross-linked or physically cross-linked, as described below.6, 83
1.3.1. Covalently cross-linked glassy polymers

This type of SMP is covalently cross-linked glassy polymers below their $T_g$ and rubbery elastic above $T_g$. It shows excellent shape fixity and shape recovery due to the nature of permanent cross-linking, that can be adjusted through the extent of cross-linking. However, since the primary shape is covalently fixed, once finally processed (casting or molding) these materials are difficult to reshape thereafter. Typical examples are thermosetting styrene-butadiene copolymer, polyethylene, thermosetting polyurethanes, co-polyester etc.\(^6\)

1.3.2. Covalently cross-linked semi-crystalline elastomers

It is similar to the above type of SMP where the permanent shapes are established through the cross-linking. However the temporary shape can be controlled through deformation above $T_m$ of the crystallization region and subsequent cooling below the crystallization temperature. This is because of the fact that both $T_g$ and $T_m$ can be used as a transition temperature for this type of SMP, though in most of the cases $T_m$ is used, as stated earlier. The shape fixity of this type of SMP can be improved by choosing a relatively lower temperature compared to $T_{trans}$ and that low temperature should be such so that it allows to a high degree of crystallization. The shape recovery speed is generally faster for this type of SMP as $T_m$ is a first-order transition and a sharp transition. This class of materials includes bulk polymers, such as semi-crystalline polymers, liquid crystal elastomers and hydrogels with phase separated crystalline microdomains. Thermosetting semicrystalline polyisoprene, polycyclooctenes, polycaprolactone etc. are examples of this class.\(^6\)

1.3.3. Physically cross-linked glassy polymers

In this SMP, the rigid amorphous domains serve as physical cross-links through the van der Waals forces, polar-polar interactions, hydrogen bonding etc. and afford the required elasticity for shape memory effect. These are mainly phase-separated block copolymers. When the temperature is higher than the $T_g$ of these discrete physical domains, the material will be deformed easily that can be processed and reshaped. Another phase of lower $T_g$ which softens to a rubbery state and fixes a secondary shape on cooling below $T_g$, present in the system. The
majority of SMP in this category are segmented shape memory thermoplastic amorphous polyurethanes.

1.3.4. Physically cross-linked semi-crystalline block copolymers

In this SMP the soft domains are crystallized and \( T_m \) is used as the transition temperature for shape recovery. These polymers generally have hard and soft domain structures. The properties can be tailored by varying the hard to soft domain ratio. The secondary shapes are thus fixed by crystallization of the soft domains. The polyethylene oxide-co-polyethylene terephthalate, polystyrene-co-poly(butadiene) and the thermoplastic segmented shape memory semi-crystalline polyurethanes fall in this category.

1.4. Classification of polymer nanocomposites

Depending on the dimension of the nanomaterials, nanocomposites can be divided into three different categories. In the first category of polymer nanocomposites, all three dimensions of the nanomaterials are in the nano region. The spherical nanoparticles like zeolites, metal, metal oxides etc. containing polymer nanocomposites fall in this category.

In the second class of polymer nanocomposites, two dimensions of the nanomaterials are in the nano region, whereas the third dimension may be a few micrometers. Carbon nanotube, carbon nanofibre etc. nanomaterials based polymer nanocomposites are the examples of this class.

The polymer nanocomposites, where only one dimension of the nanomaterials is in the nano region, while other two dimensions are in micrometer size are categorized in third class of nanocomposites. Most of the cases the nanomaterials are in layer structure like silicate layers, clay etc. and such nanomaterials based polymer nanocomposites are included in this category.

1.5. Materials and methods

1.5.1. Materials

Polyurethane
Polyurethanes are linear polymers that have a molecular backbone containing carbamate groups (-NHCOO-). These groups, called urethane, are produced through a rearrangement reaction between a diisocyanate and a polyol. The polyols used in preparation of polyurethanes are of two types, viz. macroglycol and chain extender. The brief descriptions of these components are presented below.

**Diisocyanate**

Isocyanates are highly reactive compounds and can readily react with the groups containing active hydrogen. These reactions are most important in the formation of polyurethanes. The properties of the polyurethane largely depend on the structure of isocyanate. The most commonly used diisocyanates in polyurethane synthesis are listed in Table 1.2. The most widely used diisocyanates for the preparation of polyurethanes are toluene diisocyanate (TDI) and 4,4′-diphenylmethane diisocyanate (MDI). In most of the cases TDI used is a mixture of the 2,4- and 2,6- isomers in 80:20 mol ratio. Similarly, MDI has three isomers namely 4,4-, 2,4-, and 2,2-diphenyl methane diisocyanates. However, 4,4-isomer is used in most of the commercial polyurethanes. Though aromatic diisocyanates are more reactive than aliphatic one but polyurethanes obtained from the aromatic diisocyanates have lower oxidation and weaker ultraviolet stabilization than the polymers with aliphatic diisocyanates. However, the aromatic diisocyanates based polyurethanes exhibited good shape memory behaviors.

