

# Crosslinking of Biocatalytically Synthesized Organosilicone Copolymers for Flame Retardant Applications

VIJAYENDRA KUMAR<sup>1,2</sup>, BHAVNA GUPTA<sup>1,3</sup>, ABDULLAH KHAN<sup>4</sup>, RAVI MOSURKAL<sup>5</sup>,  
SUNIL K. SHARMA<sup>1,3,4</sup>, VIRINDER S. PARMAR<sup>1,3,4</sup>, JAYANT KUMAR<sup>1,3</sup>, LYNNE A. SAMUELSON<sup>5</sup>,  
KRISHNA KUMAR<sup>2</sup>, and ARTHUR C. WATTERSON<sup>1,3\*</sup>

<sup>1</sup>Institute of Nano-science and Engineering Technology, Department of Chemistry, University of Massachusetts Lowell, Lowell, MA

<sup>2</sup>Howard University, School of Pharmacy, Washington, DC

<sup>3</sup>Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA

<sup>4</sup>Bio-organic Laboratory, Department of Chemistry, University of Delhi, Delhi, India

<sup>5</sup>U.S. Army Natick Soldier Research Development and Engineering Center, Natick, MA

Crosslinking of polymers using crosslinking agents has been widely utilized to further improve the mechanical and thermal properties of the polymers. We have explored various aliphatic and aromatic dicarboxylic acids such as malonic acid, glutaric acid, isophthalic acid, terephthalic acid and terephthaloyl chloride as crosslinking agents to crosslink polydimethylsiloxane copolymer [poly{poly(dimethylsiloxane-1000)-propylamine-5-aminoisophthaloyl}] to improve its flame retardant properties. We have also used nanoclays [Cloisite 20A, 2C<sub>18</sub> MMT (dimethyldialuminumammonium-/ dimethyldioctadecylammonium-modified montmorillonite)] along with the crosslinker during crosslinking process to further reduce the flammability of the crosslinked polymers. Among all the crosslinkers investigated, isophthalic acid with the nanoclay was found to have the best performance for flame retardant applications. The present work provides a basis to further improve the performance of silicone-based polymers for the flame retardant applications.

**Keywords:** Novozyme-435, *Candida antarctica* Lipase B, organosilicone co-polymers, flame retardant polymers, crosslinked polymers, nanoclay, thermogravimetric analysis (TGA), pyrolysis-combustion flow calorimetry (PCFC)

## 1 Introduction

Polycarbosiloxanes have been attracting attention as potential substitutes for conventional flame retardant materials owing to their exceptional thermal and flame retardant properties (1–4). The combustion products of these polymers are non-toxic cyclic siloxanes as well as branched siloxane structures (5). However, the existing brominated fire retardants (BFRs) and chlorinated fire retardants (CFRs) have already been restricted because of their persistence in the environment and/or their toxic health effects (6). Polychlorinated biphenyls (PCBs) previously used as chlorinated flame-retardants, were banned in 1977. EU has banned several types of brominated flame retardants as of 2008. The objectives of flame retardant polymers are twofold; first, to increase ignition resistance and second, to

reduce the rate of flame spread. To meet these stipulations, additives, which interfere in various ways with the chemical exothermic chain of combustion have been used.

It is anticipated that small amounts of well-dispersed natural clay can lead to environmentally friendly and inexpensive plastic composites with improved specialized properties (7). When polymers with clay incorporated in their structures burn, the clay forms a char layer on the outside of the polymeric material that insulates the material beneath. The polymer clay blends (nanocomposites) do not alter the normal production and processing of the clayless polymer. The addition of clay can make polymers less permeable to liquids and gases; enhance flame retardancy and make them tougher. The natural clays such as bentonites and montmorillonites are already in use in paints to prevent dripping and in cosmetics to prevent shine. Further, there is no problem in incorporating them into polymeric materials that come in contact with foods, medicines, beverages or plastics used in biomedical devices, since the U.S. Food and Drug Administration has already approved them for use.

