Thermoreversible Block Copolymer/Clay Nanocomposite via Surface Initiated ATRP (SI-ATRP) and “Click Reaction” in Clay Surface

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Abstract

This investigation reports the preparation and characterization of a reactive block copolymer/clay nanocomposite from nanoclay surface via SI-ATRP and its post polymerization modification to prepare thermoreversible polymer via Diels-Alder (DA) and retro-DA (rDA) reaction. In this case, the block copolymer of 2-ethylhexylacrylate (EHA) and furfuryl methacrylate (FMA), a reactive methacrylate was prepared from suitably modified nanoclay surface via SI-ATRP. The furfuryl group of PFMA unit of block copolymer PEHA-b-PFMA/clay nanocomposite (BCP/clay) was used as a diene in DA reaction with bismaleimide (BM) as dienophile. This DA cross-linked block copolymer/clay composite had successfully undergone retro-DA reaction at higher temperature showing reversible characteristics. The block copolymer was characterized by ¹H-NMR, GPC, TEM, TGA, DSC analysis. The thermoreversible properties of block copolymer/clay nanocomposite were characterized by FT-IR and DSC analysis.

Keywords: Diels-Alder (DA) reaction; Surface-initiated ATRP; Block copolymer; Nano clay; DA cross-linked polymer

1. Introduction

In recent years, the thermally reversible compounds became the focus in materials research due to its self-healing properties (Chen et al, 2003; Gandini et al, 2008; Kavitha and Singha, 2009; Gotsmann et al, 2006; Liu et al, 2008; Tesoro and Sastri, 1986). In these thermo-reversible materials the click chemistry of Diels-Alder (DA) and retro-DA (rDA) reactions involving furfuryl moiety and maleimide functional group as diene and dienophile, respectively, is often used. As DA and rDA reactions are thermoreversible in nature, these materials can be used to prepare thermally...
amendable materials for the application in self-healing and autonomic reshaping etc. Wudl et al. reported the thermally amendable polymeric network based on furfuryl moieties and studied its self-healing property through DA and rDA reaction (Chen et al, 2002; Bergman and Wudl 2008; Veldman et al, 2009; Murphy and Wudl, 2010). Several research groups prepared polymers based on furfuryl methacrylate (PFMA) via conventional free radical polymerization and followed by DA reactions between PFMA and bismaleimide (Gousse and Gandini, 1999; Abid et al, 2004; Gandini et al, 2009 and 2010; Goiti et al, 2001; 2003 and 2004). We have first reported the preparation of tailor-made homo, random and block copolymers of furfuryl methacrylate (PFMA) via different controlled radical polymerizations (CRP) and we also reported thermally amendable polymeric materials via DA reactions between these PFMA and different bismaleimides (Kavitha and Singha 2007 (a), 2007 (b) and 2010; Pramanik et al, 2013).

