# Toughening of Bone Cement Using Nanoparticle: The Effect of Solvent

**Nira Misra,[1] Govinda Kapusetti,[1] Shilpa Jaiswal,[1] Pralay Maiti[2]**

[1]*School of Biomedical Engineering, Institute of Technology, Banaras Hindu University, Varanasi 221 005, India*
[2]*School of Materials Science and Technology, Institute of Technology, Banaras Hindu University, Varanasi 221 005, India*

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**ABSTRACT:** Drawbacks of poly(methyl methacrylate) (PMMA)-based bone cement as a grouting agent for *in vivo* fixation of orthopedic and dental implants such as considerable low mechanical strength have been improved using nanotechnology. Bone cement-layered silicate nanocomposites have been prepared without any heat treatment in the presence of polar (dimethyl formamide, DMF) and nonpolar (benzene) solvents. Solvents have been removed completely from the bone cement after its preparation. Nanostructure is very much dependent on the solvent used for nanocomposite preparation, and benzene-based nanocomposites are highly intercalated, whereas DMF-based nanocomposites do not exhibit intercalation. Thermal stability of bone cement has improved in the presence of nanoclays. The relative enhanced interaction in case of benzene-based nanocomposites has been shown through FTIR and UV–vis studies. The significant improvement in modulus and toughness of bone cement has been demonstrated in the presence of minimum amount of nanoclay for benzene-based nanocomposites, whereas no change in modulus and reduced toughness have been observed for DMF-based nanocomposites. The decrease of contact angle has been witnessed with increasing nanoclay concentration indicating better hydrophilic materials suitable for biomedical applications for greater cell growth. The reason for varying property enhancement in different solvents has been discussed considering the polarity effect and interactions.  J Appl Polym Sci 121: 1203–1213, 2011

**Key words:** bone cement; nanocomposite; mechanical properties; solvent; adhesion

## INTRODUCTION

Poly(methyl methacrylate) (PMMA) is widely used in biomedical applications from the early development of biomaterials,[1–3] as it has excellent biocompatibility,[4–7] physical properties, and good hydrophilic/hydrophobic balance required for living systems. PMMA is used in various biomedical applications mainly (i) orthopedic and dental applications; (ii) contact and intraocular lenses; (iii) filler material in different bone cavities, etc. One of the world famous orthopedic surgeons as well as scientist John Cherli was the first person successfully introduced PMMA as a bone cement in total hip replacement surgery.[8] PMMA is the major component in bone cement. PMMA tolerates the capability to resist the fatigue-related cracking.[9] Now, the cement is currently being used in hip and knee replacement surgeries. Cement is applied as a grouting agent between the prosthesis.[10] In a cemented total joint replacement, the interface between a prosthetic implant and the bone is filled with viscous PMMA-based bone cement, whose primary function is to provide a stable interface between the prosthetic implant and the surrounding bone by forming a mechanical bond between the bone and implant. It acts as a stress transfer agent between metalic implant and bone. Therefore, it increases the load carrying capability of the implant. It provides rapid fixation of prosthesis for patient to enable the artificial implant in hours after the insertion of bone cement.[11] In total joint replacement, the use of cemented hip prosthesis gives excellent clinical results, and the success rate increases up to 89–96% in last 6–18 years.[12]

Bone cement has lot of clinical advantages, particularly in orthopedics, but still it cannot fulfill all the requirements of patient because of the lack of enough mechanical properties.[13] In general, the cemented total hip implants undergo cyclic loads of up to five to eight times of the body weight.[14] Under high cyclic loads on prosthesis, debonding takes place between bone cement and implant or bone and bone cement resulting in failure of prosthesis.[15,16] The most common failure of bone cement is

*Correspondence to:* P. Maiti (pmaiti.mst@itbhu.ac.in).
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**TABLE I**
**Chemical Compositions of Bone Cement**

| S. no | Component | Chemical | Present (w/w) | Function |
|---|---|---|---|---|
| 1 | Solid component | Polymethyl methacrylate | 88.85 | |
| | | Benzoyl peroxide | 2.05 | Initiator |
| | | Barium sulfate | 9.10 | Radiopaque agent |
| 2 | Liquid component | Methyl methacrylate | 98.50 | |
| | | Hydroquinone | 75 (ppm) | Stabilizer |
| | | *N*,*N*-Dimethyl-*p*-toluidine | 1.50 | Promoter |

fatigue failure,[17,18] which is initiated by microcracking on cement mantel leading to aseptic loosing.[19–22] Repetition of a surgery is very painful, time consumption, and economical burden to the patient. To overcome this failures, many experts all over the world have put efforts to enhance the mechanical properties of bone cement by many ways mainly by increasing the cement mantel thickness, but it is not a suitable method as it offers large gap between bone and implant, and second, one has to reinforce the bone cement matrix with suitable filling material to resist the growth of microcracks. Different types of reinforcing materials may have been incorporated to bone cement matrix to improve the mechanical properties and fracture toughness of the bone cement, for example, kelver fibers have slightly improved the toughness at low percentage of fiber reinforcement but the modulus was not changed[23]; polyethylene fibers have offered significant enhancement in toughness but not the modulus.[24] On the other hand, carbon fibers have improved significantly all the mechanical properties.[25,26] Hydroxyapatite (HA) enhanced the fracture resistance, flexural modulus, and yield stress up to certain content. Beyond a certain limit, properties undergo deterioration because of the accumulation of HA. In addition, HA affects the cement porosity[27] and reduces flexural strength and flexural modulus.[28] Steel fibers have increased the modulus and toughness,[29] and titanium fibers have improved the tensile and fracture properties of bone cement.[30,31] Glass fibers have slightly been improved the modulus but toughness was reduced with respect to pure bone cement[32]; graphite fibers have increased the stiffness twofold without compromising the flexural strength of the material, but the compressive strength decreased significantly.[33]

Nanotechnology in present years is rapidly developing with potential to become an essential element in our everyday lives. The principal difference between nanosize particles and their micron-size counterpart is of greatly increased surface area to volume ratio. The reinforcement of nanoparticle in the biomaterial gives not only enhancement of mechanical, physical, and biological properties of the material but also reduces the detrimental effects caused by micron-size particles.[34–36] In this work, we used nanoclay (layered silicate) as filler material to reinforce the bone cement matrix to enhance the mechanical properties, as nanoclay is a biocompatible and economically viable. The effect of solvents during bone cement/composite preparation has been investigated to verify the property improvement in different solvents-derived nanocomposites.