We have established the synthesis of organic-inorganic hybrid polydimethylsiloxane copolymers under mild

\*Address correspondence to: Arthur C. Watterson, Institute of Nano-science and Engineering Technology, Department of Chemistry, University of Massachusetts Lowell, Lowell, MA, 01854 and Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA 01854. E-mail: arthur\_watterson@uml.edu

reaction conditions in bulk by a chemoenzymatic approach using *Candida antarctica* lipase (Novozyme 435) (8–11). We have already demonstrated the effect of crosslinking in these polymers by using crosslinkers such as hexamethylene tetramine (12) and pyromellitic dianhydride (13), which considerably decreased their flammability. In this paper, we have explored various aliphatic and aromatic dicarboxylic acids such as malonic acid, glutaric acid, isophthalic acid, terephthalic acid and terephthaloyl chloride as crosslinking agents to crosslink polydimethylsiloxane copolymer [poly{poly(dimethylsiloxane-1000)-propylamine-5-aminoisophthaloyl}] in order to decrease its flammability. Further, in this study, we chose nano clay [Cloisite 20A, 2C<sub>18</sub> MMT (dimethylditallowammonium-/dimethyldioctadecylammonium-modified montmorillonite)] along with the crosslinker during crosslinking process to further reduce the flammability of the crosslinked polymers. The effect on thermal properties and flammability by crosslinking of polydimethylsiloxane copolymer with and without nanoclay has been studied.

## 2 Experimental

### 2.1. Materials

Novozyme-435, an immobilized enzyme, was a gift from Novozyme, Denmark. Aminopropyl terminated polydimethylsiloxane (DMS-A12,  $M_w$  900–1000) was purchased from Gelest Inc., USA. Malonic acid, Glutaric acid, Isophthalic acid, Terephthalic acid and Terephthaloyl chloride were purchased from Aldrich. All other chemicals and solvents were of analytical grade and were used as received unless otherwise noted.

### 2.2. Characterization

Gel permeation chromatography (GPC) was used to determine the molecular weights and molecular weight distributions,  $M_w/M_n$  of polymers. The <sup>1</sup>H-NMR spectra were recorded on a Bruker Instrument Inc. DPX 500 spectrometer at 500 MHz using TMS as internal standard. Infrared spectra were recorded as neat samples on a Nicolet 4700 Fourier transform infrared (FT-IR) spectrometer by Thermo Electron Corporation. Thermal decomposition was studied under air at the rate of 10 mL/min and ramping at 10°C/min using a TA Instruments, Q 50 thermogravimetric analyzer (TGA). Flammability was measured using a pyrolysis-combustion flow calorimeter (PCFC, FAA microcalorimeter) (14). In this apparatus, samples of  $1.0 \pm 0.1$  mg were pyrolyzed at 1200°C at 1°C s<sup>-1</sup> under nitrogen using a flash pyrolyzer (Pyroprobe 2000, CDS Analytical, Inc.).

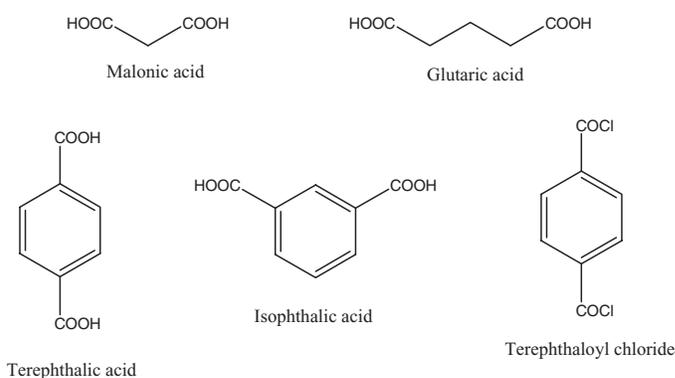


Fig. 1. Structures of crosslinkers.