**Macroglycol**

The diols/polyols with number average molecular weight 500 to 5000 g/mol are used as a macroglycol in the preparation of polyurethane. The polyols are generally categorized into two groups viz. polyether polyol and polyester polyol. The structure of the macroglycol is an important factor in governing the ultimate properties of the polyurethanes. Polyester polyols are widely used macroglycols as they exhibited excellent mechanical properties, thermal stability, outstanding tear strength and shape memory behaviors.
### Table 1.2: Diisocyanates used for the synthesis of polyurethanes

<table>
<thead>
<tr>
<th>Name of diisocyanate</th>
<th>Abbreviated name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4- and 2,6-Toluene diisocyanate</td>
<td>TDI</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>4,4′-Methylenediphenyl diisocyanate</td>
<td>MDI</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>1,5-Naphthalene diisocyanate</td>
<td>NDI</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>1,6-Hexamethylene diisocyanate</td>
<td>HMDI</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>1,4-Cyclohexyl diisocyanate</td>
<td>CHDI</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>4,4′-Dicyclohexylmethane diisocyanate</td>
<td>DCHMDI</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>Isophorone diisocyanate</td>
<td>IPDI</td>
<td><img src="image7" alt="Structure" /></td>
</tr>
<tr>
<td>Norbornane diisocyanate</td>
<td>NBDI</td>
<td><img src="image8" alt="Structure" /></td>
</tr>
<tr>
<td>p-Phenylene diisocyanate</td>
<td>PDI</td>
<td><img src="image9" alt="Structure" /></td>
</tr>
</tbody>
</table>
Among them, further the crystalline polycaprolactone (PCL) diol based polyurethane is the most convenient to use for the shape memory studies. The melting temperature can be used as the transition temperature. A few macroglycols used for the synthesis of polyurethanes are listed in Table 1.3.

**Table 1.3: Macroglycols used for the synthesis of polyurethanes**

<table>
<thead>
<tr>
<th>Name of Polyol</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene oxide (PEO)</td>
<td><img src="image" alt="PEO structure" /></td>
</tr>
<tr>
<td>Polypropylene oxide (PPO)</td>
<td><img src="image" alt="PPO structure" /></td>
</tr>
<tr>
<td>Polytetramethylene oxide (PTMO)</td>
<td><img src="image" alt="PTMO structure" /></td>
</tr>
<tr>
<td>Polycaprolactone (PCL)</td>
<td><img src="image" alt="PCL structure" /></td>
</tr>
<tr>
<td>Polyethylene adipate (PEA)</td>
<td><img src="image" alt="PEA structure" /></td>
</tr>
</tbody>
</table>

**Chain extender**

Chain extenders are low molecular weight (generally, below 400 g/mol) hydroxyl or amine compounds. The choices of chain extender and the diisocyanate determine the characteristics of the hard segment and the physical properties of the polyurethane. The most commonly used chain extenders are mentioned in Table 1.4.

1.5.2. Nanomaterials

The nanomaterials with at least one of the dimensions in the region of 1-100 nm can be used as a nano-reinforcing agent in the polymer nanocomposites. The incorporation of nanomaterials in the polymer matrix significantly improves the mechanical, thermal, electrical and shape memory properties along with others. The properties of nanomaterials are remarkably
different from the bulk counterpart due to the confinement of electron wave function, their high surface area to volume ratio, and extremely high proportion of surface atom. They are of different types, though metals or their oxides and carbon nanotubes are only discussed here as these are widely used nanomaterials for tuning of shape memory property of polymers.

**Table 1.4: Chain extender used for the synthesis of polyurethanes**

<table>
<thead>
<tr>
<th>Name of chain extender</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>HO(-)OH</td>
</tr>
<tr>
<td>1,4-Butanediol</td>
<td>HO(-)OH</td>
</tr>
<tr>
<td>1,6-Hexanediol</td>
<td>HO(-)OH</td>
</tr>
<tr>
<td>Ethylene diamine</td>
<td>H(_2)N(-)NH(_2)</td>
</tr>
<tr>
<td>Ethanolamine</td>
<td>HO(-)NH(_2)</td>
</tr>
<tr>
<td>Glycerol</td>
<td>HO(-)OH</td>
</tr>
<tr>
<td>Trimethylol propane</td>
<td>HO(-)OH</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>HO(-)OH</td>
</tr>
</tbody>
</table>

**Metal/metal oxide nanoparticle**

Nanoparticles are the three dimensional nanomaterials with an average diameter smaller than 100 nm. These nanoparticles are synthesized by different methods such as co-precipitation, sol-gel, hydrothermal, microwave, sonochemical, template synthesis etc. The properties of the nanomaterials depend on the size, shape and distribution, which can be changed by changing the reaction parameters. Fe\(_3\)O\(_4\) nanoparticles are most widely studied metal oxide nanoparticles due to their easy synthesis, biocompatibility, magnetic property, microwave absorption characteristics etc. in shape memory polyurethane based nanocomposites.
Carbon nanotube

Carbon nanotubes (CNT) are one dimensional tubular structure of graphitic sheet consisting of covalently bonded carbon atoms in hexagonal-type arrangement. CNT are generally classified into two classes: single wall carbon nanotube (SWCNT) and multi-walled carbon nanotubes (MWCNT) (Fig. 1.2 (a, b)). CNT are synthesized by the different techniques such as laser ablation technique, chemical vapor deposition, gas phase pyrolysis, arc discharge etc. CNT possess excellent elastic modulus (~1 TPa), strength (~200 GPa) electrical conductivity (1000 times of copper) and thermal conductivity (~3000 Wm\(^{-1}\)K\(^{-1}\)).\(^{84, 85}\) The dispersion of CNT in the polymer matrix is very difficult because of their strong van der Waals forces and numerous \(\pi-\pi\) interactions between the tubes. Two different techniques are used for the modification of CNT viz. covalent and non-covalent techniques. Covalent modification based on the formation of covalent bond between the CNT and the attached functionality. On the other hand, non covalent modification is mainly the adsorption of functional molecules on the surface of the nanotube through various interactions such as van der Waals forces, hydrogen bonding, hydrophobic interaction, electrostatic forces and \(\pi-\pi\) interactions.\(^{86, 87}\) Again the decoration of CNT with the nanomaterials like ZnO, Cu, Fe, Fe\(_3\)O\(_4\) etc. increases the dispersion as well as modifies the intrinsic properties of the CNT. In the recent years, extensive studies have been made to decorate the CNT with magnetic nanomaterials due to their potential applications in magnetic recording media, electrical devices, color imaging, heterogeneous catalysis, magnetic force microscopy as nanoprobes, microwave absorption materials and smart materials.\(^{88-90}\) Besides these, other nanomaterials like organically modified nanoclay, cellulose nanofibre, graphene etc. are also used to enhance the performance of the shape memory polymers. However these are not discussed here as these nanomaterials are not used in the present study.