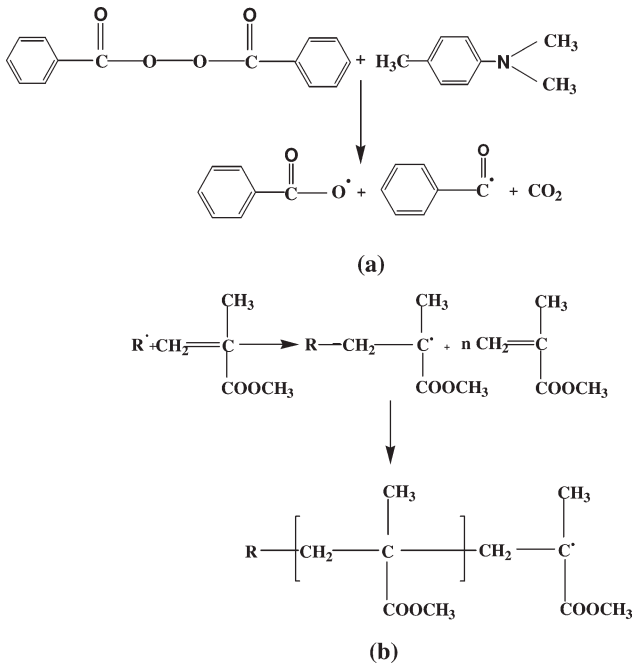
## EXPERIMENTAL

### Materials

Commercially available (Jhonson & Jhonson, Depy CMW-1) bone cement was used in this work. The bone cement is two-pack systems of finely divided white powder and a colorless liquid. The powder is composed of PMMA and benzoyl peroxide to initiate the cement polymerization when the powder and liquid components are mixed. Barium sulfate ($BaSO_4$) was used as radiopaque agent. The liquid was composed of methyl methacrylate monomer, hydroquinone, used as stabilizer to prevent premature polymerization, which may occur when the liquid is exposed to heat or light, and *N*,*N*-dimethyl-*p*-toluidine to promote cement polymerization. Table I shows the chemical composition of bone cement and solid and liquid components. An organically modified clay, Cloisite 30B [bis(hydroxyethyl)methyl tallow ammonium ion exchanged montmorillonite], purchased from Southern Clay Products (Gonzales, TX), was used as the nanofiller. Benzene (nonpolar) and *N*,*N*-dimethyl formamide (DMF) (polar) solvents were purchased from Merck, India, and were used as solvents for proper mixing of bone cement.[37]

### Preparation of bone cement nanocomposite

Bone cement samples were prepared by mixing powder and liquid components manually[37] with the help of glass rod in Petri dish for 2 min at room temperature. Nanocomposites have been prepared using different percentages of nanoclay (1, 2, and 4 wt %) with respect to the powder component of bone cement using both the solvents separately. The nanoclay was added to the solvent followed by the



**Scheme 1** Polymerization process in bone cement: (a) initiation reaction and (b) chain growth reaction.[37]

liquid and powder components in a Petri dish and mixed simultaneously with the help of a glass rod for 2 min at ambient temperature. Polymerization is one of the major phenomena during mixing in which initiator plays an important role. Scheme 1 shows the polymerization reaction with the help of initiator (benzoyl peroxide) and promoter (*N*,*N*-dimethyl-*p*-toluidine).

Henceforth, we will use the notation of BC-B, BC-D, BC-B-NC, and BC-D-NC for bone cement prepared from benzene, bone cement prepared from DMF, bone cement nanocomposite prepared from benzene, and bone cement nanocomposite prepared from DMF, respectively. The number after NC indicates the weight percentage of nanoclay used for nanocomposite preparation. After polymerization, the samples have been dried initially at room temperature for 2 days in air followed by its drying under reduced pressure at 80°C for 24 h.

## Characterization

### Light transmission

Transparency of the bone cement was examined with the help of digital camera using thin films of bone cement and bone cement nanoclay composites for comparison purpose. Pure bone cement and 4 wt % nanoclay composite thin films of 0.06-mm thickness, 3.5-mm length, and 2.5-mm width have been prepared using both benzene and DMF through solvent casting technique. The light transmittance was also quantitatively calculated using photodetector.

### UV–visible spectroscopy

The UV–visible measurements have been carried out by using Shimadzu (UV-1700), Pharma Speck, UV–Vis spectrophotometer operating in the spectral range of 200–1100 nm. Transparent thin film samples have been prepared from bone cement and its nanocomposite using benzene and DMF solvents of ~30-μm thickness on quartz plates to obtain good absorbance.

### X-ray diffraction

The degree of bone cement intercalation and/or exfoliation of layered silicate nanoclay was examined by using an advance wide-angle X-ray diffractometer with Cu Kα radiation and a graphite monochromator (wavelength, $\lambda = 0.154$ nm, Bruker AXS D8, Germany). Thin sheet of the samples was placed on a quartz sample holder at room temperature and was scanned at diffraction angle 2θ from 1° to 50° at the scan rate of 1°/min.

### FTIR

FTIR technique was applied to detect the functional group and to understand the nature of interaction between bone cement and nanoclay. FTIR was performed in absorbance mode at room temperature from 400 to 4000 $cm^{-1}$ wavenumber using Nicolet 670 FTIR with a resolution of 4 $cm^{-1}$. The bubble-free thin films were prepared by compressing polymer melt in between cover slips with a special care.

### TG/DTA

Thermal stability of bone cement and its nanocomposites using benzene and DMF solvents was examined by using thermogravimetric analyzer (TGA) (Mettler-Toledo) fitted with differential thermal analyzer (DTA). Data were taken from 40 to 550°C. All the experiments were performed using the heating rate of 20°C/min in nitrogen atmosphere.

### Mechanical properties

Young's modulus and toughness were determined using rectangular strips of $1 \times 15 \times 70$ $mm^3$, prepared by compression molding technique, by using Instron 3369 tensile testing machine. Samples were stretched uniaxially at a rate of 5 mm/min. Several samples were tested to get good error estimates.