In recent years inorganic-organic materials esp. polymer/clay composite have got great interest, because of their high performance properties. In these composites inorganic materials, e.g. clay as core render good mechanical strength and excellent thermal properties. The functional polymeric material, a relatively soft material as shell determines the chemical properties of the composites. These composite materials are prepared via solution blending, insitu polymerization as well as via surface initiated polymerization (SIP) from inorganic nanoparticles. In SIP the nanoparticle surface is suitably modified and then the polymerization is carried out from this modified surface. Among the different CRP methods, surface initiated atom transfer radical polymerization (SI-ATRP) has been successfully demonstrated from different inorganic surfaces like silica (Xu et al, 2004; Xiao and Wirth 2002; Paripovic and Klok, 2011), clay (Datta et al, 2008; Kim et al, 2003; Haloi et al, 2012), gold (Kim et al, 2000 and 2005), and magnesium hydroxide surface (Liu and Yi, 2009). In this investigation we were interested to develop tailor-made DA polymer/clay nanocomposite via SI-ATRP and DA click reaction. Liu et al (2008) synthesized nanocomposite of poly-(p-phenyleneethynylene) (PPE) gold nanoparticles via grafting of maleimide functionalized gold nanoparticles onto PPE chain by DA reaction which enhanced electronics communication between the copolymer and inorganic particles. Costanzo and Bayer (2007) also used reversible DA chemistry to develop polymeric film based on furfuryl terminated poly(ethylene glycol) as diene and maleimido functionalized silica nanoparticles as dienophile. After that the pegylated silica nanoparticles were distributed within poly(methyl methacrylate ) matrix resulting an optically transparent film in which the change in optical clarity was thermally triggered. Rahman et al (2008) grafted the free maleimide functional groups through nucleophilic addition onto the surface of amino-functionalized silica nanoparticles. However, in all those cases no CRP was used to graft polymer in nanoparticle surface. Recently Engel and Kickelbick (2014) reported self-healing nanocomposite materials based on silica-polymer core-shell nanoparticles using SI-ATRP technique. In this case, they prepared copolymer of butyl methacrylate (BMA) and furan protected maleimidopropyl methacrylate (pMiMA) via ATRP process and they used maleimido functionality. To the best of our knowledge there is no report on the preparation of thermally amendable DA block copolymer (BCP)/clay nanocomposite based on furfuryl methacrylate (FMA) via SI-ATRP and DA chemistry on clay surface. Block copolymer are interesting materials which applications in emulsifier, shape memory material, smart paints and coating and in different other specialty applications.
Our goal is to prepare the reactive BCP of FMA on clay surface via SI-ATRP and to study the reversible DA chemistry in the block copolymer (BCP)/clay nanocomposite materials which can have applications in potential thermoreversible paints and coatings. In this approach we first prepared poly(2-ethylhexylacrylate)-block-poly(furfuryl methacrylate) (PEHA-b-PFMA)/clay nanocomposite from clay surface via SI-ATRP and then modified this block copolymer (BCP)/clay composite via DA reaction. We were interested in poly(2-ethylhexyl acrylate) (PEHA) as a soft block in this diblock copolymer, because PEHA has long chain branched alkyl group, good film formation properties and its polymers are used in coating and adhesive applications. The BCP/clay nanocomposite was characterized by 1H-NMR, GPC, TEM, XRD, TGA and DSC analysis. The thermoreversible properties of the DA cross-linked BCP/clay nanocomposite were characterized by FT-IR and DSC analysis.

2. Experimental Section

2.1. Materials
The nanoclay, Cloisite Na⁺ (gallery spacing \(d_{001}\) = 11.7 Å, surface area \(\sim\) 750 m²/g) was purchased from Southern Clay Products, Gonzales, TX, U.S.A. 2-Ethylhexylacrylate (EHA) (98%, Aldrich), N, N', N″, N‴-pentamethyl diethylenetriamine (PMDETA) (99%, Aldrich), furfuryl methacrylate (FMA) (97%, Aldrich) and 1,1-(methylene di-4,1-phenylene)bismaleimide (BM) were purchased from Sigma-Aldrich. Toluene (Merck) and N,N-dimethyl formamide (DMF) (Merck) were purified by vacuum distillation over CaH₂ and used.

Preparation of Bromo-Functionalized Nanoclay

Using the esterification reaction between the hydroxyl group present on the surface of Cloisite Na⁺ and 2-bromopropionyl bromide the bromo functionalized nanoclay was prepared. In this process in a 100 ml round bottom flask 60 ml dichloromethane was taken. After 10 min, Cloisite Na⁺ (3.0 g) and dry triethylamine (1 mL, 7 mmol) were added to the flask. To this ice-cold mixture, 2-bromopropionyl bromide (0.7 mL, 7 mmol) was added dropwise from a dropping funnel. After 10 min, the ice-bath was removed and the reaction mixture was continuously stirred overnight at room temperature. The free 2-bromopropionyl bromide present in the mixture was removed by diluting with THF and decanting the liquid until it becomes colorless. The free amine present in the modified nanoclay was removed by washing with water. Finally, the modified nanoclay was dried in a vacuum oven at 50 °C for 4 days to remove water. Conversion = 48 %.

