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Nanocomposites and Blends of Biocatalytically Synthesized Organosilicone Co-Polymers for Flame Retardant Applications

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The great synthetic flexibility of organosilicone polymers, their ease of processing, low cost, and nontoxic nature present an attractive alternative solution over current flame retardant materials. Novozyme-435 catalyzed amidation reaction with silicone-based oligomer was carried out to scale up the synthesis of co-polymer which was fully characterized from its detailed spectroscopic studies. Synthesized co-polymer was compounded in polyolefins for flame retardant applications. Nanoclay [Cloisite 20A, $2C_{18}$ MMT (dimethylditallowammonium-/dimethyldioctadecylammonium-modified montmorillonite)] was used as a potential additive in co-polymer, which was then blended with polyolefins to improve their thermal as well as flame retardant properties. The present work provides an initial exciting basis for the enzymatic synthesis of silicon based co-polymers in bulk and their flame retardant applications.

Keywords: Novozyme-435, *Candida Antarctica* Lipase B, Organosilicon co-polymer, flame retardant polymers, nanocomposites, nanoclay, polypropylene, polyethylene, thermogravimetric analysis (TGA), pyrolysis-combustion flow calorimetry (PCFC)

1 Introduction

Organosilicone polymers, especially polycarbosiloxanes have been attracting attention as potential substitutes for conventional flame retardant materials owing to their exceptional thermal stability and low flammability (1–4). The combustion products of these polymers are benign, nontoxic, cyclic siloxanes as well as branched siloxane structures (5) rather than the typical toxic halogenated combustion products.

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). Polycholorinated biphenyls (PCBs) previously used as chlorinated flame-retardants, were banned in 1977. EU has banned several types of brominated flame retardants as of 2008.

Enzymatic chemistry has been used to carry out the condensation polymerizations (7, 8) having polydimethysiloxane segments (9, 10). The ability to make fire retardant polymers cost effectively has been a technological challenge since the early development of plastics. Plastics are synthetic organic materials with carbon and often high hydrogen content, so they are combustible, and must meet flame retardancy requirements. Today, due to their rapidly expanding use in construction products, automotives and electronics, more work than ever is being done on a variety of flame retardant systems for resins such as polyolefins (polyethylene and polypropylene) which are flammable and burn with a hot and clean flame, accompanied by melting and subsequent dripping or flowing of the molten polymer. The objectives in flame retarding polymers are twofold; first, to increase ignition resistance and second, to reduce the rate of flame spread. To meet these stipulations, additives are used that interfere in various ways with the chemical exothermic chain of combustion.

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It is anticipated that small amounts of well-dispersed natural clay can lead to environment friendly and inexpensive plastic composites with improved specialized properties (11). When polymers with clay incorporated in their structures burn, the clay forms a char layer on the outside of the plastic that insulates the material beneath. The polymer clay blends (nanocomposites) do not alter the normal production and processing of the clayless polymer. Addition of clay can make plastics less permeable to liquids and gases; enhances flame retardancy and makes them tougher. The natural clays such as bentonites and montmorillonites are already in use in paints to prevent dripping, in cosmetics to prevent shine and in pharmaceuticals. Further, there is no problem in incorporating them into plastics 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.

In this paper, we have scaled up the lipase catalyzed synthesis of siloxane based polyamides. This biocatalytic route has several advantages including environmental compatibility, economic synthesis, ease of processability and stability. Herein, we have blended siloxane co-polymer with polyolefins as flame retardant additives. Further, in this study, we chose natural clay as a potential additive in our siloxane based co-polymer and this mixture was then blended with polyolefins. The effect of these additives on thermal properties and flammability has been studied.

2 Experimental

2.1 Materials

Novozyme-435, an immobilized enzyme, was a gift from Novozyme, Denmark. All other chemicals and solvents were of analytical grade and were used as received unless otherwise noted. Aminopropyl terminated polydimethylsiloxane (DMS-A12, M_w 900–1000) was purchased from Gelest Inc., USA. Powdered polypropylene (PX PH350) resin and polyethylene resin were gifts from Basell, MD and Exon Mobile, respectively and were used as received.

2.2 Characterization

Gel permeation chromatography (GPC) was used to determine the molecular weights and molecular weight distributions, M_w/M_n of polymers. ^{1}H-NMR spectra were recorded on a Bruker Instrument Inc. DPX 500 spectrometer at 500 MHz using TMS as internal standard. Blending of siloxane co-polymer with polyolefins was carried out in C. W. Brabender Instruments, Inc. twin screw mixer bowl. 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-combusion flow calorimeter (PCFC, FAA microcalorimeter). In this apparatus, samples of 1.0 ± 0.1 mg were pyrolyzed at 1200°C at 1°C s^{-1} under nitrogen using a flash pyrolyzer (Pyroprobe 2000, CDS Analytical, Inc.).