### Contact angle

Contact angle measurement for biomedical implant material is very important as it gives the information about the hydrophilicity of the material. Ultimate

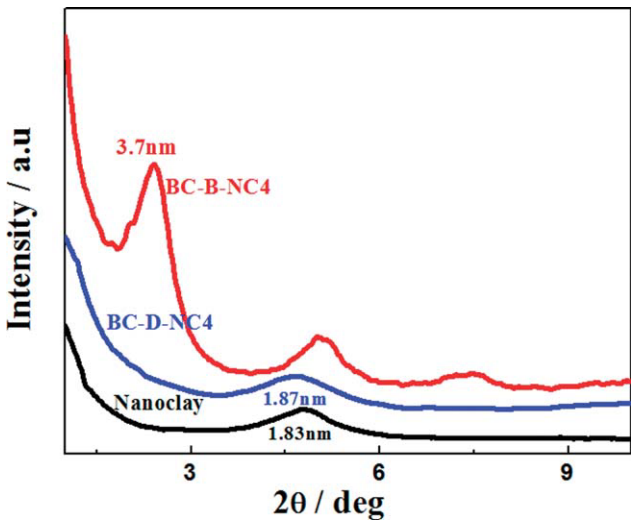



**Figure 1** X-ray diffraction patterns of indicated (1) nanoclay, (2) BC-D-NC4, bone cement nanoclay composite in DMF solvent, and (3) BC-B-NC4, bone cement nanoclay composite in benzene solvent. *Y*-axis has been shifted for better clarity of the diffraction peaks. The numbers indicate $d_{001}$-spacing in nanometers for the respective system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

result can be achieved through adhesion of the implant material with body system and body fluid. Kruss F-100 tensiometer was used for contact angle measurement for thin strip ($1 \times 10 \times 20$ mm$^3$) of pure bone cement and its various nanocomposites at room temperature in water medium.

## RESULTS AND DISCUSSION

### Nanostructure

Figure 1 shows the XRD patterns of the nanoclay and its nanocomposites with bone cement prepared using benzene and DMF as solvents. Low-angle XRD studies provide the information about nanostructure of the material. The diffraction peak (001 plane) of nanoclay was appeared at $2\theta = 4.8^\circ$ corresponding to the *d*-spacing of 1.83 nm. The 001 peak was observed for BC-B-NC4 and BC-D-NC4 at 2.4° and 4.7°, corresponding to the *d*-spacing of 3.7 and 1.87 nm, respectively. Diffraction peak has been shifted toward low angle region, and basal plane of silicate layers is enlarged more than two times for bone cement composites prepared using benzene (BC-B-NC4) because of the insertion of polymer chains of bone cement into nanoclay galleries. However, in case of BC-D-NC4, diffraction peak remain unchanged, suggesting no alteration of *d*-spacing of silicate layers for nanocomposite prepared using DMF. Therefore, huge amount of intercalation takes place in benzene as media, whereas no intercalation occurs in DMF solvent for the same set of bone cement and nanoclay. The extent of intercalation of polymer chains of bone cement exhibits strong solvent dependency phenomena. The plausible reason may lie on the polarity of the solvent. Highly polar DMF can interact strongly with PMMA chains causing less interaction of polymer–organically modified nanoclay, whereas nonpolar benzene cannot interact with PMMA molecules, thereby having enough scope of stronger interaction between bone cement and nanoclay. Better interaction between polymer and organically modified nanoclay leads to greater intercalation for benzene case, whereas PMMA chain strongly interacts through dipolar interaction with DMF solvent causing less intercalation. Moreover, the intense 001 peak of BC-B-NC4 followed by 002 and 003 plane strongly supports the ordered stacking of nanoclay layers in nanocomposites. It is noteworthy to mention that PMMA nanocomposite is a rare case where up to third order of reflection is prominent.

### Structure

XRD analyses were carried out for pure bone cement and nanoclay dispersed in bone cement. Bone cement showed peaks assigned to $BaSO_4$ (matched with JCPDS file)[25] and an amorphous halo responsible for amorphous PMMA in bone cement. Figure 2(a,b) shows XRD patterns of the bone cement and its nanocomposite in benzene and DMF solvents, respectively. Interestingly, diffraction peaks of BC-B-NC4 were slightly shifted toward lower angle when compared with BC-B in Figure 2(a), whereas the diffraction peaks shifted to higher angle region and for BC-D-NC4 with respect to BC-D in Figure 2(b). Table II shows the *d*-spacing of bone cement and its nanocomposite prepared using benzene as solvent. The *d*-spacing has increased in BC-B-NC4, indicating the fact that defects have been introduced into the crystal of $BaSO_4$ in the presence of nanoclay. On the contrary, *d*-spacing of BC-D-NC4 was almost constant when compared with BC-D system (Table III), indicating similar structure before and after the addition of nanoclay. Structural analyses exhibit that the clay has been introduced into the system in a better way when the composite was prepared using benzene as solvent, whereas composite prepared using DMF has similar structure even after the addition of nanoclay.

### Optical transparency

Light transmission through a material reveals the optical clarity of the material, and it gives the information about its transparency as well. Figure 3 shows the optical images of thin films of pure bone cement and its 4 wt % nanoclay composite prepared

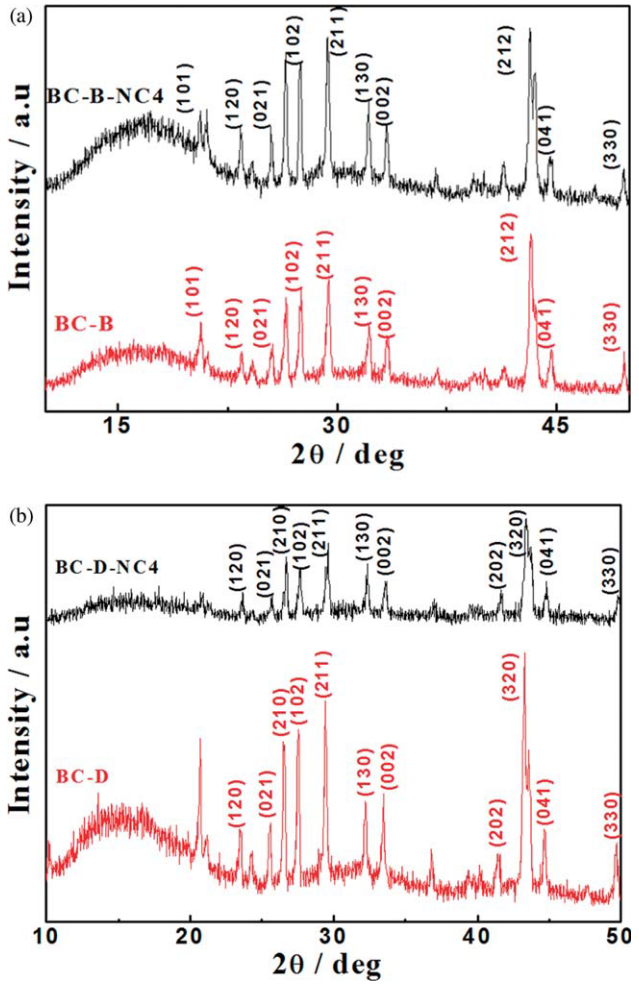



**Figure 2** (a) XRD patterns of the bone cement and its composite using benzene as solvent, in indicated samples. (b) XRD patterns of bone cement and its nanoclay composite using DMF solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