Preparation of poly(2-ethylhexyl acrylate) (PEHA)/Clay Nanocomposites via SI-ATRP from Bromo-Functionalized Nanoclay

PEHA/clay nanocomposite was prepared via the SI-ATRP of 2-ethylhexyl acrylate (EHA) shown in Scheme-1. In a typical SI-ATRP polymerization reaction, in a Schlenk tube modified nanoclay (0.18 g) was taken. After that CuBr (0.0171 g, 1.2 × 10⁻⁴ mol) was added to the Schlenk tube that was sealed with a silicone rubber septum. Nitrogen was purged through it for 10 min to remove the oxygen present inside the Schlenk tube. The ligand PMDETA (0.03 g, 1.8 × 10⁻⁴ mol) in acetone (1 mL) was transferred to the Schlenk tube with continuous purging of nitrogen. EHA (5 mL, 2.4 × 10⁻² mol) was then added into the mixture. The mixture was stirred for 30 min and the polymerization
reaction was carried out at 90 °C. Conversion = 80 %, \( M_n(\text{Theo}) = 88300 \text{ g/mol} \), \( M_n(\text{GPC}) = 97200 \text{ g/mol} \), PDI = 1.52.

**Preparation of PEHA-b-PFMA/Clay (BCP/Clay) Nanocomposite via Si-ATRP**

The BCP/clay nanocomposite was prepared from PEHA/clay nanocomposite as shown in Scheme 1. This Clay-PEHA-Br (\( M_n = 97200 \text{ g mol}^{-1} \)) was used as macroinitiator to polymerize FMA to prepare the PEHA-b-PFMA block copolymers. In a typical block copolymerization reaction, the macroinitiator (1.08 g) was taken in a Schlenk tube and was sealed with a rubber septum. Nitrogen was purged through the reaction system to make the system oxygen free. CuBr (0.0017 g), PMDETA (0.002 g) and toluene (3 mL) were added to the tube. On continuous stirring, FMA (2 mL) was added into the reaction mixture. The reaction mixture was heated at 90 °C and the reaction was run for 6 h. The final polymer was purified and characterized by different characterization techniques. Conversion = 45%, \( M_n(\text{NMR}) = 130400 \text{ g mol}^{-1} \), \( M_n(\text{GPC}) = 125500 \text{ g mol}^{-1} \), PDI = 1.35.

**Preparation of cross-linked BCP/Clay Nanocomposite via DA Reaction between BCP/Clay Nanocomposite and bismaleimide**

The preparation of cross-linked BCP/clay nanocomposite via DA reaction was shown in Scheme 2. In a typical reaction set up, a mixture of block copolymer (1.0 g) and stoichiometric amount of bismaleimide (0.4 g) were mixed in dimethyl formamide (DMF) (8 ml) solvent in schlenk tube. The reaction mixture was stirred at 60 °C for 24 hrs under nitrogen atmosphere and then the solvent was evaporated at 60 °C in vacuum oven. The final product was characterized by FT-IR and DSC analysis.

**Scheme 1** Schematic representation of preparation of BCP/clay nanocomposite from clay surface via SI-ATRP.
Scheme 2 The cross-linked BCP/clay nanocomposite via DA reaction between BCP/clay nanocomposite and BM at 60 °C.

2.2. Characterization

*Gel Permeation Chromatography (GPC)*

GPC analysis was carried out at ambient temperature on a Viscotek GPC instrument (model VE 3580) which was equipped with refractive index detector. The polymer solution was passed through two ViscoGel GPC columns (model GMHR-M #17392) having pore size 30-650Å connected in a series. We used tetrahydrofuran (THF) as an eluent at room temperature with flow rate of 1.0 mL min⁻¹ and narrow disperse poly (methyl methacrylate) (PMMA) as calibration standard. Data analysis was performed using Viscotek OMNI-01 software.

The polymer chains were cleaved from the nanoparticles surface by using previously reported method for the GPC and NMR characterization (Engel et al, 2014).

*Nuclear Magnetic Resonance Spectroscopy (NMR)*

Bruker 400-MHz spectrometer was used to record ¹H-NMR spectra of polymers usingCDCl₃ as a solvent, which contained a small amount of tetramethysilane (TMS) as internal standard.

*Fourier Transform (FT-IR) Analysis*

IR spectrum was recorded using Perkin-Elmer FT-IR spectrometer, Inc. version 5.0.1. Polymer solution in chloroform was cast over KBr cell and then FT-IR spectra were recorded. FT-IR spectra were recorded in the range of 400-4000 cm⁻¹.