2.3 Method of Scale Up of Polymerization

Dimethyl 5-hydroxyisophthalate (1 mol, 25 g) and aminopropyl terminated polydimethylsiloxane (MW 1000) (DMS-A12) (1.5 mol, 179.4 g) were placed in a round bottom flask under nitrogen, 10% by weight of the enzyme Novozyme-435 (immobilized *Candida antarctica* lipase B, protein content 1%) (20.4 g) and 10% by weight of 4A° molecular sieves (20.4 g) with respect to the weight of monomers were added. The resulting mixture was stirred at 90°C for 48 h using magnetic stir bar under vacuum. The reaction mixture was completely viscous. It was then stirred for another 48 h under vacuum using a mechanical stirrer. After completion, the reaction was quenched by adding chloroform and filtering off the enzyme and molecular sieves. The solvent was removed under reduced pressure to obtain the polymer in 85% yield, which was analyzed by different spectroscopic methods.

2.3.1. *^{1}H-NMR (δ_H $CDCl_3$, 500 MHz)*

0.10 (brs, methyl protons of dimethyl siloxane main chain, C-1H), 0.58 (t, 2H, C-2H), 1.20 (s, NH_2, exchanges with D_2O), 1.58 (m, 2H, C-3H), 3.35 (t, 2H, C-4H), 3.86 (s, COOCH_3 end group), 6.25 (brs, CON*H*), 7.71 (s, 1H, C-10H), 7.83 (s, 1H, C-12H), 7.96 (s, 1H, C-8H)

2.3.2. *^{13}C-NMR (δ_C $CDCl_3$, 125 MHz)*

0.50(C-1), 15.89(C-2), 29.85(C-3), 43.73(C-4), 52.82(O*C* -H_3, end gp), 118.42 and 120.47(C-8 and C-10), 122.86(C-6), 132.0 and 135.95(C-7 and C-11), 157.08(C-9), 166.26(CONH, main chain), 166.86(COO, end gp.).

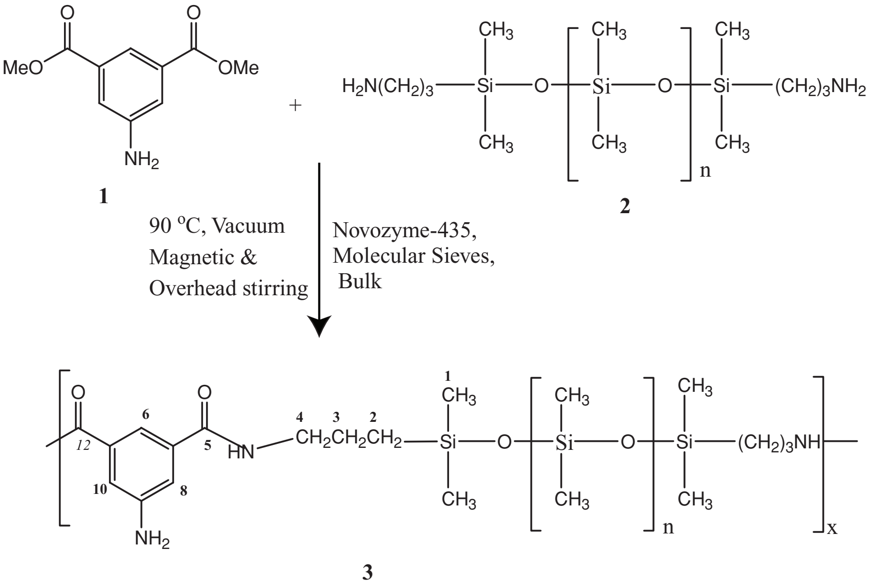
IR ν_{max}: 2961, 1642, 1541, 1411, 1257, 1009, 863, 786, 701 cm^{-1}.

UV λ_{max}($CHCl_3$): 304 nm

M_n(GPC), 11000 Da.; **PD** 1.34; **Isolated Yield** 85%.