![Fig. 1.2: (a) Single walled carbon nanotube (SWCNT) and (b) Multi-walled carbon nanotubes (MWCNT)](image-url)
1.5.3. Method

1.5.3.1. Preparation of polyurethane

One-shot and pre-polymer methods are used for the preparation of polyurethanes (Fig. 1.3 and 1.4). In the one-shot method all the reactants namely macroglycol, diisocyanate and chain extender are added at once at the starting of the polymerization reaction. This process is easier, faster and more reproducible. A high order of crystallinity is obtained in this process. However controlling of reaction is difficult. In contrary, in the pre-polymerization method –NCO or -OH terminated pre-polymer is prepared by reacting a diisocyanate with a macroglycol in the first step. Then a chain extender is added to the pre-polymer in the second step and high molecular weight polyurethane is obtained. More regular chain sequences of polyurethane are obtained in the pre-polymerization technique. The solvents like xylene, dimethylformamide, dimethylacetamide etc. are generally used for the preparation of polyurethanes.

Fig. 1.3: Schematic representation of the one shot method for the synthesis of polyurethane

1.5.3.2. Preparation of polymer nanocomposite

The polymer nanocomposites are generally prepared by three different methods as discussed below.
**Fig. 1.4:** Schematic representation of the pre-polymerization method for the synthesis of polyurethane

**Solution method**

In this method nanomaterials are swelled and dispersed by solvent in a polymer solution. The layers may be delaminated in a solvent or a solvent mixture due to the interactions of nanomaterials and the solvent molecules. Polymer chains are then adsorbed onto the delaminated individual layers or particles. However upon removal of the solvent, the layers or particles can reassemble to reform the stack with polymer chains sandwiched in between and forming a well-ordered intercalated nanocomposite. The formation of exfoliated nanocomposite is very rare by this technique. This technique is used in many cases in the laboratory for the preparation of nanocomposites but industry used only when water is used as the solvent. However this technique is not well accepted for the commercial production of nanocomposites due to the requirement of large volume of solvent and phase separation of the prepared product.\(^{91}\)

**In situ polymerization**
In this method the nanomaterials are first dispersed in the liquid monomer or pre-polymer solution before polymerization. Polymerization can be initiated either by heat or radiation, or by the diffusion of a suitable initiator or catalyst inside the nanomaterials before the swelling step by the monomer. Polymerization produces long chain polymers within the nanomaterials. The homogeneous distribution of nanomaterials is obtained by using a high shear device because of the gradual increment of viscosity of the reaction mixture with progress of polymerization. Well-exfoliated nanocomposites can be prepared by this method and has been applied to a wide range of polymer systems. This technique is suitable to prepare clay/polymer and metal/polymer nanocomposites. This method is particularly useful for the thermosetting polymers.

Melt-Mixing technique

This method involves the mechanical mixing of a polymer with nanomaterials using extrusion and injection molding above the softening point or at processing temperature of the polymer. The intercalation or exfoliation of nanomaterials occurs during melting of polymer under shear conditions. The processing conditions play an important role on the structure evaluation of such polymer nanocomposites. Generally, temperature is kept well below the decomposition temperature of all the components of the nanocomposites. The absence of a solvent makes direct melt intercalation an environmentally sound and an economically favorable method for industries. Thus this technique has wide application for commercial production of polymer nanocomposites.

1.6. Characterization

Polymers and their nanocomposites are characterized by different analytical and spectroscopic techniques as discussed below.

1.6.1. Nuclear magnetic resonance (NMR) spectroscopy

NMR is used to determine the structure of the polymers. Mainly proton (\(^1\)H) and carbon (\(^{13}\)C) NMR spectroscopic as NMR technique is utilized for this purpose. This technique is used to investigate the molecular weight, degree of branching, repeating units and distribution, tacticity as well as the presence of the non-reacted monomers. This spectroscopic technique can
also be used to study the kinetic of the polymerization reaction, cross-linking reaction, composition of copolymer, degradation nature etc. NMR study of the polymer can be done in the solid state or in the swollen state. This technique can also be utilized to explain the effect on the nanomaterials with the polymer matrix.

1.6.2. X-ray diffraction (XRD) study

XRD is used to study the degree of crystallinity, amorphousness, size of crystals and crystal structure of polymers. Polymer nanocomposites can be characterized by this technique. Two types of X-ray diffraction used for polymers. These are wide angle X-ray diffraction (WAXD) and small angle X-ray diffraction (SAXD). WAXD provides the information about the degree of crystalinity, orientation of crystalline region and nature of ordering structure. On the other hand the SAXD is utilized to obtain information on the dimension of small crystalline regions as lamellae and the presence of voids and their shapes. The combined study of WAXD and SAXD present the quantitative characterization of nanostructure and crystalline structure of polymer nanocomposites.