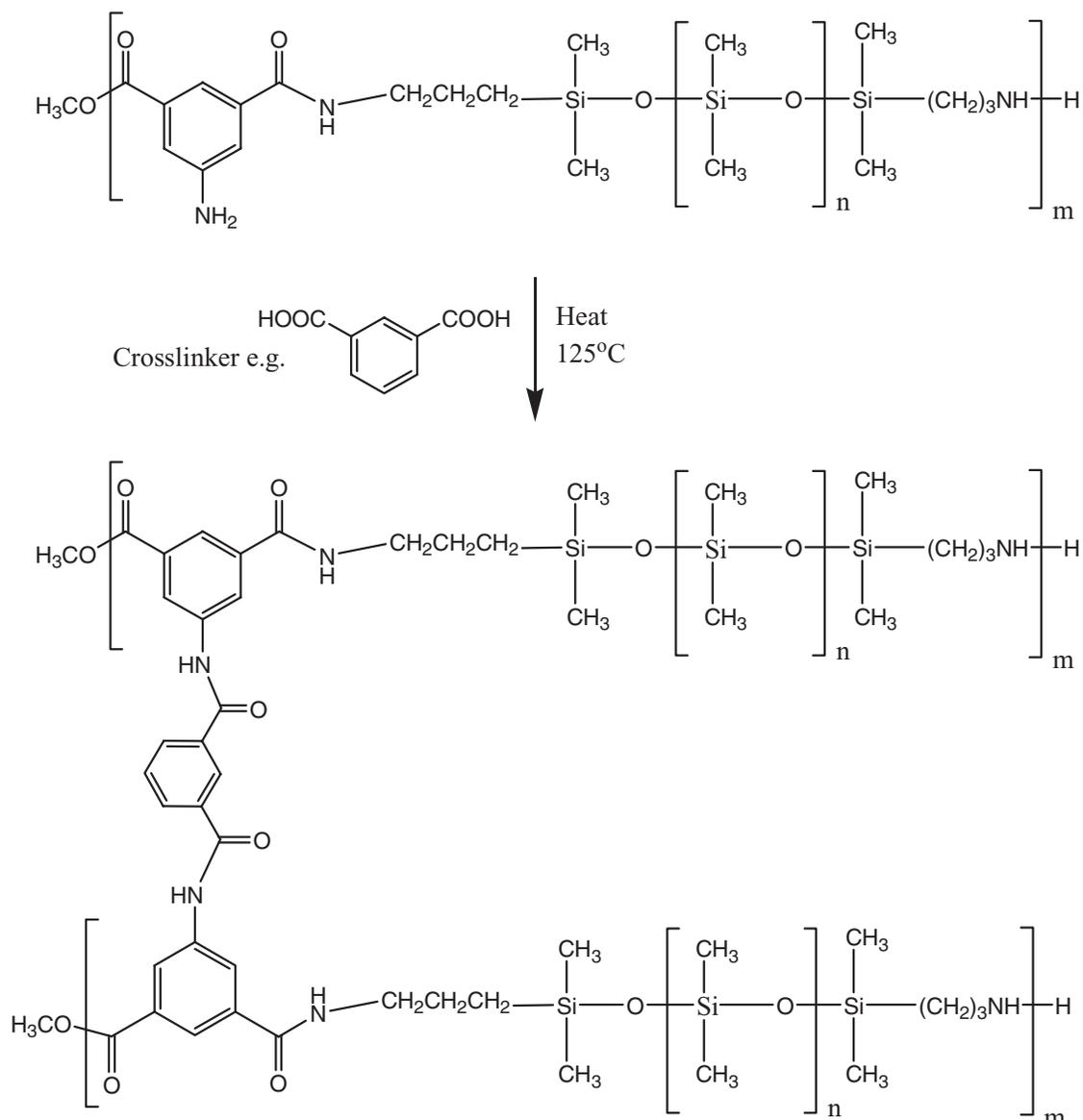
### 2.3. General Method of Synthesis and Crosslinking of Polydimethylsiloxane Copolymer [Poly{poly(dimethylsiloxane-1000)-propylamine-5-aminoisophthaloyl}]