2.4 General Method of Blending Siloxane Co-polymer [Poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl]] with Polyolefins

We have blended siloxane co-polymer in polyolefins in two ways. In the first method, we have blended the siloxane co-polymer Poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl] in polypropylene at 185°C and in polyethylene at 160°C using twin screw mixer bowl. In the second method, we initially mixed siloxane co-polymer with nanoclay [Cloisite 20A, 2C_{18} MMT (dimethylditallow-ammonium-/dimethyldioctadecylammonium-modified montmorillonite)] at room temperature followed by



Sch. 1. Synthesis of Poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl].

blending of this mixture with polypropylene at 185°C and with polyethylene at160°C using twin screw mixer bowl.

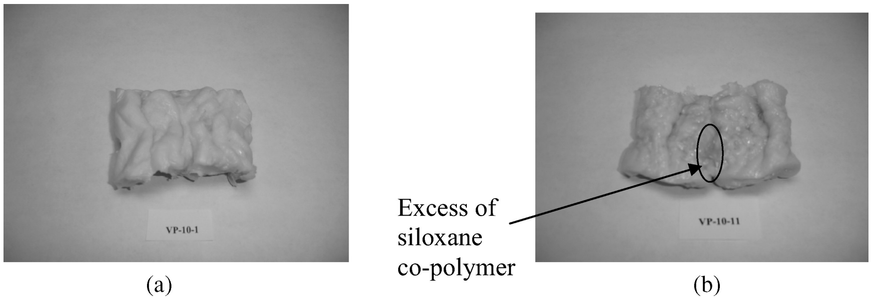
3 Results and Discussion

Herein, we have described a very flexible biocatalytic methodology using Novozyme-435 (immobilized *Candida antarctica* lipase B) for the scaled-up synthesis of siloxane-based co-polymers and their use in polyolefins as flame retardant additives. The silicone-based co-polymers were synthesized in large amounts by lipase catalyzed amidation polymerization of the diester, dimethyl 5-aminoisophthalate **1** and amino terminated polydimethylsiloxane **2** as shown in Scheme 1.

The ^{1}H-NMR spectrum of the co-polymer **3** showed the amidation between the methyl ester moiety of dimethyl 5-hydroxyisophthalate **1** and amino group of aminopropyl terminated siloxane **2**. The structure of the repeat units in the co-polymer formed was determined from its ^{1}H-NMR spectra. We have already shown the detailed synthesis and characterization of siloxane based organic-inorganic hybrid polymers (9). The number average molecular weight of the co-polymer **3** was found to be 11000 Da (PD 1.34), as determined by GPC. The degree of polymerization and molecular weight were also determined from proton NMR on the basis of end group analysis and was determined as 14000 Da. For this purpose, integration of methoxy end group at δ 3.86 and integration of α-CH_2 of the amide bond at δ 3.35 were used. We have blended the synthesized siloxane co-polymer with polyolefins with and without nanoclay [Cloisite 20A, $2C_{18}$ MMT (dimethylditallowammonium-/dimethyldioctadecylammonium-modified montmorillonite)].

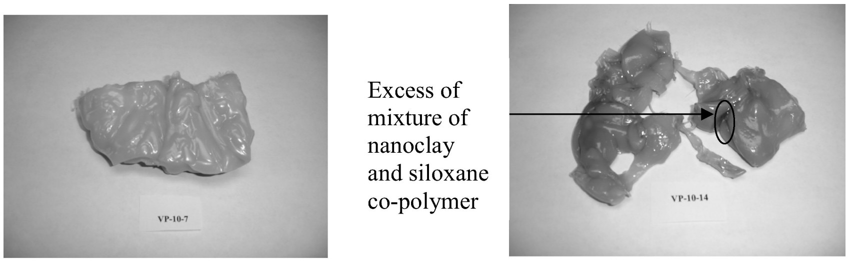
3.1 (A) Polypropylene

Twin screw mixer bowl was maintained at 185°C to blend siloxane co-polymer, Poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl] with polypropylene in different concentrations. Optimum concentration of siloxane co-polymer in polypropylene was found to be 10% (Fig. 1a). However, at 25% concentration complete blending did not occur and separation was observed as shown



(a) (b)

Fig. 1. (a) 10% siloxane copolymer in Polypropylene; (b) 25% siloxane copolymer in Polypropylene.



(a) (b)

Fig. 2. (a) 20% of [5% clay in polysiloxane] in polypropylene (b) 25% of [5% clay in polysiloxane] in polypropylene.

in Figure 1b. Blended polypropylene samples are shown in Figure 1.