1.6.3. Fourier transformed infrared spectroscopy (FTIR)

FTIR spectroscopy is a commonly accepted method for characterizing the polymeric materials. This spectroscopy records the absorbance or transmittance intensity in percentage as a function of wavenumber (cm\(^{-1}\)) or wavelength (nm) of the polymers under investigation. The rotational and vibration energies of any specific group or atom fall in the infrared region resulted the characteristic absorption band. So this spectroscopy is largely used to determine the functional groups present in the structure of the polymer. This technique is also used to identifying a polymer, monitoring the polymerization stage, and to characterize the structural changes under different conditions. The formation of nanocomposites can also be characterized by this technique.

1.6.4. Scanning electron microscopy (SEM)

The scanning electron microscope is a type of electron microscope that creates images by the electrons emitted when the primary electrons coming from the source strike the surface and are
in-elastically scattered by atoms in the sample. The morphological study of the polymeric materials and nanocomposites is done by using the scanning electron microscopic technique. SEM is usually used to study topography such as three dimensional images of polymer blends, block and graft copolymers. Furthermore it can also be used to get information of crystallographic orientation and composition of polymeric materials by help of energy dispersive spectroscopic (EDS) attachment. The phase separated morphology of the SMP can be characterized by this technique in terms of domain sizes and number of phases.

1.6.5. Transmission electron microscopy (TEM)

TEM is used to investigate the distribution of different phases, internal structure, defects structure etc. present in the nanocomposites. It can be used to get the information about crystallography and chemical composition of the materials. In TEM, the electron beam is allowed to penetrate to the very thin film and the transmitted electrons are directly used to produce the image of the specimen by the help of lenses. Varying the electron density in regions with different morphology leads to a contrasted image.

1.6.6. Thermo-gravimetric analysis (TGA)

TGA is a very useful technique to determine the thermal stability of polymeric materials. The TGA thermogram is obtained by recording the change of weight of the polymer sample either with temperature or with time. The amount of moisture or any other volatiles, plasticizer, inorganic nanomaterials etc. present in the polymer can also be obtained from the TGA thermogram.

1.6.7. Differential scanning calorimetry (DSC)

DSC is a very potential tool to evaluate the thermal properties of the polymeric materials. The glass transition temperature ($T_g$), melting temperature ($T_m$), crystallinity, kinetic of reaction, amount of endothermic or exothermic energy etc. can be studied by DSC. It can reveal the mobility of molecular chains by specific thermal energy variation.
1.6.8. Raman spectroscopy

Raman spectroscopy relies on the inelastic scattering of monochromatic light usually from a laser in the visible, near infrared or near ultra-violet range with materials. Raman spectroscopy is highly sensitive to the material crystallinity, orientation and temperature. This is useful for analyzing molecules without a permanent dipole moment. This technique is mostly used for the study of carbon nanotube. It is used to determine the G band that represents the graphitic level of the tubes and the D band that is indicates the presence of disorder.

1.6.9. Vibrating sample magnetometeric study

Vibrating sample magnetometer (VSM) is used to measure saturation magnetization, initial magnetization and Curie temperature of magnetic materials. VSM consists of an electromagnet assembly, a magnet power supply rack, a control electronics rack and a computer. It is based upon the Faraday’s law according to which an electromagnetic frequency is induced in a conductor by a time varying magnetic flux.

1.6.10. Biodegradation testing

The biodegradability of the polymers provides novel and additional properties which may also be beneficial for their uses. Different methods such as field test, simulation test, laboratory test etc. are used to study the biodegradation of the polymeric materials. Field tests such as burying plastic samples in soil, placing it in a river or full-scale composting performed represent ideal practical environmental conditions. However this method has some disadvantages. The environmental conditions such as temperature, humidity, or pH, cannot be efficiently controlled in nature. Simulation test has been developed to overcome the problems of field test. Here, the test for degradation is performed in a controlled laboratory reactor using a real environment (e.g. soil, compost or sea water). The most reproducible biodegradation tests are laboratory tests, where defined media with a mixed microbial population or individual microbial strains are used.

1.6.11. Testing for shape memory behavior

Different testing methods are used to study the shape memory behaviors of SMP as discussed below.
**Stretching technique**

In this technique the specimens are heated above the transition temperature \( (T_s) \) and then they are stretched to twice of their original length \( (L_0) \) and the stretched length is denoted as \( L_1 \). Immediately, the stretched samples are put into the low temperature (much below transition temperature) to fix the temporary shape for the specified period of time, and length is measured as \( L_2 \) after releasing the stretch. The cooled samples are reheated at the same elevated temperature for the same period of time, and the length obtained is denoted as \( L_3 \). The percentage of shape recovery and percentage of shape fixity are calculated by using the following equations.

\[
\text{Shape recovery (\%) } = \left( \frac{L_1 - L_3}{L_0} \right) \times 100 \quad \text{(1.1)}
\]

\[
\text{Shape fixity (\%) } = \left( \frac{L_2 - L_0}{L_0} \right) \times 100 \quad \text{(1.2)}
\]

**Bending technique**

In this technique the specimens are heated above the transition temperature \( (T_s) \) for the specified period of time and then they are folded to a ring shape. Immediately, the folded samples are put into the fixing temperature (much below \( T_s \)) for specified period of time to fix the temporary shape. Subsequently, they are reheated at the same elevated temperature for the same period of time for the shape recovery study. The shape recovery and shape fixity are two shape memory parameters calculated from the following equations:

\[
\text{Shape recovery (\%) } = \left( \frac{90 - \theta}{90} \right) \times 100 \quad \text{(1.3)}
\]

\[
\text{Shape fixity (\%) } = \left( \frac{\theta}{90} \right) \times 100 \quad \text{(1.4)}
\]

where \( \theta \) in degree denotes the angle between the tangential line at the midpoint of the sample and the line connecting the midpoint and the end of the curved sample.