*X-ray diffraction (XRD) Analysis*

XRD analysis was carried out on an analytical high resolution XRD-II, PW 3040/60 with crystal monochromatic CuKα (λ = 1.548 Å) radiation in the angular range of 2 to 10 ° (2θ) with a 40-kV operating voltage and a 30 mA current. The samples were scanned from 2θ = 2 to 10 ° at the step-
scan mode (step size 0.04°, time per step 2 s), and the diffraction pattern was recorded using a scintillation counter detector.

**Transmission Electron Microscopy (TEM) Analysis**

The dispersion of nanoclay into the polymer matrix and the morphology of the polymer were studied by High Resolution (HR) TEM (JEOL 2000) operated at accelerated voltage of 200 kV. The sample was prepared using drop casting method. In this case very dilute solution of polymer/clay nanocomposite in THF was casted on copper grid and examined under microscope.

**Differential Scanning Calorimetry (DSC) Analysis**

The DSC analysis was conducted on a DSC 200 F3 instrument (Netzsch, Germany). In case of block copolymer the sample was heated from -100 °C to + 100 °C under nitrogen atmosphere at a heating rate 10 °C/min. But in case of cross-linked Diels-Alder polymer the sample was heated from -25 °C to + 250 °C at a heating rate of 20 °C/min under nitrogen atmosphere. Nitrogen was used as an inert atmosphere with a flow rate 50 mL/min. The temperature against heat flow was recorded. The enthalpy was calibrated with an indium standard supplied by Netzsch.

**Thermogravimetric Analysis (TGA)**

TGA analysis was performed on a TA (TGA Q50 V6.1 Build 181) instrument. In this case small amount (10 mg) of sample was heated from 30 °C to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

### 3. Results and Discussion

In this case BCP/clay nanocomposite was prepared by ATRP using CuBr/PMDETA as catalyst and clay-PEHA-Br as macroinitiator (Scheme-1). This clay-PEHA-Br macroinitiator was prepared via SI-ATRP of EHA from bromo-functionalized ATRP initiator on clay surface (Haloi and Singha, 2012). Figure 1 shows the comparative GPC traces of the PEHA-Br macroinitiator and of PEHA-b-PFMA block copolymer. Shift of GPC traces of PEHA-Br to lower retention volume i.e. towards higher molecular weight in case of block copolymer indicates living nature of >CH-Br in PEHA-Brand successful block copolymerization via SI-ATRP. 1H- NMR analysis shows the different protons of the block copolymer of PEHA-b-PFMA prepared via SI-ATRP in Figure 2. The two distinct resonances at δ = 5.0 ppm and at δ = 4.0 ppm are due to the ethoxy (−O−CH₂−) protons in PFMA and PEHA respectively. The resonances at δ = 7.4 (1H, H₄) and 6.4 (2H, H₂&3) are due to the different aromatic protons in furfuryl ring in FMA as designated in Figure 2. The presence of these aromatic protons and quantitative comparison of integral areas of these protons to −OCH₂− protons in FMA at δ = 5.0 ppm (e.g. H₂&3; H₅ = 1 : 1) indicates that furfuryl group was not affected during polymerization (Goiti et al, 2001; Kavitha and Singha, 2007). The resonances at δ = 0.8 to 2.5 ppm are due to the different aliphatic protons in the pendant alkyl group of PEHA block as well as in the main polymer chain, as clearly designated in Figure 2. It is reported that conventional free radical polymerization (FRP) of FMA leads to gel formation, because of the side reactions involving several labile protons in FMA (Canary and Stevens, 2009; Gousse et al, 1998). In this case the block copolymer was free from gel
formation and was soluble in many solvents like CHCl₃ and THF etc. The molar composition of EHA and FMA in the block copolymer was determined by using the following equation

$$\% \text{FMA} = \frac{A}{A+B} \times 100$$ (1)

where A & B are integral areas at δ = 5.0 & 4.0 ppm of $-\text{OCH}_2-$ protons of PFMA and PEHA respectively. The molar composition of PEHA: PFMA unit in block copolymer was determined to be 60: 40 by ¹H-NMR analysis. The molecular weight of the block copolymer by this compositional analysis was calculated to be $M_n(\text{GPC}) = 125500 \text{ g.mol}^{-1}$.

**Fig. 1.** GPC traces of ATRP macroinitiator (PEHA-Br) as dotted line and the block copolymer PEHA-b-PFMA as solid line.