We have mixed siloxane co-polymer with 5% of nanoclay in a high speed mixer at room temperature and then this mixture was blended with polypropylene in a twin screw mixer bowl at 185°C temperature at varying polymer concentrations ranging from 10% to 25%. The optimum concentration of nanoclay mixed siloxane co-polymer in polypropylene was found to be 20% (Fig. 2a). As the concentration of nanoclay and polymer mixture was increased up to 25%, complete blending did not occur as shown in Figure 2b. Blended polypropylene samples are shown in Figure 2.

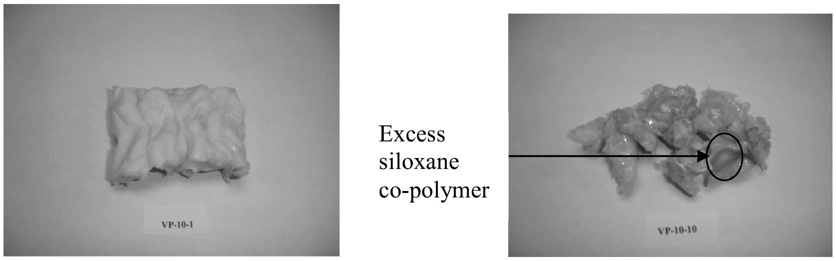
Table 1. TGA values of blended polypropylene

Polymer	*TGA Degradation temperature at 20% weight loss (°C)*
Poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl]	395
Polypropylene	385
10% siloxane co-polymer in polypropylene	435
10% of [5% clay in siloxane co-polymer] in polypropylene	448
20% of [5% clay in siloxane co-polymer] in polypropylene	445

3.2 Thermal Analysis

Thermal properties of polypropylene blended with and without nanoclay were studied based on their decomposition temperature and results are summarized in Table 1. Polypropylene was found to lose 20% weight at 385°C and siloxane co-polymer, Poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl] lost 20% weight at 395°C. 20% weight loss was found at 435°C for polypropylene blended with siloxane co-polymer, while this temperature goes up to 448°C for polypropylene blended with nanoclay mixed siloxane co-polymer. Addition of siloxane co-polymer in polypropylene improved the thermal stability of polypropylene by 50°C, whereas the improvement in thermal stability of polypropylene goes up by 63°C when polypropylene was blended with nano clay mixed siloxane co-polymer. Thus, on the basis of decomposition temperatures, polypropylene blended with mixture of nanoclay and siloxane co-polymer was found to be relatively more heat-resistant and can therefore be used at fairly high temperatures.

Flame retardant properties of blended polypropylene 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 (12). 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 948 $Jg^{-1}K^{-1}$



(a) (b)

Fig. 3. (a) 10% Polysiloxane in polyethylene; (b) 25% Polysiloxane in polyethylene.

Table 2. Flammability characteristics of blended polypropylene

Polymer	*Heat Release Capacity (J/gK)*	*Total Heat Release (KJ/g)*	*Char Yield (%)*
Poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl]	185.8	20.0	0
Polypropylene	947.8	39.8	0
10% siloxane co-polymer in polypropylene	963.0	37.4	1.1
10% of [5% clay in siloxane co-polymer] in polypropylene	985.9	38.7	0.5
20% of [5% clay in siloxane co-polymer] in polypropylene	880.4	37.0	3.3

for polypropylene, while it drops to about 880 $Jg^{-1}K^{-1}$ for polypropylene blended with mixture of nanoclay and siloxane co-polymer, Poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl]. Mixture of clay and siloxane co-polymer showed better performance in terms of heat release capacity as compared to siloxane co-polymer in polypropylene. Decrease of 67.4 $Jg^{-1}K^{-1}$ in heat release capacity was observed from polypropylene to polypropylene blended with nano clay and siloxane co-polymer. Flammability characteristics of blended polypropylene are summarized in Table 2.

3.3 B) Polyethylene

Twin screw mixer bowl was maintained at 160°C to blend siloxane co-polymer Poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl] with polyethylene at different concentrations. In this case also, optimum concentration of siloxane co-polymer in polyethylene was found to be 10% (Fig. 3a). Blending of 25% polysiloxane co-polymer with polyethylene did not give a uniform distribution indicating excess of siloxane co-polymer (Fig. 3b). Blended polyethylene samples are shown in Figure 3.