**Thermo-mechanical cyclic tensile technique**

In this technique the specimen is stretched to a maximum strain \( (\varepsilon_m) \) of 100% with a constant cross-head speed above transition temperature \( (T_s) \). Immediately it is cooled to a low temperature (much below \( T_s) \) to fix the deformed shape and the force of the specimen is released. Then the unloaded sample is reheated to study the shape recovery behavior. The shape recovery
ratio ($R_t$) and shape fixity ratio ($R_f$) are two shape memory parameters calculated from the following equations:

$$R_t = \frac{[\varepsilon_m - \varepsilon_p(N)]}{\varepsilon_m}$$

$$R_f = \frac{\varepsilon_u(N)}{\varepsilon_m}$$

Where $\varepsilon_m$ denotes the maximum strain in the tensile test, $\varepsilon_p(N)$ is the residual strain after shape recovery in the $N$th cycle and $\varepsilon_u(N)$ is the residual strain at stress free state of $N$th cycle.

1.7. Property

The desired properties like mechanical, thermal, biodegradability, shape memory etc. at required values of polymers and their nanocomposites are useful for SMP and hence discussed below.

1.7.1. Mechanical property

Mechanical properties of polymers and the nanocomposites are very important for applications as SMP. The mechanical properties include tensile strength, elongation at break, scratch hardness, impact resistance, fracture toughness etc. Very low loading of suitable nanomaterials drastically improved the mechanical properties of many polymers in their nanocomposites. The extent of improvement depends on the functionalization, dispersion, size and shape, orientation, aspect ratio etc. of the nanomaterials. However the high level of loading of the nanomaterial deteriorated the mechanical properties of the nanocomposite. This is due to the agglomeration of the nanomaterials in the nanocomposite. Tensile strength of the nanocomposites increased due to the efficient load transfer from the matrix to the nanomaterial. However the elongation at break is generally decreased in the nanocomposites. This is due to the restricted movement of the polymer chains on the surface of the nanomaterials. Scratch hardness of the nanocomposites increases with the increase of toughness and rigidity of the material. Impact strength of the material may be defined from the angle of toughness of the films that is the ability to absorb the applied external energy as well as the transfer of energy to its adjacent molecular chains. Impact resistance of the nanocomposites also increases with the increase of toughness of the nanocomposites. The fracture toughness of the nanocomposites measures the
ability of the material containing a crack to resist the fracture. It depends on the strength and flexibility of the material.

1.7.2. Thermal property

Thermal properties of nanocomposites are very important for their service life. Various thermal techniques such as TGA, DSC, DTA etc. are available for this purpose. Thermal stability of the nanocomposites is determined by using TGA. The thermal stability of the nanocomposites generally increases due to the restriction of thermal motion of the macromolecular chains on incorporation of nanomaterial in the polymer matrix. Also nanomaterials act as physical barrier, so the volatile products formed during the thermal decomposition process have to overcome longer zigzag path to escape the matrix. Moreover the nanomaterials may act as a superior insulator and assist the formation of char after the thermal decomposition. DSC is used to investigate the thermal transition behavior such as glass transition temperature and melting temperature. The glass transition temperature may be shifted to higher region due to the increased toughness and rigidity of the nanocomposites as compared to the pristine polymers.

1.7.3. Magnetic property

Recently magnetic nanomaterials taking tremendous attention in the polymer domain due to their potential applications in magnetic recording media, electrical devices, color imaging, heterogeneous catalysis, magnetic force microscopy as nanoprobes, microwave absorption materials and smart materials. Most of the shape memory materials are actuated by the direct heating, which have the adverse effect in the biomedical applications. Magnetic nanoparticles based nanocomposites have added advantages in this respect as shape memory materials. This type of shape memory materials can be actuated by the non-contact mode using the alternating magnetic field.

1.7.4. Biodegradation behavior

Biodegradable polymers have attracted great attention for the protection of natural wealthy environment. Again biodegradable shape memory polymers have potential application in biomedical field. The interesting and exciting aspect of polymer nanocomposites is their
significant improvement of biodegradability. The improved biodegradability may be due to the catalytic role of the nanomaterials in the biodegradation mechanism. The biodegradation process involves mainly in the four steps viz. water absorption, ester cleavage and formation of oligomeric fragments, solubilization of oligomer fragments and finally utilization of soluble oligomers by the bacteria. Thus any factor which increases the hydrolysis tendency of the polymer influences the biodegradation process.

1.7.5. Shape memory property

The following properties of SMP are very important and hence mentioned here.

*Shape fixity*

Shape fixity is proposed to depict the extent of a temporary shape being fixed in one cycle of shape memory test. It is similar to strain fixity and shape retention. Shape fixity \( (R_f) \) is equal to the amplitude ratio of the fixed deformation to the total deformation of the sample. The shape fixity is thus equal to the percentage of the ratio of fixed deformation to total deformation.

*Shape recovery*

Shape recovery \( (R_r) \) define how well an original shape can be memorized by SMP. The shape recovery of SMP is therefore percentage of the ratio of the deformation recovered by specimen in a complete cycle of test to the deformation taken place to the specimen in the first cycle.

