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Crosslinking of Polydimethyl Siloxane Copolymers with Aromatic Dianhydrides: The Study of Thermal and Flame Retardant Properties[†]

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Aromatic dianhydrides have been identified as potential candidates for crosslinking with biocatalytically synthesized siloxane copolymers containing a functional amino group on the isophthalate moieties. We present the synthesis, characterization, thermal and flame retardant properties of this novel class of crosslinked organo-siloxane copolymers. We also discuss the effect of the concentration of one of the crosslinkers, 1,2,4,5-benzenetetracarboxylic dianhydride (DAH), on thermal decomposition and flame retardant properties using thermogravimetric analysis (TGA) and pyrolysis combustion flow calorimetry (PCFC) studies. The char yields were improved in all the polymers crosslinked with the various aromatic dianhydrides. The heat release capacity of a polymer crosslinked with 20% DAH, compared to the pure polymer, was tremendously reduced from 190 J/gK to 100 J/gK. The decomposition kinetics from TGA showed that the crosslinked polymer is thermally more stable than the non-crosslinked polymer.

Keywords: Polysiloxane copolymers, crosslinking, dianhydride, flame retardant

1 Introduction

Biocatalytic synthesis methods using enzymes have been proven to be environmentally friendly techniques (1). We have utilized lipase catalysis to synthesize organic-inorganic hybrid polysiloxane copolymers to improve the thermal stability and processability of inherently stable polydimethylsiloxanes (2). The thermal stability was further improved in enzymatically synthesized polysiloxane copolyimides using polydimethyl siloxanes with amino end groups and aromatic dianhydrides (3). The copolyamides synthesized using environmentally benign synthetic routes have been shown to possess a high degree of flame retardancy (4). However, the products remained as waxy or viscous liquids with heat release capacities around 200–260 J/g-K. Thus, there is a need to improve the mechanical and flammability properties in these polymers.

Crosslinking of polymers using various crosslinking agents is well known in the literature to further improve mechanical and thermal properties of the polymer. Flame retardant properties such as heat release capacity and total heat release were drastically improved in a siloxane copolyamide when they were crosslinked using hexamethylenetetramine (HMTA) as a crosslinking agent (4). The increase in percentage of HMTA drastically decreases the heat release capacity of the polymer. However, due to its aliphatic nature, HMTA tends to decompose and burn easily, which in turn did not improve the char yields and total heat release in any HMTA compositions. Thus, we need rigid, aromatic and thermally stable crosslinkers for further improvement of flame retardant properties of our materials. We report a simple crosslinking method to crosslink biocatalytically synthesized siloxane copolyamides and amino terminated polydimethyl siloxanes using aromatic dianhydrides which enhanced thermal as well as flame retardant properties of polysiloxane copolymers.

2 Experimental

2.1 Materials and Methods

Novozyme-435, an immobilized enzyme, was received gratis from Novozymes, Denmark and used as received.

[†] Dedicated to the memory of Professor Sukant K.Tripathy.