Polydimethylsiloxane copolymer poly[poly(dimethylsiloxane-1000)-propylamine-5-aminoisophthaloyl] was synthesized using a previously reported procedure (8, 9, 11) and characterized by <sup>1</sup>H-NMR spectroscopy. Crosslinking of the polydimethylsiloxane copolymer was carried out using various aliphatic and aromatic dicarboxylic acids as crosslinking agents such as malonic acid, glutaric acid, isophthalic acid, terephthalic acid and terephthaloyl chloride (Fig. 1). In a typical crosslinking procedure, the polydimethylsiloxane copolymer and crosslinker (10 wt%) were dissolved in a mixture of solvents chloroform and acetone (1:1) by heating, and the resultant clear solution was heated slowly on a hot plate at 60°C to remove the solvent for 15 min. Further heating was performed at 125°C for 15 min to crosslink the copolymer. The crosslinked product was then oven-dried under vacuum at 100°C overnight to remove any residual solvents. The yield of the crosslinked products was found in the range of 90–95%. We have also used nanoclay [Cloisite 20A, 2C<sub>18</sub> MMT (dimethylditallowammonium-/dimethyldioctadecylammonium modified montmorillonite)] (10 wt%) along with the crosslinker during the crosslinking process. The crosslinked polymers were found to be insoluble in common organic solvents. The insoluble products were characterized by FTIR spectroscopy.

## 3 Results and Discussion

### 3.1 Synthesis and characterization

The silicone-based co-polymer was synthesized by lipase catalyzed amidation polymerization of the diester, dimethyl 5-aminoisophthalate and amino terminated polydimethylsiloxane using Novozyme-435 (immobilized *Candida antarctica* lipase B) (8–13). The <sup>1</sup>H-NMR spectrum



**Sch. 1.** Crosslinking of polydimethylsiloxane copolymer poly[poly(dimethylsiloxane-1000)-propylamine-5-aminoisophthaloyl] with isophthalic acid.

of the siloxane co-polymer showed the amidation between the methyl ester moiety of dimethyl 5-aminoisophthalate and amino group of aminopropyl terminated siloxane. The structure of the repeat units in the co-polymer formed was determined from its  $^1\text{H-NMR}$  spectra. We have already shown the detailed synthesis and characterization of siloxane based organic-inorganic hybrid polymers (8–13). The number average molecular weight of the co-polymer was found to be 11,000 Da (PD 1.34), as determined by GPC.

Herein we have described the crosslinking of polydimethylsiloxane copolymer using various aliphatic and aromatic dicarboxylic acids as crosslinking agents such as malonic acid, glutaric acid, isophthalic acid, terephthalic acid and terephthaloyl chloride and are

shown in Figure 1. We have also mixed 10% nanoclay [Cloisite 20A, 2C<sub>18</sub> MMT (dimethyldialuminum/dimethyldioctadecylammonium modified montmorillonite)] while crosslinking with isophthalic acid. Schematic representation of crosslinking of polydimethylsiloxane copolymer poly[poly(dimethylsiloxane-1000)-propylamine-5-aminoisophthaloyl] with isophthalic acid is shown in Scheme 1.

The crosslinked polymers were found to be insoluble in common organic solvents. We have characterized crosslinked polydimethylsiloxane copolymers by FTIR spectroscopy. FT-IR spectra of crosslinked polymer of polydimethylsiloxane copolymer [poly{poly(dimethylsiloxane-1000)-propylamine-5-aminoisophthaloyl}] using