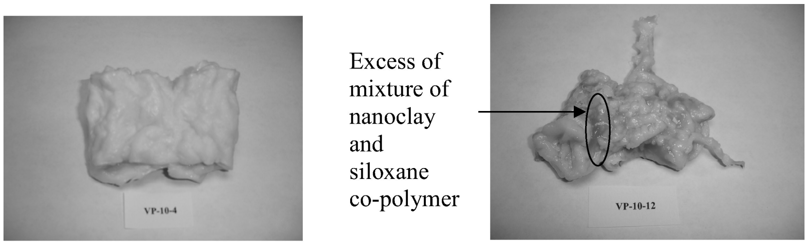
We have also mixed siloxane co-polymer with 5% of nanoclay in a high speed mixer at room temperature and then mixture of nanoclay and siloxane co-polymer was blended with polyethylene in twin screw mixer bowl at 160°C temperature. We have taken different concentrations of mixture of nanoclay and siloxane co-polymer ranging from 5% to 25% in polyethylene. Optimum concentration of nanoclay mixed siloxane co-polymer in polyethylene was found to be 15% (Fig. 4a). As the concentration was increased to 25%, uniform mixing could not be achieved as excess of mixture of nanoclay and siloxane co-polymer was observed (Fig. 4b). Blended polyethylene samples are shown in Figure 4.

Table 3. TGA values of blended polyethylene

Polymer	*TGA Degradation temperature at 20% weight loss (°C)*
Poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl]	395
Polyethylene	415
10% siloxane co-polymer in polyethylene	450
5% of [5% clay in siloxane co-polymer] in polyethylene	452
10% of [5% clay in siloxane co-polymer] in polyethylene	458
15% of [5% clay in siloxane co-polymer] in polyethylene	455

3.4 Thermal Analysis

Thermal properties of polyethylene blended with and without nanoclay were studied based on their decomposition temperature and results are summarized in Table 3. Polyethylene was found to lose 20% weight at 415°C and siloxane co-polymer, Poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl] lost 20% weight at 395°C. 20% weight loss was found at 450°C for polyethylene



(a) (b)

Fig. 4. (a) 15% of [5% clay in polysiloxane] in polyethylene; (b) 25% of [5% clay in polysiloxane] in polyethylene.

Table 4. Flammability characteristics of blended polyethylene

Polymer	*Heat Release Capacity (J/gK)*	*Total Heat Release (KJ/g)*	*Char Yield (%)*
Poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl]	185.8	20.0	0
Polyethylene	1158.8	41.9	0
10% siloxane co-polymer in polyethylene	1023.1	36.8	0
5% of [5% clay in siloxane co-polymer]in polyethylene	1078.8	38.2	0
10% of [5% clay in siloxane co-polymer]in polyethylene	1001.9	37.9	0
15% of [5% clay in siloxane co-polymer]in polyethylene	1003.2	145.0	1.9

blended with siloxane co-polymer, while this temperature goes up to 458°C for polyethylene blended with mixture of nanoclay and siloxane co-polymer. Addition of siloxane co-polymer in polyethylene improved the thermal stability of polyethylene by 35°C, whereas the improvement in thermal stability of polyethylene goes up by 43°C when polyethylene was blended with nano clay mixed siloxane co-polymer. Thus, on the basis of decomposition temperatures, polyethylene blended with mixture of nanoclay and siloxane co-polymer was found to be relatively more heat-resistant and can be used up to fairly high temperatures.

Flame retardant properties of blended polyethylene 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(12). 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 1159 $Jg^{-1}K^{-1}$ for polyethylene, while it drops to about 1003 $Jg^{-1}K^{-1}$ for polyethylene blended with mixture of nanoclay and siloxane co-polymer, poly[poly(dimethylsiloxane-1000)-propylamine-5-hydroxyisophthaloyl]. Mixture of clay and siloxane co-polymer showed better performance in terms of heat release capacity as compared to siloxane co-polymer in polyethylene. Decrease of 135.7 $Jg^{-1}K^{-1}$ in heat release capacity was observed from polyethylene to polyethylene blended with siloxane co-polymer whereas this decrease in heat release capacity from polyethylene to polyethylene blended with nano clay and siloxane co-polymer was found to be of 156.9 $Jg^{-1}K^{-1}$. Flammability characteristics of blended polyethylene are summarized in Table 4.

4 Conclusions

Synthesis of siloxane-based hybrid polymer having organic and inorganic components was successfully scaled up by a green chemistry approach using lipase (Novozyme 435) catalysis under mild and solvent-less conditions. Synthesized silicon co-polymer was blended with polypropylene and polyethylene with and without nanoclay. Blends of polyolefins with a mixtures of silicon co-polymer and nanoclay have shown enhanced thermal properties as compared to polyolefins and blend of polyolefins with silicon co-polymer.

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