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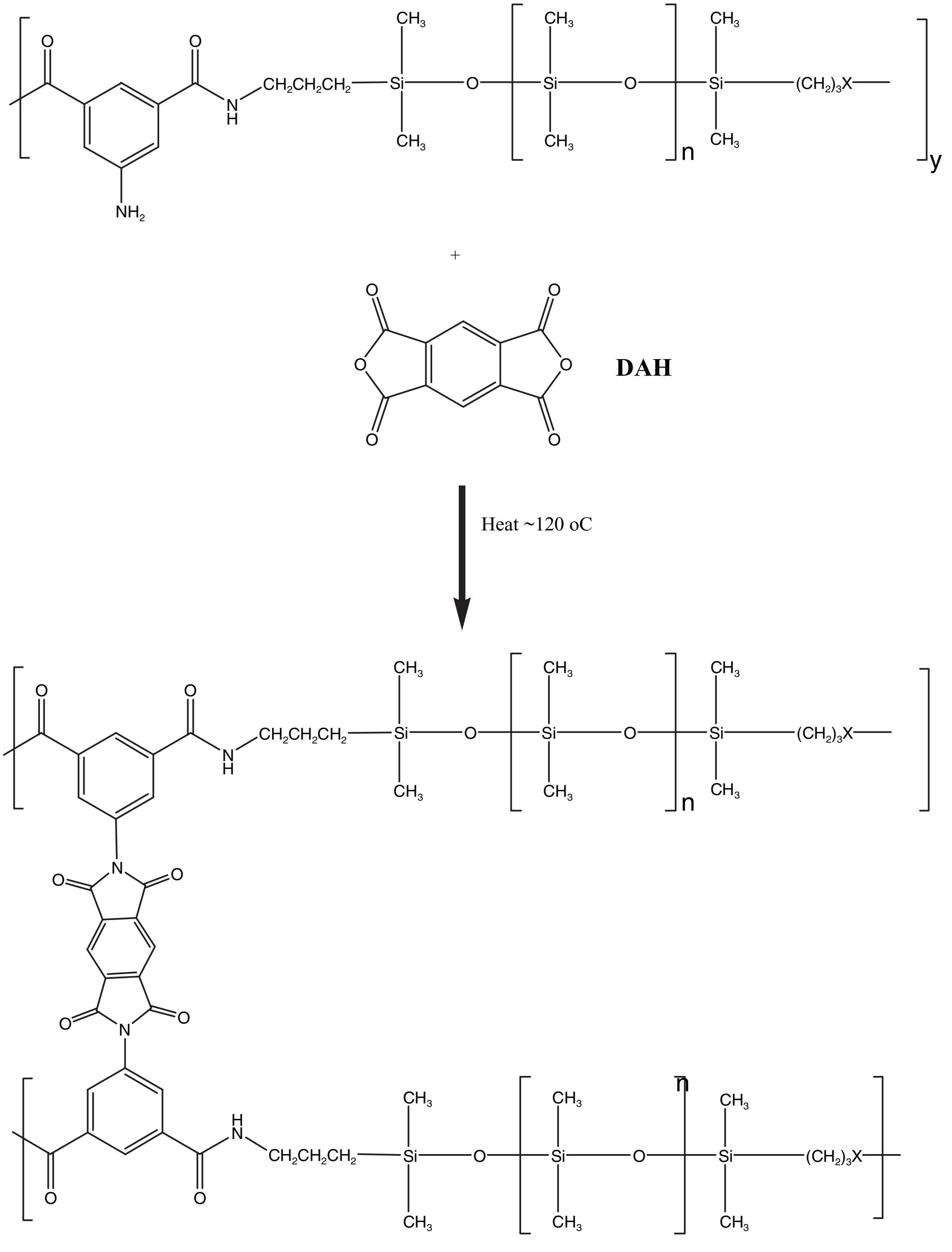
All other chemicals and solvents were used without further purification. Aminopropyl terminated polydimethylsiloxane (A12-Silox) (Mw 900-1100) was purchased from Gelest Inc. Dimethyl 5-aminoisophthalate, 4,4′-oxydiphthalic anhydride, 1,2,4,5-benzenetetracarboxylic dianhydride and 4,4′-biphthalic anhydride were purchased from Aldrich. Thermal decomposition temperatures and char yields were obtained under air atmosphere using a TA Instruments 2050 thermogravimetric analyzer (TGA). Flammability properties were measured using a pyrolysis-combustion flow calorimeter (PCFC, FAA micro calorimeter). Three measurements were carried out for each sample and the average of all three is reported. ^{1}H-NMR spectra of the polymers were obtained on a Bruker 200 MHz ARX



Sch. 1. Crosslinking of Siloxane copolyamide(IPNH) with an aromatic dianhydride, DAH (5–30 wt%), to obtain CL-IPNH-DAH.

Table 1. :Thermal decomposition temperatures, char yields and flame retardant properties of the siloxane copolymer and the crosslinked polymers (20 wt% of the various crosslinkers)

	TGA (in Air)[a]		*PCFC*		
Polymer	T_d *(°C)*[b]	*Char Yield*[c] *(%)*	*HRC (J/g-K)*	*Total HR (kJ/g)*	T_d *max (°C)*
IPNH	431.2	13.17	190.0	18.1	508.4
CL-IPNH-DAH	411.1	20.73	100.1	11.6	522.0
CL-IPNH-OXY	427.6	18.85	208.5	21.3	523.6
CL-IPNH-BPA	419.3	15.05	159.6	16.0	500.3

[a]at heating rate of 20°C/min; [b]decomposition temperature at 20% wt. loss; [c]residual char at 800°C; [d]temperature at maximum heat release.

spectrometer. FTIR-ATR spectra were recorded on a Thermo Nicolet 4700 FTIR-ATR spectrophotometer.