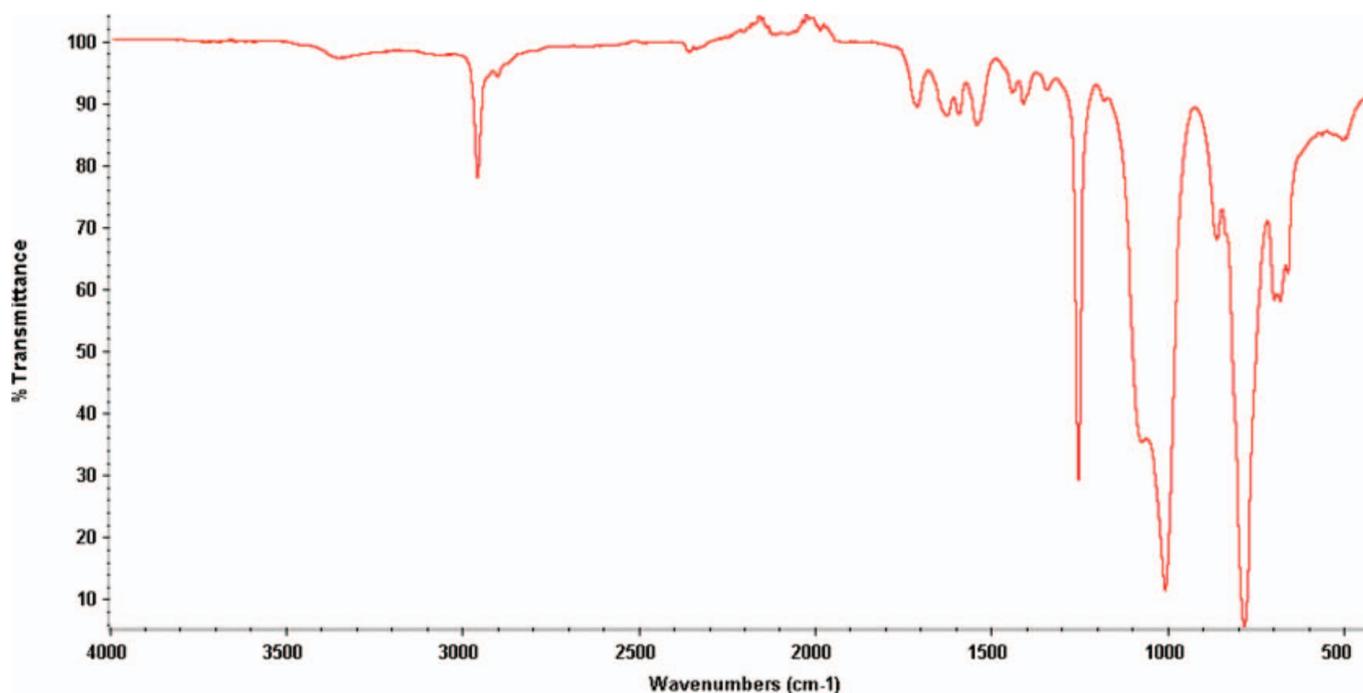


Fig. 2. FT-IR spectra of crosslinked polydimethylsiloxane copolymer. (Color figure available online.)

10% isophthalic acid as crosslinker is shown in Figure 2. In FT-IR spectrum of crosslinked copolymer, an amidic carbonyl stretching frequency can be seen at  $1720\text{ cm}^{-1}$  and NH stretching can be seen at  $2962\text{ cm}^{-1}$ , indicating crosslinking of the polymer.