*Recovery rate*

This parameter describes the speed i.e. the rate of recovery from a fixed temporary shape to its original shape during the recovery process of SMP under the application of appropriate stimulus. It can also be said as speed of recovery process or shape recovery speed.
1.8. Applications of shape memory polymers

SMP have different applications such as sensors and actuators, aerospace engineering, textile engineering, deployable structure, packaging, self-peeling reversible adhesive and biomedical field. SMP have wide applications in biology and medicine, especially for biomedical devices, which might open new medical procedure of minimally invasive surgery. The bulky SMP device can be inserted into the body in a small fixed shape by a small laparoscopic and the permanent shape can be recovered under the application of suitable stimulus. Again the biodegradable SMP can be used as short term implant as they are degraded to non toxic substances in the body environment. The different biomedical fields of applications are given below.

Clot removal device

SMP can be utilized for the treatment of ischemic stroke. The Maitland research group has developed SMP devices for the clot removal. These devices were designed to be delivered through a catheter and punctured the clot in a narrow form, and then actuated by the radiation into a clot-grabbing form for clot extraction (Fig. 1.5).

Fig. 1.5: (a) The device first punctures the clot, (b) activate to a form of coil shape on the distal side of the clot and (c) pulled to remove both the device and clot simultaneously (Reproduced from Small, W., et al. Laser-activated shape memory polymer intravascular thrombectomy device, Opt. Expr. 13 (20), 8204-8213, 2005)

Dialysis needle

SMP adapter for a kidney dialysis needle has been developed to decrease the hemodynamic stresses during dialysis. A SMP adapter has been proposed to pass through the dialysis needle in a compact form, thermally expanded upon heating to body temperature, and be
retracted when the procedure is completed (Fig. 1.6). Flow visualization experiments exhibited that the wall shear stresses were decreased by the adapter’s elimination of jet impingement.

**Fig. 1.6:** A dialysis needle (a) is shown to produce jet impingent of flow (b), however, with the SMP adapter (c) the turbulence of the flow is decreased (d) *(Reproduced from ref. 98)*

**Vascular stent**

SMP can be utilized as stent applications because of their less thrombogenesis and intimal hyperplasia, biodegradability and high elongation. Vascular stents are tiny tubular scaffolds used to retain the patency of an artery. They are extensively used in conjunction with transluminal angioplasty in the treatment of arterial stenosis to avoid acute vessel closure (Fig. 1.7).^{15}

**Orthodontic wire**

Orthodontics is an area in which polymeric materials are required for both their esthetic appeal and shape-memory effect (Fig. 1.8). Nakasima et al. proposed the concept of using a thermoresponsive SMP arch wire in orthodontic braces for aligning teeth and noting that the recovery force was sufficient for moving teeth and that the SMP was more aesthetically appealing than a metallic archwire.^{99} Jung and Cho reported the use of shape-memory polyurethanes for archwires.^{100}
Fig. 1.7: The representative image of the vascular stents (*Reproduced from Small, W., et al. Shape memory polymer stent with expandable foam: a new concept for endovascular embolization of fusiform aneurysms, IEEE Trans. Biomed. Eng. 54 (6), 1157-1160, 2007*)

Fig. 1.8: The utilization of shape memory wire in orthodontic application (*Reproduced from ref. 100*)

*Suture*

SMP can be used as surgical suture, which will play a significant role in endoscopic surgery.\(^\text{14}\) Generally the sutures are to be stitched very carefully. They may damage the cells of the skin if the threads are stitched very tightly; on the other hand, if the threads are too loose, it will not do the function properly. SMP if used, the threads can be stitched loosely and when the threads come into contact with the body temperature, it tightened as required (Fig. 1.9).
1.9. Short review on shape memory polyurethane nanocomposites

Introduction

Nowadays shape memory polyurethane nanocomposites are widely used to fulfill the demand of advanced applications such as aerospace engineering, automotive engineering, self deployable structure etc. The segmented polyurethanes usually show the shape memory behaviors. The hard and soft segments are responsible for the shape memory effect of the polyurethanes. The shape memory behavior of polyurethanes can be tuned by changing the nature and composition of reactants as well as the ratio of hard to soft segment. The observed shape recovery and shape fixity of such polyurethanes are not sufficient to meet the demands for some advanced applications. From the literature it has been seen that on incorporation of nanomaterials the shape memory behaviors of the polyurethanes increased. It is reported that due to the presence of nanomaterials the stored strain energy in the system increased and thereby increased the shape recovery and shape fixity.\textsuperscript{71, 101} Moreover the shape recovery speed and reproducibility of the nanocomposites increased. Different nanomaterials such as nanoclay, metal oxides, carbon nanotubes, carbon nanofiber etc. can be used for the preparation of polyurethane nanocomposites. The performance including the shape memory behaviors of the nanocomposites depend on the size and shape, aspect ratio, surface modification etc. of the nanomaterials. Furthermore, the non contact actuation of shape memory polymer is more important in some specific applications. Incorporation of suitable nanomaterials in the shape memory polymer helps to actuate them by the magnetic field, electric field, radiation etc. in non contact mode.\textsuperscript{22, 23} The research in this area is gaining importance in the recent times.
Background

Meng et al. studied MWCNT based polyurethane nanocomposites that exhibited enhanced recovery ratio and recovery force. According to the report MWCNT helped to store the internal elastic energy during stretching and fixing. Cao et al. reported that the shape recovery force of shape memory polyurethane can be increased significantly with the addition of small amount of reactive nanoclay particles. Jang et al. reported that 2 wt% surface modified silica nanoparticles/polyurethane nanocomposites showed over 99% shape fixity. Jana et al. reported the enhancement of mechanical and shape memory properties of polyurethane nanocomposites reinforced with poly(ε-caprolactone)-grafted carbon nanotubes. Luo et al. reported the path dependent and multi-shape recovery of polyurethane/cellulose whisker nanocomposites. Haghayegh et al. studied shape memory, thermal and mechanical properties of polyurethane/clay nanocomposites. From the study it was found that on incorporation of nanoclay shape recovery behavior found to enhance. Recently authors studied the shape memory behaviors of polyurethane nanocomposites by employing non contact actuation strategy. Razzaq et al. studied the shape recovery behavior of magnetite filled polyurethane nanocomposites. Sahoo et al. reported that carbon nanotubes based polyurethane nanocomposites exhibited the good shape recovery (90-95%) under the actuation of electric field. Yoo et al. reported the carbon nanotube based polyurethane nanocomposites as electro-active shape memory materials. The prepared materials exhibited the enhanced mechanical and shape memory behaviors. Cai et al. reported the synthesis and properties of magnetic responsive shape memory Fe$_3$O$_4$poly(ε-caprolactone)-polyurethane nanocomposites.