2.2 Synthesis and Crosslinking

Polysiloxane copolyamides with an amino group at 4-position on the isophthalate moiety were synthesized using a previously reported procedure (2) and characterized by ^{1}H-NMR spectroscopy. Crosslinking of these siloxane-copolyamide polymers was carried out using aromatic dianhydrides (Fig.1). In a typical crosslinking procedure (Scheme 1), the copolyamide and dianhydride (20 wt%) were dissolved in a mixture of chloroform and acetone (1:1) solvents by heating, and the resultant clear solution was heated slowly on a hot plate at 60°C to remove the solvent mixture for 10 min. Further heating was performed to crosslink at 120°C for 10 min and obtain an insoluble transparent glassy material. The crosslinked product was then oven-dried under vacuum at 90-120°C overnight to remove any residual solvents and water. The insoluble product was characterized by FTIR-ATR spectroscopy.

3 Results and Discussion

3.1 Synthesis and characterization

The siloxane copolyamide (IPNH) crosslinked with aromatic dianhydrides (CL-IPNH-DAH, Sch. 1) resulted in a highly insoluble glassy material and is very different from the original waxy polymer. The crosslinking was carried out at various concentrations (5, 10, 15, 20, 25, 30%) of the crosslinker, but 20% of the crosslinker in IPNH was found to be optimum. The IPNH crosslinked with 20% DAH was characterized by ATR-IR and is shown in Figure 1. As can be seen from the IR stretching frequencies in Figure 2, the carbonyl stretching frequency corresponding to an imide bond appeared at 1723 cm^{-1} in the crosslinked polymer in addition to an amide carbonyl stretching frequency at 1630 cm^{-1}. The imide formation in this polymer is only possible between the amino group on isophthalate moiety and the aromatic dianhydride as shown in Scheme 1.

3.2 Thermal and Flame Retardant Properties

Thermal and flame retardant properties were investigated for all the crosslinked polymers and the non-crosslinked polymer. Table 1 provides thermal decomposition temperatures (T_d), char yields, heat release capacities (HRC), total heat release (THR) and temperature at maximum heat release (T_{max}) values for all of the polymers. The flame retardant properties measured using pyrolysis combustion flow calorimetry (PCFC) revealed that both DAH and BPA crosslinked polymers had tremendously improved their HRC compared to the non-crosslinked polymer, IPNH. Surprisingly, the 20% Oxy crosslinked polymer, CL-IPNH-OXY, increased the HRC and total HR somewhat compared to the non-crosslinked polymer. The crosslinked polymer (20% DAH), CL-IPNH-DAH, exhibited the lowest heat release capacity (100 J/gK) and total heat release (11.6 kJ/g) compared to all of the polymers studied. The TGA studies showed that this crosslinked polymer has a good decomposition temperature (411°C) and the highest char yield (21%). This could be due to the rigid nature of the DAH. All other dianhydrides studied have single bonds within the molecule, which allow for rotation and could lead to an entirely different degradation mechanism. The temperatures at maximum heat release (T_{max}) also called 'ignition temperature' from PCFC are found to be around 500°C in all of these polymers, which also makes them interesting candidates for flame retardant applications.

Table 2 provides T_d, HRC and THR values of the DAH-crosslinked polymers at various concentrations of DAH. The decomposition temperatures decreased from 431 to

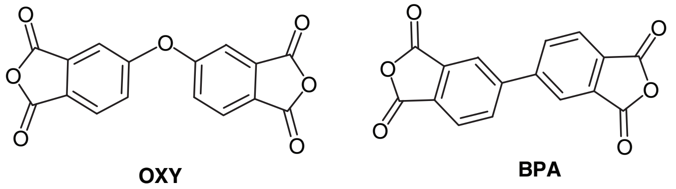


Fig. 1. Structures of other anhydride crosslinkers considered in this study.

Table 2. PCFC heat release capacity and total heat release of crosslinked polymer CL-IPNH-DAH at various concentrations of the crosslinker, DAH

% DAH in IPNH	*T_d^a(°C)*	*HRC (J/g-K)*	*Total HR (kJ/g)*
0	431.2	190.0	18.1
5	438.8	177.0	16.3
10	435.0	177	19.7
15	429.3	144.9	18.7
20	411.1	100.1	11.6
25	401.8	133.8	19.6
30	415.1	133.5	20.7

[a] decomposition temperature at 20% wt. loss in air.

411°C from pure polymer to 20% DAH crosslinked polymer (CL-IPNH-DAH) due to faster degradation in the presence of DAH. However, it is interesting to note that, an increase in the DAH concentration decreased the HRC, which depend entirely on various factors (global activation energy for pyrolysis, the temperature of maximum mass loss rate, the heat of combustion, char yield) of combustion process (5) of the crosslinked polymer until a critical concentration of 20% was reached. At 20% DAH, the crosslinked polymer had the lowest HRC (100 J/gK). This could be the maximum amount of DAH that the polymer can crosslink, and therefore no noticeable improvement in the properties above this concentration level is observed. The thermal decomposition kinetics of the 20% DAH crosslinked sample were studied using the Kissinger method (6) and the results were compared with the pure polymer, IPNH. The activation energy of decomposition was determined based on changes in thermogravimetric data at various heating rates (2, 5, 10, 15, 20, 25°C/min) (7). As we anticipated, the activation energy of decomposition for the crosslinked polymer was found to be higher (92 kJ/mol) than the pure polymer (79 kJ/mol), which is well correlated with the flame retardant properties.

