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Synthesis, Characterization and Material Applications of Unsaturated Polyamide Containing

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Abstract

Unsaturated polyamides (USPA) containing 5,5-dimethylhydantoin in the main chain were prepared by polycondensation reaction of bisamic acid **(1a-h)** with 5,5-dimethylhydantoin **(2)** using thionyl chloride and pyridine as condensing agents and N-methyl-2-pyrolidone as solvent. These new polymers **(3a-h)** were obtained in good yield. The resultant USPA polyamides were characterized by elemental analysis, thermal gravimetric analysis, solubility test and FT-IR spectroscopy. The interacting blends of these USPAs with commercial unsaturated polyester (CUPE) and epoxy resin at 30:60:10 ratio were prepared and processed for glass reinforced composites.

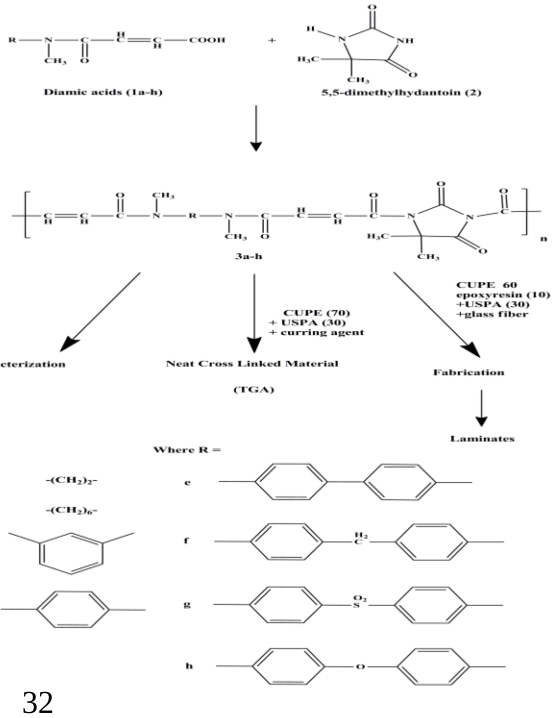
Keywords: Unsaturated Polyamides, Interacting Blends, Polyester, 5, 5-Dimethyl Hydantoin, Reinforced Composites.

Introduction

High performance polymers have received remarkable attention in current age due to growing demands in industrial applications like the replacement for metals or ceramics in automotive, aerospace and microelectronic industries[1-4]. One of important class of high-temperature polymers i.e. aryl polyamide have found application in the aviation, automotive and electronic industries[5-7]. However these polymers are difficult to process due to their infusibility and insolubility in common organic solvents[8,9]. Therefore, more studies attempts were made to process modify these polymers without dilution of their properties[10-14].

One of the authors [HSP] developed unsaturated polyester containing epoxy residue[15]. In extension of this work the present work comprising the USPA containing 5, 5 -dimethyl hydantoin. Though such 5, 5-dimethylhydantoin containing polyamides are reported earlier[16]. The present work is shown schematically as follow:

Scheme 1



Experimental

Materials

All chemicals were procured as pure grade. Bisamic acids were prepared by method [17] reported. 5,5-dimethylhydantoin was prepared by laboratory method [18,19]. Commercial unsaturated polyester was obtained from sympol industry, Vatva, Ahmedabad. Glass cloth Satin (2/2) weave (polyamide compatible) woven fabric, 0.25 thick, E-glass, 270 g/m^2 (obtained from Unnati Chemicals, Ahmadabad, India), was used for laminate preparation.

Methods

The C, H and N contents of all the USPA were estimated by means of a Carlo Erba elemental analyzer (Italy). The FTIR spectra were taken in KBr using a Perkin-Elmer 983 spectrophotometer. All polymer samples were subjected to thermogravimetric analysis (TGA) (Du Pont 950 thermogravimetric analyzer) in air at a heating rate of 10 K min^{-1}.

Synthesis of 5, 5-dimethylhydantoin (2)

Acetone cyanohydrin (0.05mol) and freshly powdered ammonium carbonate (0.078mol) were added to a 250mL round-bottomed flask, which contained a stirring bar. The mixture was heated to 50°C for 30 min, and then heated to 70-80°C for 3h. Next, it was heated to 90°C and was maintained at this point until the mixture was quiescent. The colorless residue was solidified on cooling. Then the crude product was recrystallized with hot water and the yield of pure product **(2)** was 62 %.