using benzene and DMF solvents. It is clear that there is no difference in contrast between pure and composite thin films prepared using both benzene and DMF. Visibly, the films (pure and nanocomposite) are white when they are prepared using benzene and slight orange while prepared using DMF. This result reflects that there is no considerable loss of optical transparency in nanocomposite when compared with pure bone cement. Quantitatively, we have measured the transparency by getting the intensity of light passing through the polymer film when the same intense light falls on every film. The intensity of the transmitted light was measured by using a photodetector in the other side of the polymer film. The values are 450 and 420 for BC-B and BC-B-NC4, respectively, whereas 410 and 370 for BC-D and BC-D-NC4, respectively. From these values, it is clear that nanocomposite film prepared using benzene is more transparent, and the transparency did not loose much in the presence of nanoclay, especially in benzene-derived nanocomposites.

**TABLE II**
***d*-Spacing of Different Planes of Bone Cement and Its Nanocomposite Prepared Using Benzene**

| | | BC-B | | BC-B-NCB | |
|---|---|---|---|---|---|
| S. no | Plane | 2θ | *d*-space (Å) | 2θ | *d*-space (Å) |
| 1 | (101) | 20.69 | 4.17 | 20.59 | 4.28 |
| 2 | (120) | 23.44 | 3.69 | 23.33 | 3.71 |
| 3 | (021) | 25.54 | 3.39 | 25.44 | 3.40 |
| 4 | (102) | 27.55 | 3.15 | 27.45 | 3.16 |
| 5 | (221) | 29.44 | 2.95 | 29.34 | 2.96 |
| 6 | (130) | 32.19 | 2.70 | 32.18 | 2.70 |
| 7 | (002) | 33.45 | 2.60 | 33.55 | 2.61 |
| 8 | (212) | 43.26 | 2.03 | 43.2 | 2.04 |
| 9 | (041) | 44.64 | 1.97 | 44.56 | 2.00 |
| 10 | (330) | 49.69 | 1.78 | 49.59 | 1.79 |

**TABLE III**
***d*-Spacing of Different Planes of Bone Cement and Its Nanocomposite Prepared Using DMF Solvent**

| | | BC(D) | | BC+NC(D) | |
|---|---|---|---|---|---|
| S. no | Plane | 2θ | *d*-space (Å) | 2θ | *d*-space (Å) |
| 1 | (120) | 23.44 | 3.69 | 23.64 | 3.66 |
| 2 | (021) | 25.55 | 3.39 | 25.76 | 3.37 |
| 3 | (210) | 26.49 | 3.82 | 26.71 | 3.24 |
| 4 | (102) | 27.55 | 3.15 | 27.65 | 3.13 |
| 5 | (221) | 29.44 | 2.95 | 29.63 | 2.92 |
| 6 | (130) | 32.19 | 2.70 | 32,40 | 2.68 |
| 7 | (002) | 33.45 | 2.60 | 33.66 | 2.59 |
| 8 | (212) | 43.26 | 2.03 | 43.46 | 2.02 |
| 9 | (041) | 44.74 | 1.97 | 44.84 | 1.96 |
| 10 | (330) | 49.69 | 1.78 | 49.80 | 1.78 |

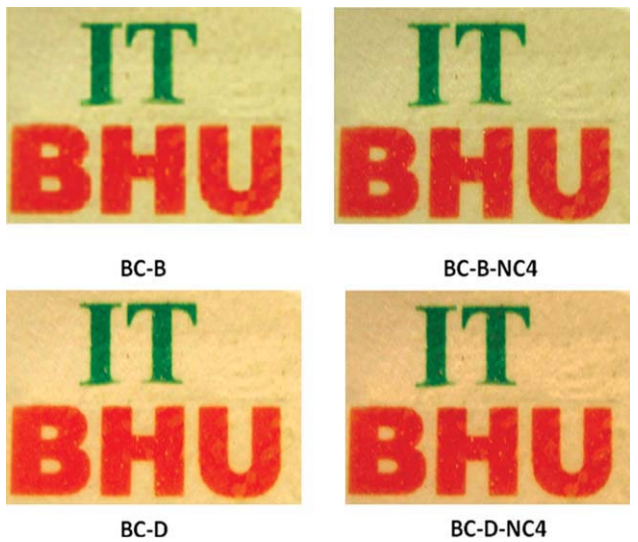



**Figure 3** Light transmission (optical images) through thin films of bone cement and nanoclay composites for indicated samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