**Fig. 2.** ¹H-NMR spectrum of PEHA-b-PFMA block copolymer (60:40).
Formation of well defined block copolymer was also revealed by DSC analysis. DSC traces of PEHA-b-PFMA/clay nanocomposite showed two $T_g$'s, one at $-68 \, ^\circ C$ and another at $+59 \, ^\circ C$ which are due to the soft segment of PEHA and hard segment of PFMA respectively. (DSC traces are shown in Supplementary Section).

**Morphological study of BCP/Clay Nanocomposite**

Morphology of the BCP/clay nanocomposite was studied by XRD and TEM analysis. Figure 3 shows the characteristics diffraction peaks of the unmodified clay Cloisite Na$^+$ and the BCP/clay nanocomposite at $2\theta = 2^\circ$ to $10^\circ$ in WAXD analysis. XRD analysis of Cloisite Na$^+$ shows an intense peak at $2\theta = 7^\circ$-$8^\circ$. The intensity of the peak decreases and the peak is broadened in the BCP/Cloisite Na$^+$ composite. This is due to some agglomeration caused by poor dispersion of clay particles. In the present case due to the presence of bulky long chain in the PEHA as well as the bulky furfuryl group in PFMA, the entry of the block copolymer into the gallery spacing of the Cloisite Na$^+$ nanoclay is somewhat restricted as the gallery spacing is less in case of cloisite Na$^+$ ($d_{001} = 11.7 \, \text{Å}$). So, it leads to intercalated morphology along with some aggregation. The intercalation phenomena were also studied by TEM analysis. Figure 4 shows the TEM data of pure clay cloisite Na$^+$ and BCP/clay nanocomposite. Neat clay, Cloisite Na$^+$ mainly shows agglomerated morphology, whereas BCP/clay nanocomposite showed the intercalated morphology. In this case the polymer chains are intercalated into the gallery spacing of Cloisite Na$^+$ (Haloi and Singha, 2011 and 2012; Singha et al, 2012).

![Fig. 3. Wide angle XRD pattern of Cloisite Na$^+$ (A) BCP/clay nanocomposite (B).](image-url)
**Fig. 4.** TEM images of pure clay Cloisite Na⁺ (a) & (b) and BCP/clay nanocomposite (c) & (d).

**DA cross-linked BCP/Clay Nanocomposite and its thermoreversible properties**

BCP/Cloisite Na⁺ composite was reacted with bismaleimide (BM) in DMF to carry out the DA reaction. Retro-DA reaction (rDA) in this DA polymer-composite was carried out at 160 °C. The thermoreversibility of the DA-BCP clay composite was characterized by FT-IR as well as heating-cooling cycle in DSC analysis. Figure 5 shows the FT-IR analysis of the DA adducts of PEHA-b-PFMA/clay & BM and its rDA product after heating at high temperature. The different characteristic
absorption bands of maleimide group, at 829 cm\(^{-1}\) (for C-H out of plane), 691 cm\(^{-1}\) (for maleimide group deformation) and 1603 cm\(^{-1}\) for C=C bond of maleimide group disappeared indicating the successful DA reaction. Appearance of new peak at 1775 cm\(^{-1}\) clearly indicates the successful DA reaction between the furan and maleimide group (Engel and Kickelbick, 2013; Varganici et al, 2013; Parker et al, 1990; Tian et al, 2010; Imai et al, 2000). When the cross-linked DA polymer was heated at 160 °C for 30 min, the above absorption bands of maleimide groups in the FT-IR spectra appeared again. This indicates the rDA reaction took place at higher temperature. The process of DA and rDA is shown in (Scheme 2).

![FT-IR spectra of cross-linked DA polymer of BCP/clay nanocomposite & bismaleimide(a) and its rDA product after heating at 160 °C (b).](image)

**Fig. 5.** FT-IR spectra of cross-linked DA polymer of BCP/clay nanocomposite & bismaleimide(a) and its rDA product after heating at 160 °C (b).