### 3.2. Thermal and Flame Retardant Analysis

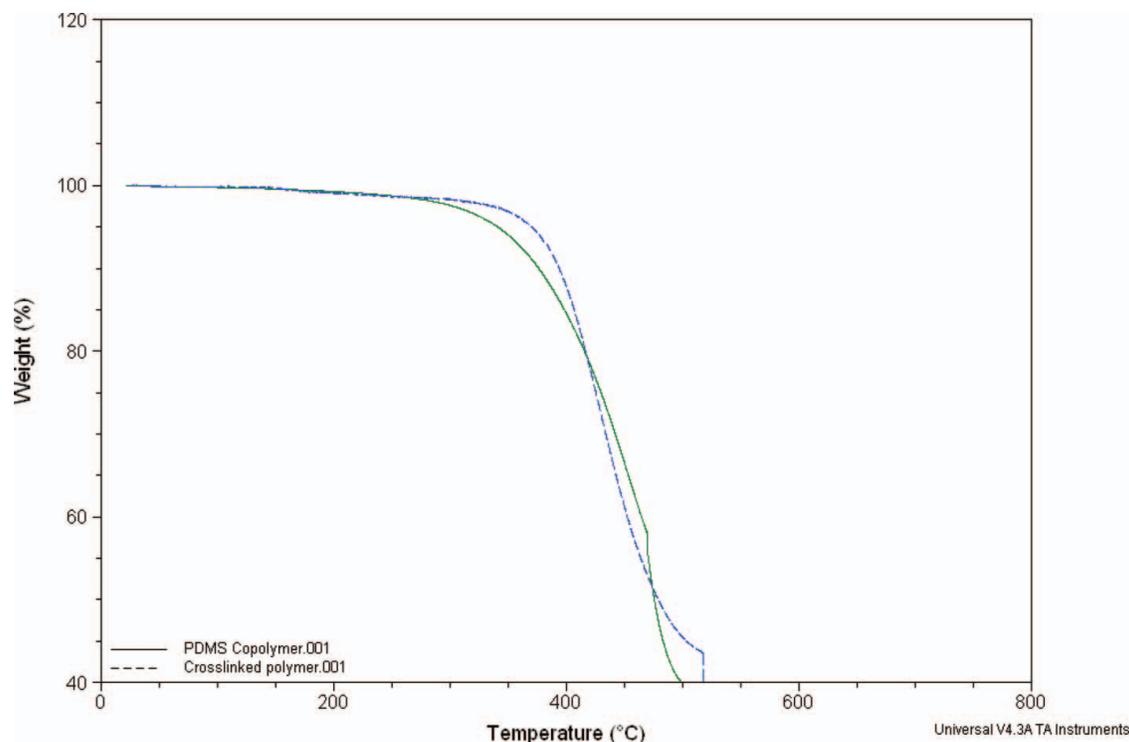
The thermal properties of crosslinked polydimethylsiloxane copolymers were studied based on their onset decomposition temperature and results are summarized

Table 1. TGA values of crosslinked polydimethylsiloxane copolymers

Polymer Description	Degradation Temperature by TGA $T_{\text{onset}}$ ( $^{\circ}\text{C}$ )
Polydimethylsiloxane copolymer	378.2 $^{\circ}\text{C}$
Polydimethylsiloxane copolymer was crosslinked by heating at 125 $^{\circ}\text{C}$ with 10% <b>malonic acid</b>	378.6 $^{\circ}\text{C}$
Polydimethylsiloxane copolymer was crosslinked by heating at 125 $^{\circ}\text{C}$ with 10% <b>glutaric acid</b>	375.9 $^{\circ}\text{C}$
Polydimethylsiloxane copolymer was crosslinked by heating at 125 $^{\circ}\text{C}$ with 10% <b>Terephthalic acid</b>	357.1 $^{\circ}\text{C}$
Polydimethylsiloxane copolymer was crosslinked by heating at 125 $^{\circ}\text{C}$ with 10% <b>Isophthalic acid</b>	<u>385.6<math>^{\circ}\text{C}</math></u>
Polydimethylsiloxane copolymer was crosslinked by heating at 125 $^{\circ}\text{C}$ with 10% <b>Terephthaloyl chloride</b>	335.7 $^{\circ}\text{C}$

in Table 1. Comparison of degradation profile of polydimethylsiloxane copolymer [poly{poly(dimethylsiloxane-1000)-propylamine-5-aminoisophthaloyl}] and its crosslinked polymer using 10% isophthalic acid as crosslinker is shown in Figure 3. Degradation Temperature [ $T_{\text{onset}}$  ( $^{\circ}\text{C}$ )] for polydimethylsiloxane copolymer was found to be 378.2 $^{\circ}\text{C}$  and for polydimethylsiloxane copolymers crosslinked with malonic acid, glutaric acid, terephthalic acid and terephthaloyl chloride were found to be 378.6 $^{\circ}\text{C}$ , 375.9 $^{\circ}\text{C}$ , 357.1 $^{\circ}\text{C}$  and 335.7 $^{\circ}\text{C}$ , respectively, while polydimethylsiloxane copolymer crosslinked with isophthalic acid showed the degradation temperature [ $T_{\text{onset}}$  ( $^{\circ}\text{C}$ )] at 385.6 $^{\circ}\text{C}$ . Thus on the basis of decomposition temperatures, polydimethylsiloxane copolymer crosslinked with isophthalic acid was found to be relatively more heat-resistant and can therefore be used at fairly high temperatures.