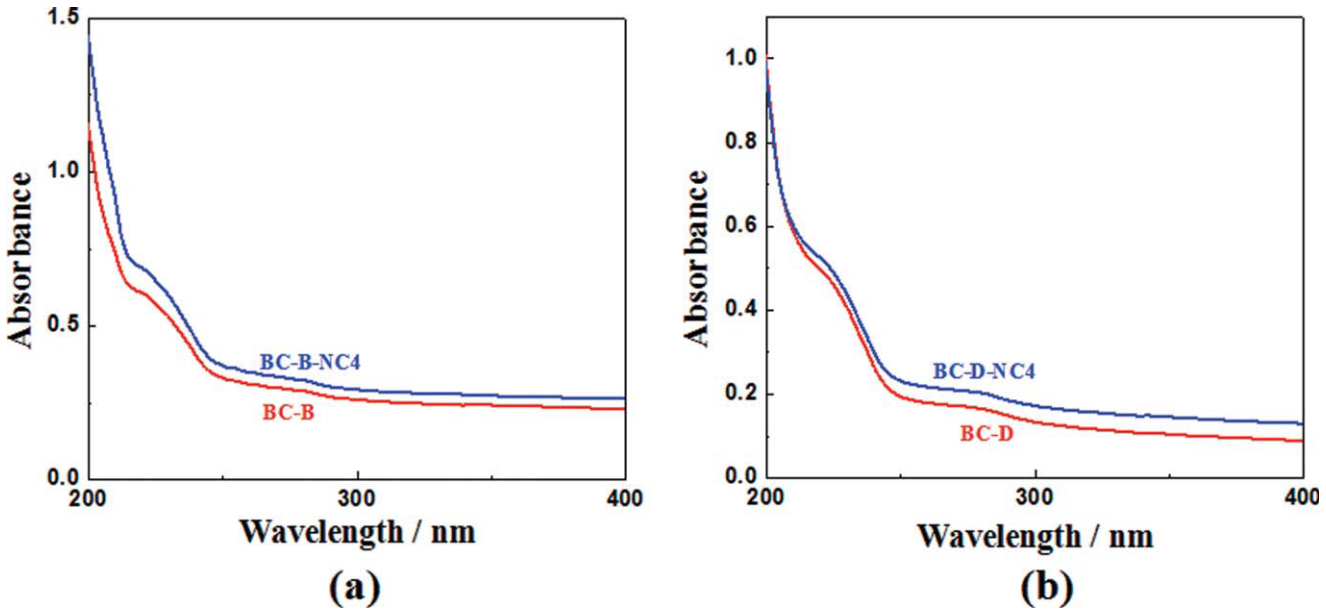



**Figure 4** UV/Vis spectra of bone cement and its nanocomposites in (a) BC-B, pure bone cement, and BC-B-NC4, 4% nanoclay bone cement composite using benzene solvent, and (b) BC-D, pure bone cement, and BC-D-NC4, 4% nanoclay bone cement composite using DMF solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

### UV–visible spectroscopy

The absorbance of light energy by polymeric materials in UV–visible region is mainly attributed to electronic transitions between σ, π, and n energy levels from ground state to higher energy state. The UV–vis scans in the wavelength range of 200–1100 nm for bone cement and its nanocomposites using benzene and DMF solvents have been shown in Figure 4(a,b), respectively. One peak has been observed nearly at 218 nm in all scans is due to $n \rightarrow \sigma^*$ transition for PMMA.[38] Another absorbance peak has been observed around 273–280 nm may be attributed to $\pi \rightarrow \pi^*$ transition, which arises from unsaturated bonds mainly >C=O.[39] There is no shifting of peak position of nanocomposite of BC-D-NC4 in either side may be attributed to noninteracting nature of the nanocomposite [Fig. 4(b)], whereas the high intense peak and slight shifting of peak toward lower wavelength region in nanocomposite (BC-B-NC4) indicate strong interaction between bone cement and nanoclay composite derived from benzene [Fig. 4(a)].[38]

### Interaction through spectroscopy

Figure 5(a,b) shows the FTIR spectra of the bone cement and its nanocomposites prepared using benzene and DMF as solvents. Peak of carbonyl (>C=O) stretching frequency was observed at 1726 $cm^{-1}$ in BC-B, and this peak has been shifted to lower wavenumber region to 1717 and 1700 $cm^{-1}$ for BC-B-NC2 and BC-B-N4, respectively, because of favorable interaction between bone cement and nanoclay. The shifting of peak position gradually increases with increasing nanoclay content in the composite, indicating a better interaction in the presence of greater amount of nanoclay. In contrast, there is no shifting at all for nanocomposites prepared using DMF for same amount of nanoclay [Fig. 5(b)], suggesting insignificant interaction between bone cement and nanoclay for DMF-derived nanocomposites. This evidence further strengthens the nanostructural observation that the extent of intercalation strongly depends on the interaction between the two components while prepared using two different kinds (polarity) of solvent. It is expected that the interaction between DMF and PMMA is stronger because of dipole–dipole interactions. The interaction is purely physical and stronger in case of PMMA-DMF as the dipole of DMF is much higher when compared with benzene. In addition, there is an extra peak at 2377 $cm^{-1}$ for BC-D-NC4, which does not appear in benzene-based nanocomposites, and the cause of the appearance of this peak is unknown but the said peak is reproducible.

### Thermal stability

Thermal stability can be measured when the specimens are subjected to continuous heating program and monitoring its weight like in TGA. Figure 6(a,b) shows the weight loss behavior of pure bone cement and its nanocomposites as a function of temperature. The temperature corresponding to 5 wt % loss of