Preparation

The polyurethane nanocomposites are also prepared by utilizing the similar technique as discussed in subsection 1.5.3.2. These nanocomposites can be prepared by in situ or ex situ polymerization technique. The nanocomposites prepared by the in situ polymerization technique generally provide high tensile strength, high thermal stability etc. This is due to the well dispersion of nanomaterials in the polymer matrix. Meng et al. prepared the shape memory polyurethane by the pre-polymerization technique taking polycaprolacton diol (PCL) for soft segment, and diphenylmethane-4,4-diisocyanate (MDI) and molecular chain extender 1,4-
butanediol for hard segment. Jang et al. prepared the polyurethane tacking the poly(tetramethylene glycol), isophorone diisocyanate, butyl amine and glycidol by the pre-polymerization technique. Deka et al. prepared the shape memory polyurethane using the PCL for soft segment, and toluene diisocyanate, bio-based chain extender monoglyceride of the Mesua ferrea L. seed oil and multifunctional moiety glycerol for hard segment by the pre-polymerization technique. The nanocomposites of the same were prepared by the in-situ polymerization method using the acid treated MWCNT. Choi et al. reported the preparation of graphene based shape memory polyurethane nanocomposites. In this preparation the dispersed graphene was first reacted with PCL and then reacted with the required amount of MDI and finally reacted with the chain extender butanediol under proper conditions. Chung et al. reported the preparation of nanocomposites of covalently bonded surface modified montmorillonite nanomaterials with the polyurethane by the melt-mixing method. Lee et al. reported the preparation of polyurethane from PCL, MDI and 1,4-butanediol by two step polymerization method and then polyurethane/SWCNT is prepared by the solution polymerization technique. Cai et al. prepared the Fe$_3$O$_4$ based polyurethane nanocomposites by the in situ polymerization technique at molar ratio of polycaprolacton diol: diphenylmethane-4,4-diisocyanate:1,4-butanediol=1:4:3 with different loading of Fe$_3$O$_4$.

Characterization

The shape memory polyurethane nanocomposites are characterized by the different techniques as discussed in section 1.6. The presence of different types of interaction between polyurethane and the nanomaterial of the nanocomposites can be characterized by the FTIR study. The shifting and broadening of the peaks implies the interaction of nanomaterials with the polymer matrix. The transmission electron microscopic study also confirmed the formation of nanocomposites. The homogeneous distribution of nanomaterials in the polymer matrix confirmed the presence of interactions with the polymer matrix. The thermal behaviors of the polyurethane nanocomposites are characterized by the TGA and DSC analyses. The thermal stability is determined by using the TGA analysis. The thermal transition behaviors are characterized by the DSC study. The $T_g$ and $T_m$ are very important parameters for the shape memory polyurethane nanocomposites because they can act as switching temperatures. The
shape memory properties of the nanocomposites are evaluated by using the bending or stretching technique as discussed in subsection 1.6.11. Rana et al. characterized the prepared polyurethane-carbon nanotube nanocomposites by XRD, SEM, TEM, TGA and DSC studies. The shape memory behavior was studied as thermo-responsive shape memory materials using the bending test. Jang et al. characterized the surface modified silica particles based shape memory polyurethane by FTIR and TEM studies. The shape memory behaviors were studied by the thermo-mechanical cyclic test. Cai et al. characterized the polyurethane–carbon nanotube hybrid by the XRD, TGA and DSC. The shape recovery was studied (at 30 V and 0.1 A) as electro-active noncontact actuation method. Yoo et al. characterized the polyurethane-carbon nanotube nanocomposites by using DSC, SEM and AFM. The authors also studied the shape recovery using electric field of 50 V.

Property

The properties required to study for polyurethane nanocomposites are same as discussed for pristine polyurethanes. However, the polyurethane nanocomposites showed better performance compared to their pristine analogs. The properties of the polyurethanes were described in section 1.7.

The tensile strength of the polyurethane nanocomposites is found to be greater than the polyurethane matrix due to the homogeneous distribution of the nanomaterials in matrix. The elongation at break is generally decreased, though it may remain constant or even increased in the nanocomposites. The decrease in elongation is mainly due to the molecular restriction of polymer chains by the rigid nanomaterials. Deka et al. reported the enhancement of tensile strength of hyperbranched polyurethane/clay nanocomposites. Zhou et al. reported that the tensile strength of MWCNT/polyurethane nanocomposites increases with increase of content of surface modified MWCNT. The polyurethane nanocomposites exhibited better impact and scratch resistance as compared to the pristine polyurethane. This is due to good toughness and high elasticity of the polyurethane nanocomposites. The nanocomposites possess enhanced chemical resistance as compared to the neat polymers.