Synthesis of Unsaturated polyester by Polycondansation of bisamic acids and 5, 5-dimethylhydantoin

USPA was Prepared by following General Procedure

Bisamic acid (1mmol) was dissolved in 10ml DMF in a dry 3-necked flask. The solution was cooled to 10°C, then thionyl chloride (2.5mmol) was added and stirred for 5 min. 5, 5-dimethylhydantoin **(2)** (1 mmol) and pyridine (2.5 mmol) were added to the mixture. It was stirred for 15h at 0-5°C and then 2h at room temperature. The viscous reaction mixture was poured into 25ml of acetone. The precipitated polymer was collected by filtration and air-dried. The C, H and N contents and IR data of all the USPA were displayed in **Table-1**.

Chemical Resistance Test [20]

The resistance of chemicals of the composite samples was measured according to ASTMD543. The laminate samples (25mm x 25 mm) were immersed in 1.51 M HCL, 6.25 N NaOH, DMF, Ketones, Ethanol, DMSO, Dioxane and THF at room temperature for a week. The data are included in **Table-2**.

Mechanical Testing [20]

All the mechanical testing was done by using three test specimens.

1. The measurement of flexural properties was carried out with Universal Instron testing machine model numberA-74-37, at room temperature according to the method of ASTM D 790.
2. The compressive strength was measured according to ASTM D 695.
3. The measurement of impact strength of notched specimen was made with an Izod type impact tester at room temperature according to the testing method of ASTM D 256.
4. The Rockwell hardness was measured according to ASTM D 785.
5. The measurement of dielectric strength was carried out on a high voltage tester machine oil test set.

All the mechanical and electrical properties are furnished in **Table-2**.

Preparation of Interacting Blends

A mixture of USPA (30%) and CUPE (70%) was stirred at room temperature for 1h. The homogeneous mixture (2.0 g) was then cured in presence of MEK peroxide and cobalt octenale as acceleration at 60°C for 24h. The resultant cured material was characterized by TGA.

Fabrication

A typical method of fabrication for composites is given below.

A suspension of USPA resin and CSPE was mixed well by constant stirrer for 1 h. The MEK peroxide and cobalt octenale as acceleration were added appropriately. The suspension mixture was then applied with a brush to a 25 mm X 25 mm fiber glass cloth and the solvent was allowed to evaporate. The 10 dried prepregs thus prepared were stacked one on top of another and pressed between steel plates with a Teflon film release sheet and compressed in a flat platen press under about 70 psi pressure. The prepregs were cured by heating the press to 70-80 °C for 24h in an air circulated oven. The composite so obtained was cooled to 50°C before the pressure was released. Test specimens were made by cutting the composite and machining them to final dimensions.

Results and Discussion

Polyamides were prepared by solution polymerization of an equimolar bisamic acid with 5,5-dimethylhydantoin at stoichiometric resio using thionyl chloride and pyridine as condensing agents and DMF as solvent **(Scheme-1)**. The whole poly condensation readily proceeded to a homogeneous solution. Pasty lumps were formed when the viscous polymer solutions were poured into stirred methanol. All the polymers were obtained quantitatively.

The structures these polymers were confirmed as polyamides by FT-IR spectroscopy and elemental analyses **(Table-1)**. The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures **(Scheme-1)**. The representative FT-IR spectrum of polyamide **5b** is shown in **Figure-1**. The USPA shows absorption bands found at 1686 cm^{-1} due to carbonyl of amide group. Also absorption bands around 1450-1600 cm^{-1} show the presence of the vinyl moiety in this polymer. The weak band at 1643 cm^{-1}mainly responsible for CH=CH band. The remaining characteristic bands are found at their respective positions. The other spectra show a similar pattern.

The CHN content of all USPAs is Consistent with the Values of Predicted Structures