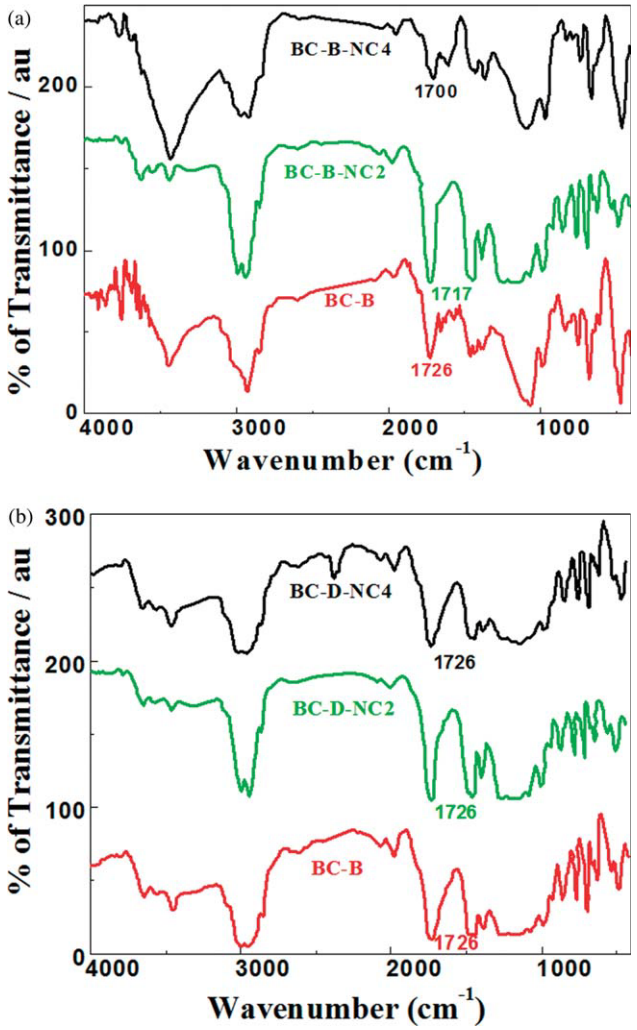



**Figure 5** (a) FTIR of bone cement nanocomposite in benzene: (1) pure BC-B, (2) BC-B-NC2, 2 wt % clay, and (3) BC-B-NC4, 4 wt % clay composites, respectively. (b) FTIR of bone cement nanocomposite using DMF solvent: (1) pure BC-D, (2) BC-D-NC2, 2 wt % clay, and (3) BC-D-NC4, 4 wt % clay composites, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymer was considered as degradation temperature. The degradation temperatures of the BC-B and BC-B-NC4 are 178 and 190°C, respectively, showing better thermal stability of bone cement in the presence of nanoclay. Two-dimensional clay particles act as a heat barrier and thereby improve the thermal stability of the composite.[40] The degradation temperatures of BC-D and BC-D-NC4 were 243 and 246°C, respectively [Fig. 6(b)], showing slight improvement for composite derived from DMF as solvent. The reason for lower degradation temperature of bone cement and its composite prepared using benzene when compared with DMF-originated bone cement and composite is not clear. However, in both the cases, two-stage degradations were observed for PMMA and are explained from the degradation of pendant acrylate group at lower temperature followed by the degradation of backbone chain at higher temperature.[41] The absolute value of the degradation temperature is less in benzene-based bone cement and its composite when compared with DMF-based bone cement and composite. We compared the increase in thermal stability of benzene-based composite with respect to pure bone cement in the same solvent (178–190°C) vis-à-vis DMF-based composite (243–246°C). Similar improvement of thermal stability of PMMA in the presence of organically modified montmorillonite has been reported in the literature.[42]

### Differential thermal analysis

Figure 7(a,b) shows the heat flow against temperature of bone cement and its composites prepared using benzene and DMF as solvents. A small endothermic peak around 80°C for BC-B is presumably due to β transition temperature, which slightly shifted to 84°C in BC-B-NC4 because of the constraint movement of side chains of polymer in the presence of significant intercalation inside the gallery (cf. nanostructure).[43] This shifting of β transition temperature is not observed in BC-D-NC4 prepared using DMF as there was no intercalation of PMMA molecules in silicate galleries. Further, the endothermic peaks at ~150°C for pure BC-B and BC-B-NC4 are related to initial weight loss observed in corresponding TG curves, and the same peak is not observed for pure bone cement and BC-D-NC4 derived using DMF as solvent as there is no such weight loss in that temperature range. Moreover, the other strong endothermic peaks associated with each degradation steps are prominent for both bone cement and its composites for both the solvents.

### Mechanical properties

Success of prosthetic implant primarily depends on the bonding strength between bone and implant. The gap between them is considerable. In general, for long survival, the gap is filled with bone cement. Mechanical properties of bone cement and its various nanocomposites have been determined from stress–strain behavior under uniaxial tension.[44] Figure 8(a,b) shows the stress–strain curves of bone cement and its nanocomposites prepared in benzene and DMF solvents. Bone cement exhibits a brittle fracture, which is similar to pure PMMA.[45] Benzene-based nanocomposites show much better stiffness (modulus) when compared with pure bone cement. The elongation at break slightly increases for lower nanoclay content followed by decreasing order with increasing nanoclay content in bone cement. Table IV shows the mechanical properties of bone cement

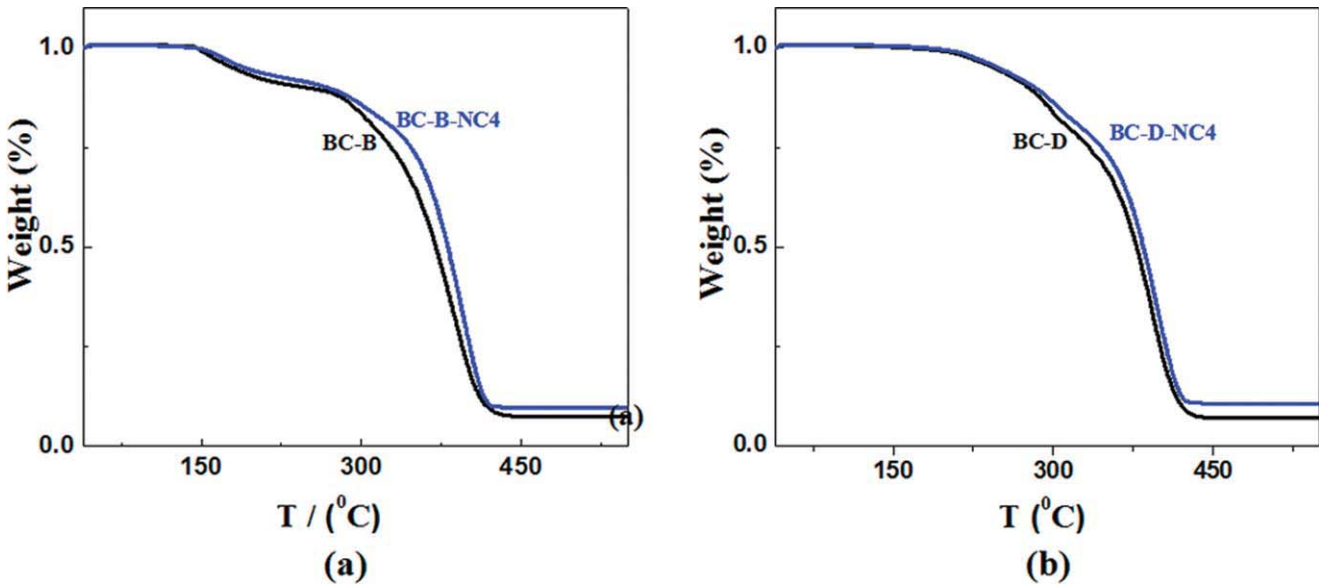



**Figure 6** Plots of the thermogravimetric analysis in inert nitrogen media: (a) pure bone cement BC-B and BC-B-NC4, bone cement with 4 wt % nanoclay in benzene solvent, and (b) pure bone cement BC-D and BC-D-NC4, bone cement with 4% nanoclay in DMF solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and nanoclay-filled bone cement. Interestingly, the brittle fracture is reduced in the presence of less amount of nanoclay, and chances of crack propagation are more for higher nanoclay content composite causing lower toughness. Toughness was measured from the area under the stress–strain curve. The percentage improvements/changes are reported in Table IV. Toughness of bone cement has improved about 30% by using minimum (1 wt %) of nanoclay. In contrast, DMF-based composite shows decrement in toughness with respect to pure bone cement irrespective of nanoclay content. Here, nanoclay acts as crack propagating agent as there is no interaction between polymer chain and nanoclay. However, nanoclay behaves like usual reinforcing agent causing small increase in stiffness of bone cement.