**Thermal properties of BCP/Clay nanocomposite and its cross-linked DA polymer**

**DSC analysis**

DSC analysis was used to study the thermoreversible property of the BCP-BM/clay nanocomposite. The heating-cooling cycles in DSC analysis of this cross-linked polymer are shown in Figure 6. In this case the polymer sample was heated from -25 °C to 230 °C with a heating rate of 20 °C/min. Three heating-cooling cycles were run to study the thermoreversible property of this cross-linked polymer. In the first heating curve there is a broad endothermic peak with an enthalpy of reaction of 8.467 J.g\(^{-1}\) at a peak temperature value of 159 °C indicating the disconnection of bond between the furan and maleimide group due to retro-DA reaction (Engel and Kickelbick, 2014; Varganici et al, 2013 (a) and 2013(b)). In the cooling curve also there is a less intense exothermic peak with an enthalpy of reaction of 2.185 J.g\(^{-1}\) indicating the disconnected bonds reconnect again via [4+2] Π cycloaddition DA reaction between the furan and maleimide groups. The second heating curve also shows a small endothermic transition with an enthalpy of reaction of 3.522 J.g\(^{-1}\), meaning reconnection of bonds (DA reaction) took place in small extent during cooling, as the period of cooling time is very short. So, the DSC traces show the endothermic as well as exothermic peak due
to disconnection and reconnection of linkage respectively between the fufuryl functionality in BCP as diene and bismaleimide as dienophile. Thus it indicates that the DA cross-linked BCP-BM/clay is thermoreversible in nature, as shown in (Scheme 2). The DSC analysis showed $T_g$ at 120 °C is for the cross-linked material (Figure 6).

**Fig. 6.** DSC thermograms of DA cross-linked BCP-BM/clay nanocomposite, 1st heating run (a), 1st cooling run (b) and 2nd heating run (c).

**TGA analysis**

**Fig. 7.** TGA thermograms of pure cloisite Na⁺ (a), clay-PEHA-Br macroinitiator (b), BCP/clay nanocomposite (c) and its DA cross-linked polymer BCP-BM/clay nanocomposite (d).
Table 1 TGA of BCP/clay nanocomposite and its DA Cross-linked polymer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_{onset}°C</th>
<th>T_{max}°C</th>
<th>Char yield at 600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay-PEHA (I)</td>
<td>322</td>
<td>385</td>
<td>4.47</td>
</tr>
<tr>
<td>BCP/Clay (II)</td>
<td>212</td>
<td>402</td>
<td>7.92</td>
</tr>
<tr>
<td>BCP-BM/Clay (III)</td>
<td>145</td>
<td>454</td>
<td>19.31</td>
</tr>
</tbody>
</table>

*T_{onset} value was measured from the TGA curve at 5% weight loss.

TGA curves for BCP/clay and DA cross-linked BCP-BM/clay are shown in Figure 7. The T_{onset} (temperature at 5% weight loss) and T_{max} (maximum degradation temperature) are shown in Table 1. This indicates that BCP/clay (II) has higher T_{onset} than DA cross-linked BCP-BM/clay (III) composite. But the latter has higher T_{max} than the former one. Goiti et al. (2004) also reported lower T_{onset} & higher T_{max} for DA polymer of PFMA/BM. But high temperature property of DA cross-linked BCP/clay nanocomposite is not reported. In this case DA cross-linked material has low T_{onset}, because at ~ 150 °C bismaleimide is cleaved from the DA polymer due to rDA reaction. But, this has greater T_{max} and higher char yield at 600 °C indicating formation of high temperature resistant infusible material which significantly improved the T_{max} of the BCP/Clay nanocomposite.

4. Conclusions

SI-ATRP method was successfully carried out to prepare block copolymer BCP/clay nanocomposite on clay surface using clay-PEHA-Br macroinitiator. GPC, NMR and DSC analysis clearly proved the formation of block copolymer. The dispersion of nanoclay in the polymer matrix was shown by XRD and TEM analysis. TEM and XRD data showed the intercalated morphology along with some aggregation of clay particles in block copolymer matrix. The reactive furfuryl group of BCP/clay was used to prepare reversible polymer through DA and rDA reaction. The DA [4+2] cycloaddition reaction in the BCP/clay nanocomposite was successfully carried out between furfuryl group of PFMA as diene and bismaleimide as dienophile. At higher temperature DA crosslinked BCP/clay composite undergoes rDA reaction leading to disconnection of DA crosslinks. The thermoreversible property of polymer/clay nanocomposite was successfully studied by FT-IR and DSC analysis. TGA analysis also showed the formation of cross-linked DA polymer and higher T_{max} of the DA cross-linked BCP/clay nanocomposite.

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