The flame retardant properties of crosslinked polydimethylsiloxane copolymer were studied by heat-release rate by pyrolysis-combustion flow calorimetry (PCFC; potential rate of heat release for combustion of the volatiles) using the oxygen consumption principle (14).<sup>1</sup> Heat release capacity was then obtained by dividing the maximum heat release rate by the sample weight and heating rate. Total heat of combustion of degradation volatiles was calculated by direct integration of the heat release rate with time. It averages  $310.1\text{ Jg}^{-1}\text{K}^{-1}$  for polydimethylsiloxane copolymer, while it drops to  $84.9\text{ Jg}^{-1}\text{K}^{-1}$  for polydimethylsiloxane copolymer crosslinked with mixture of 10% isophthalic acid and 10% nanoclay [Cloisite 20A, 2C<sub>18</sub> MMT (dimethylditallowammonium-/dimethyl dioctadecylammonium modified montmorillonite)]. We



**Fig. 3.** TGA profile of polydimethylsiloxane copolymer and crosslinked polydimethylsiloxane copolymer. (Color figure available online.)

have already published the effect of mixing nanoclay [Cloisite 20A, 2C<sub>18</sub> MMT (dimethyldiallowammonium-/dimethyldioctadecylammonium modified montmorillonite)] in the polydimethylsiloxane copolymer on thermal, as well as flame retardant properties (9). Flammability characteristics of crosslinked polydimethylsiloxane copolymers are summarized in Table 2.

#### 4 Conclusions

The synthesis of siloxane-based copolymers was successfully carried out by a green chemistry approach using lipase (Novozyme 435) catalysis under mild and solventless conditions. The synthesized polydimethylsiloxane copolymer was crosslinked using various aliphatic and

**Table 2.** Flammability characteristics of crosslinked polydimethylsiloxane copolymers

Polymer Description	PCFC (Heat Release Capacity) (J/g-K)	Total Heat Release (KJ/g)	Char Yield (%)
Polydimethylsiloxane copolymer	310.1	20.2	3.7
Polydimethylsiloxane copolymer was crosslinked by heating at 125°C with 10% <b>malonic acid</b>	248.2	19.1	7.4
Polydimethylsiloxane copolymer was crosslinked by heating at 125°C with 10% <b>glutaric acid</b>	292.9	23.4	2.3
Polydimethylsiloxane copolymer was crosslinked by heating at 125°C with 10% <b>Terephthalic acid</b>	165.2	25.2	10.9
Polydimethylsiloxane copolymer was crosslinked by heating at 125°C with 10% <b>Isophthalic acid</b>	132.4	15.9	8.3
Polydimethylsiloxane copolymer was crosslinked by heating at 125°C with 10% <b>Isophthalic acid+ 10% Nanoclay</b>	<b>84.9</b>	<b>13.2</b>	<b>12.1</b>
Polydimethylsiloxane copolymer was crosslinked by heating at 125°C with 10% <b>Terephthaloyl chloride</b>	179.7	24.3	9.3

aromatic dicarboxylic acids as crosslinking agents, such as malonic acid, glutaric acid, terephthalic acid, terephthaloyl chloride and isophthalic acid with and without nanoclay. Crosslinked polydimethylsiloxane copolymers have shown enhanced thermal as well as flame retardant properties as compared to polydimethylsiloxane copolymer, whereas, polydimethylsiloxane copolymer crosslinked with mixture of 10% isophthalic acid and 10% nanoclay [Cloisite 20A, 2C<sub>18</sub> MMT (dimethyldiallowammonium-/dimethyldioctadecylammonium modified montmorillonite)] was shown to have the best flame retardant properties.

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