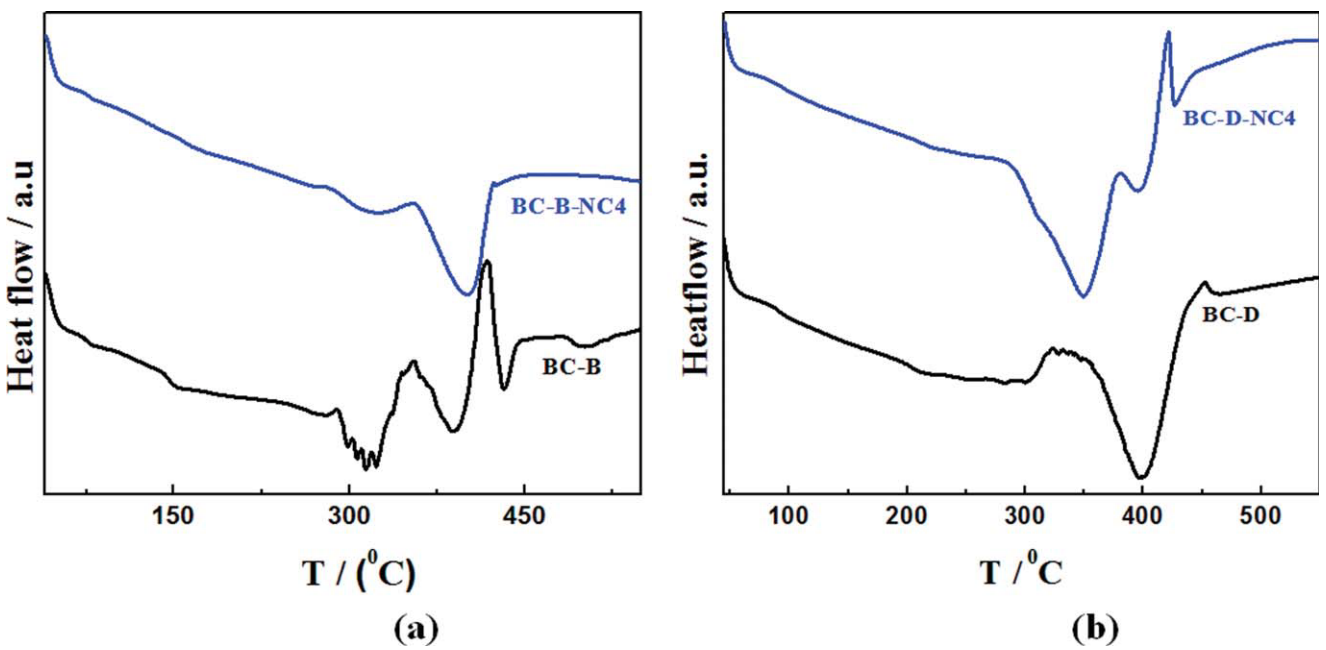



**Figure 7** Plots of DTA in nitrogen medium: (a) pure bone cement BC-B and BC-B-NC4, bone cement with 4 wt % nanoclay in benzene solvent, and (b) pure bone cement BC-D and BC-D-NC4, bone cement with 4 wt % nanoclay in DMF solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

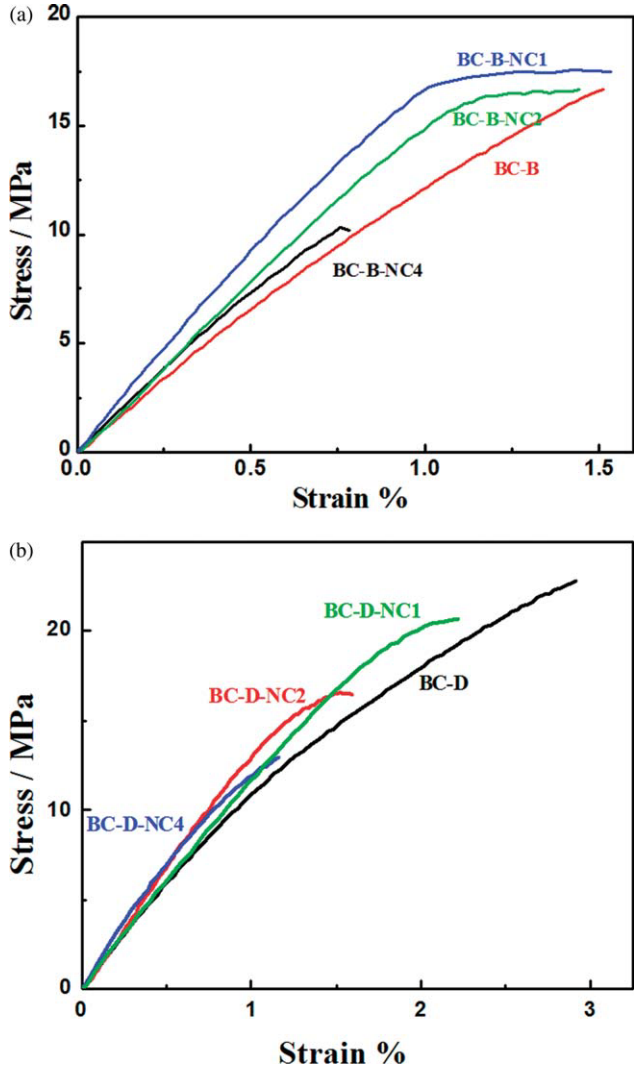



**Figure 8** (a) Stress–strain behavior of bone cement and its nanoclay composite prepared using benzene as solvent: (1) pure bone cement BC-B, (2) BC-B-NC1, 1 wt % nanoclay, (3) BC-B-NC2, 2 wt % nanoclay, and (4) BC-B-NC4, 4 wt % nanoclay composites. (b) Stress–strain curve of bone cement and its nanoclay composite in DMF solvent: (1) pure bone cement BC-D, (2) BC-D-NC1, 1 wt % nanoclay, (3) BC-D-NC2, 2 wt % nanoclay, and (4) BC-D-NC4, 4 wt % nanoclay composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Therefore, in summary, mechanical properties (both stiffness and toughness) have extremely been enhanced using benzene as solvent with respect to with pure bone cement, but DMF-based nanocomposites do not exhibit that improvement in mechanical properties. The result is explained from the interaction point of view as the benzene-based system is highly interacting, one can expect better mechanical properties while noninteracting DMF-based composites exhibit even brittle fracture as nanoclay induces more crack propagation leading to catastrophic failure. The phenomenon is also supported by using other polar solvents like chloroform and dimethyl acetamide (DMAc) where although stiffness increases but toughness decreases significantly. Benzene-based nanocomposite with lower amount of nanoclay is ideal for enhancing the mechanical properties of bone cement, which can be applied for prosthetic implant.