The polyurethane nanocomposites exhibited good thermal stability. The thermal stability of the system increased due to the increased compactness of the system as well as the presence of
highly thermo-stable nanomaterials. The $T_g$ and $T_m$ are the two important thermal transition parameters for polyurethane nanocomposites and are found to be altered from the pristine system. The changes of these parameters resulted changes in performance of the nanocomposites. Xu et al. reported the enhancement of thermal stability and the melting enthalpy ($\Delta H$) of shape memory polyurethane/silica nanocomposites.\textsuperscript{117} Suen et al. reported that $T_m$ and $T_g$ of soft segment increased with the increase of ZnC in the polyurethane.\textsuperscript{118}

The polyurethane nanocomposites showed enhanced shape recovery and shape fixity as compared to the pristine one. The shape recovery speed is also increased in the nanocomposites. This is due to various interactions in the system and thereby stored more strain energy in the system. Cai et al. reported that the shape recovery time decreased with the increase of the content of Fe$_3$O$_4$ nanoparticles in the polyurethane nanocomposites under the actuation of magnetic field.\textsuperscript{111} Cho et al. reported the electro-active shape memory behaviors of MWCNT based polyurethane nanocomposites.\textsuperscript{119}

**Application**

Shape memory polyurethane nanocomposites have potential applications in the different fields especially in the biomedical domain. It can be utilized in packaging, aerospace, automotive, sensors and actuators, robotics, textile etc. The polyurethane nanocomposites have potential application in the biomedical field such as minimally invasive surgery, drug delivery systems, tissue engineering etc. Ahmad et al. reported that polyurethane based shape memory polymer actuators have possible application in medical pressure bandages where gradient pressure is required between the ankle and the knee for treatment of leg ulcer.\textsuperscript{120} Ahn et al. reported the shape memory polyurethane membrane where the pore size can be tuned by repeating heating and cooling.\textsuperscript{121} Paik et al. reported the application of conducting shape memory polyurethane as actuators.\textsuperscript{122} Jung et al. reported a polyurethane of 4,4'-methylene bis(phenylisocyanate), poly(ε-caprolactone)diol (PCL) and 1,4-butanediol for the orthodontic application.\textsuperscript{100} Baer et al. studied that shape memory polyurethane may be suitable for the application in stents or clot extractors.\textsuperscript{123} A few applications of shape memory polyurethanes are shown in Fig. 1.10
1.10. **Scopes and objectives of the present investigation**

From the above discussion, thus, it has been found that shape memory behaviors of different polyurethanes and their nanocomposites have been studied. However the shape memory behaviors of Fe$_3$O$_4$, functionalized MWCNT and Fe$_3$O$_4$ decorated MWCNT based vegetable oil modified hyperbranched polyurethane nanocomposites are rare to find out in the literature, though they have strong potential for the same.

![Fields of application for shape memory polyurethane nanocomposites](image)

**Fig. 1.10:** Fields of application for shape memory polyurethane nanocomposites

Further, microwave actuated shape memory studies of such nanocomposites have not been explored till date, though microwave energy has largely used recently in different chemical transformations and also it could be used as a noncontact stimulant for the shape memory study. Thus the main objective of the present investigation is to develop a vegetable oil modified hyperbranched polyurethane nanocomposite as a shape memory material with tuning performance. This main objective is associated with the following sub-objectives.

1. To synthesize vegetable oil based hyperbranched polyurethanes with different compositions and to characterize them by different spectroscopic and analytical techniques.
2. To modify the above hyperbranched polyurethanes for improvement of their properties and to characterize the modified polymers by different spectroscopic and analytical techniques.
3. To prepare nanocomposites of the modified hyperbranched polyurethane with the Fe$_3$O$_4$ nanoparticles and to characterize them.
4. To prepare nanocomposites of the modified hyperbranched polyurethane with the functionalized MWCNT and to characterize them.
5. To prepare nanocomposites of the modified hyperbranched polyurethane with the magnetic nanoparticles (Fe$_3$O$_4$) decorated MWCNT and to characterize them.
6. To study the various properties such as physical, thermal, mechanical, shape memory etc. of the synthesized hyperbranched polyurethanes, modified hyperbranched polyurethanes and their nanocomposites.
7. To optimize the performance characteristics of the nanocomposites for their shape memory applications.

1.11. Plans of the present work

To fulfill the above objectives the following plans of work are demonstrated.
1. Vegetable oil based hyperbranched polyurethanes with different compositions will be synthesized by $A_2 + B_3$ approach using high the dilution and slow addition technique.
2. The synthesized polyurethanes will be modified with the epoxy resin.
3. The synthesized and the modified hyperbranched polyurethanes will be characterized by different spectroscopic techniques such as FTIR, XRD, NMR etc.
4. The nanocomposites of the synthesized hyperbranched polyurethanes and the modified hyperbranched polyurethanes with Fe$_3$O$_4$ and functionalized MWCNT will be prepared by in-situ polymerization technique as reported in the literature.
5. The magnetic nanoparticles (Fe$_3$O$_4$) decorated MWCNT/hyperbranched polyurethane nanocomposites will also be prepared by in-situ polymerization technique.
6. The prepared nanocomposites will be characterized using FTIR, XRD, TEM, SEM etc. to determine the presence of various interactions and the morphology of the nanocomposites.
7. The performance characteristics of the characterized nanocomposites will be investigated by determination of physical properties, tensile strength, elongation at break, scratch hardness,
impact resistance, thermal properties like glass transition temperature, thermo-stability etc.,
chemical resistance characteristics in different chemical media and shape memory properties.
8. Shape memory properties will be studied by stretching and bending techniques.
9. A comparative study on the performance characteristics will be conducted to find out the best
nanocomposite among the above.
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