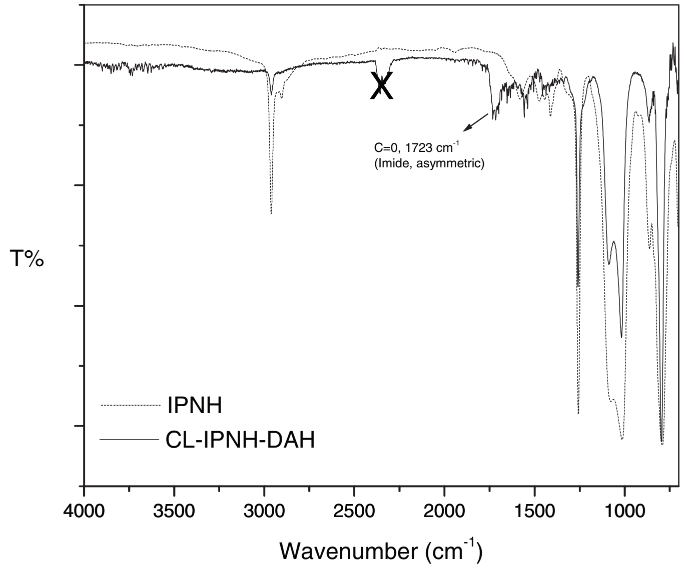


Fig. 2. ATR-IR of siloxane copolyamide films: CL-IPNH-DAH (solid) and IPNH (dotted).

4 Conclusions

Aromatic dianhydrides were found to be a new class of efficient crosslinking agents for enzymatically synthesized polysiloxane copolyamides with free amino functional groups. Due to the aromatic nature of the crosslinkers, the char yields and flame retardant properties were improved over the non-crosslinked polymer. A crosslinked polyamide with 20% DAH showed the lowest HRC, total HR and the highest char yield compared to other crosslinked polymers. These copolymers, along with the crosslinking agents, can be easily coated (in solution form) onto any substrate including fabrics and crosslinked on the surface by heat treatment. Further studies on crosslinking and coatings of these crosslinked polymers on Army fabrics are underway in our laboratory. The flame retardant properties of these new materials will be explored.

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References

1. (a) Kobayashi, S., Uyama, H. and Kimura, S. (2001) *Chem. Rev.*, 101, 3793; (b) Gross, R.A., Kumar, A., Kalra, B. (2001) *Chem. Rev.*, 101, 2097.
2. Kumar, R., Tyagi, R., Parmar, V.S., Samuelson, L.A., Kumar, J., Schoemann, A., Westomoreland, P.R. and Watterson, A.C. (2004) *Adv. Mater.*, 16, 1515.
3. Mosurkal, R., Samuelson, L.A., Parmar, V.S., Kumar, J. and Watterson, A.C. (2007) *Macromolecules*, 40, 7742.
4. (a) Mosurkal, R., Tucci, V., Samuelson, L.A., Bruno, F., Kumar, J., Westomoreland, P.R. and Watterson, A.C. (2006) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.),* 47, 1110; (b) Mosurkal, R., Tucci, V., Samuelson, L.A., Kumar, J., Watterson, A.C., Parmar, V.S., Smith, K., Westmoreland, P.R. Novel organo-siloxane coplymers for flame retardant applications. In The Science and Technology of Silicones and Silicone-modified Materials. Clarson, S. J., Fitzgerald, J.J., Owen, M.J., Smith, S.D., Van Dyke, M.E. Eds. ACS Symposium Series:

Oxford University Press, Vol. 964, in press; (c) Mosurkal, R., Samuelson, L.A., Smith, K.D., Westmoreland, P.R., Parmar, V.S., Yan, F., Kumar, J., Watterson, A.C. (2008) *J. Macromol. Sci. Part A: Pure and Appl. Chem.*, 45, 943.

5. Lyon, L.E. and Walters, R.N. (2004) *J. Anal. Appl. Pyr.*, 71, 27.
6. Kissinger, H.E. (1957) *Anal. Chem.*, 29, 1702.
7. Gaan, S. and Sun, G. (2007) *Polymer Degradation and Stability*, 92, 968.