### Contact angle measurement

Water-absorbing property or hydrophilic nature is very important for biomaterials as it promotes the cell growth and proliferation. Hydrophilicity has been evaluated through contact angle measurement. In general, PMMA bone cement has little bit of water-absorbing nature when it is placed in aqua medium.[46] Bone cements prepared using benzene and DMF as solvents show the contact angle of 103 and 111°, respectively (Fig. 9). Interestingly, the contact angle decreases with increasing nanoclay content. Contact angles of composites are 103, 101.6, 100.7, and 98.6° for pure BC-B, BC-B-NC1, BC-B-NC2, and BC-B-NC4, respectively. Contact angles are more than 10° higher for DMF-derived bone cement and its nanocomposites vis-à-vis benzene-derived bone cement and nanocomposites. However, the lowering of contact angle in nanocomposites suggests better hydrophilic systems and supposed to exhibit better cell adhesion, which will improve the biocompatibility of bone cement composite systems when compared with pure bone cement. In addition,

**TABLE IV**
**Mechanical Properties of Bone Cement and Its Various Nanocomposites in Benzene and DMF Solvents**

| | Benzene | | | DMF | | |
|---|---|---|---|---|---|---|
| Nanoclay (wt %) | Mod (GPa) | % Increment (modulus) | % Increment (toughness) | Mod (GPa) | % Increment (modulus) | % Increment (toughness) |
| 0 | 1.26 | – | – | 1.17 | – | – |
| 1 | 1.96 | 55 | 31 | 1.19 | 1.7 | −31.8 |
| 2 | 1.59 | 26 | 7 | 1.61 | 36 | −59 |
| 4 | 1.54 | 22 | −67 | 0.99 | −15 | −77.8 |

The negative sign indicates the decrement in respective properties.

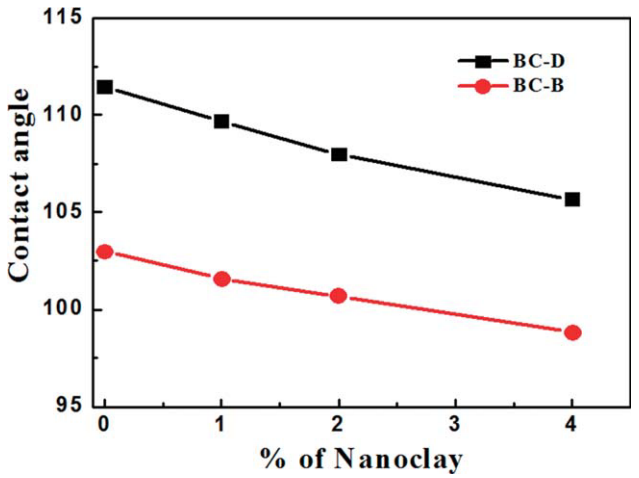



**Figure 9** Contact angle of bone cement nanoclay composite: (1) BC-B bone cement and its composites prepared using benzene and (2) BC-D bone cement and its composites prepared using DMF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

benzene-based nanocomposites show better hydrophilic properties than that of DMF-based nanocomposites. Hydrophilicity is measured through the contact angle. Theoretically, the contact angle and surface free energy are related by the following equation:

$$\gamma_{sg} = \gamma_{ls} + \gamma_{lg} \cos\theta, \quad (1)$$

where $\gamma_{sg}$, $\gamma_{ls}$, and $\gamma_{lg}$ are the surface free energy of the solid–gas, solid–liquid, and liquid–gas interface, respectively, and $\theta$ is the contact angle.

The contact angle decreases with increasing the filler content because the filler is an organically modified layered silicate and has high hydrophilic character when compared with polymer. As a result, the composites exhibit lower contact angle or higher hydrophilicity.

The significant improvement of properties including mechanical strength and wettability has been experienced for benzene-derived nanocomposites against DMF-based nanocomposites. It is surprising to understand that very different behavior of a pair of bone cement and nanoclay exhibit dissimilar property improvement when they are just prepared in two different solvents with diverse polarity. We have verified the results with other polar (DMAc and chloroform) and relatively nonpolar (toluene) solvents for preparing bone cement and its nanocomposites. The changes of properties are very similar with benzene (nonpolar) and DMF (polar) systems and will be published separately. Thus, the concept of improving properties has been testified resulting in much superior properties when prepared using comparatively nonpolar solvent for bone cement and nanocomposite preparation. Further, there is huge enhancement of stiffness (55%) and toughness (31%) of bone cement using very small amount of nanoclay (1 wt %) when compared with conventional composites where large quantity of filler is required to get the same effect on properties. However, this work signifies the role of solvent interaction during the mixing of two components. Better interacting ability of polymer and solvent restricts the interaction of polymer with nanoparticle, and, in other words, poor interaction of polymer solvent pair facilitates the interaction between polymer and nanoparticle. The developed new materials have potential use in bone surgery.

## CONCLUSIONS

Bone cement nanocomposites have been prepared with layered silicate (nanoclay) using diverse polarity of solvents to examine the improvement of properties including mechanical and wettability. Benzene-based nanocomposites exhibit intercalated structure, whereas intercalation does not take place in DMF-based nanocomposites. The significant interaction has been demonstrated through FTIR and UV–vis spectroscopy in case of benzene-derived nanocomposites, whereas there is no shifting of peaks observed in DMF-based nanocomposites indicating no interaction between PMMA and nanoclay while prepared using DMF. Thermal stability has been improved by ~12°C for benzene-based nanocomposites against hardly any improvement in DMF-derived nanocomposites. Both the stiffness and toughness increase significantly using minimum quantity of nanofiller (1 wt %) in bone cement prepared using benzene as solvent, whereas no change in modulus and detrimental toughness have been observed for DMF-based nanocomposites. The contact angle of benzene-based bone cement and its nanocomposites is less than that of samples prepared using DMF as solvent, indicating better hydrophilic nature of bone cement in the presence of nanoclay suggesting excellent material (bone cement nanocomposites) for better adhesion between bone and prosthetic implants.

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