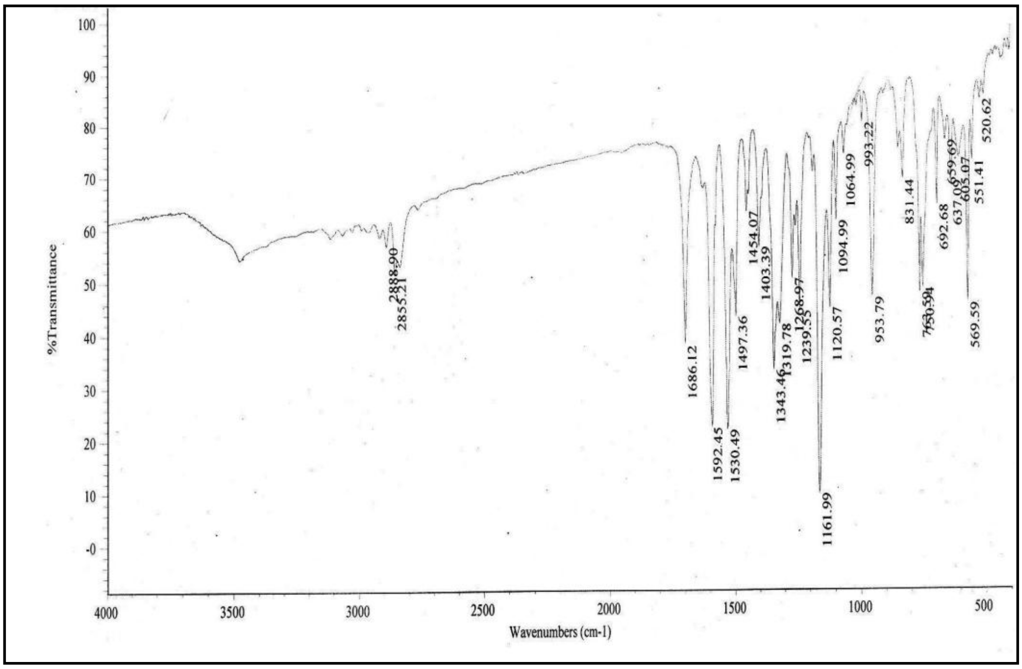


Figure-1 IR spectra of polyamide 5b

Table-1

Characterization of USPA (3a-h)

Comp.	Yield %	Elemental analysis % Calc. (Found)				% Wt. loss at various temperatures					
		C	H	N	S	300°C	400°C	500°C	600°C	700°C	750°C
3a	64	56.15 (56.1)	6.45 (6.4)	13.79 (13.7)	---	2.5	25.7	48.4	61.6	78.4	92.3
3b	68	59.72 (59.7)	7.41 (7.3)	12.11 (12.0)	---	2.5	26.5	49.5	62.8	79.7	94.2
3c	62	60.65 (60.6)	5.97 (5.9)	12.30 (12.2)	---	2.0	24.6	47.1	61.0	72.6	91.2
3d	71	60.65 (60.6)	5.97 (5.9)	12.30 (12.2)	---	2.5	21.5	43.3	59.4	73.2	90.5
3e	60	65.65 (65.6)	5.70 (5.6)	10.56 (10.5)	---	2.5	22.8	45.5	56.5	82.2	91.7
3f	69	66.16 (66.1)	5.92 (5.9)	10.29 (10.2)	---	2.0	26.4	45.0	58.6	73.4	90.2
3g	69	58.58 (58.5)	5.09 (5.0)	9.42 (9.4)	5.39 (5.3)	3.0	23.9	44.8	61.1	75.6	92.4
3h	72	63.73 (63.7)	5.53 (5.5)	10.25 (10.2)	---	3.0	23.2	46.4	59.5	73.8	91.7

Table-2

Chemical Resistance, Mechanical and Electrical Properties of Glass Reinforced Cross-Linked Polyamide Composites

Composites	Chemical Resistance %		USPA Content %	Flexural Strength (MPa)	Compressive Strength (MPa)	Impact Strength (MPa)	Hardness (R)	Electrical Strength in Air (kV/mm)
	Thickness	Weight						
C3a	1.2	1.2	35.4	374	341	370	78	21.2
C3b	1.2	1.1	34.6	447	362	364	84	22.4
C3c	1.3	1.2	37.2	361	354	359	89	27.1
C3d	1.3	1.1	37.9	355	310	305	82	29.9
C3e	1.4	1.2	38.0	395	295	314	92	28.2
C3f	1.2	1.2	39.5	336	325	302	83	24.8
C3g	1.4	1.0	36.8	312	308	306	82	25.5
C3h	1.2	1.1	37.1	305	315	310	85	24.7

The solubility of USPA (3a-h) was investigated as 0.01g of polymeric sample in 2 ml of solvent. All of these USPA are soluble in organic solvents such as DMF, DMAc, DMSO, and NMP at room temperature, and are insoluble in common organic solvents such as THF, acetone, chloroform, methylene chloride, methanol, ethanol, and water.

Thermal Properties of Blends

The TGA data of all USPA are shown in **Table-2**. Examination of TG-data reveals that the USPA starts their decomposition between 270 to 290° depending upon the nature of USPA. The rate of weight loss is high around 490°C and about 90 to 95% constantly beyond 620°C.

The TGA data of all interacting blends are shown in **Table-3**. The TG-data of blends reveals that the blends start their decomposition between 210 to 230°C. The rate of weight loss is high around 450°C and about 92 to 94% constantly beyond 610°C

Table- 3

TG data of Interacting Blends

Interacting Dlends	% Wt. loss at various temperatures					
	300°C	400°C	500°C	600°C	700°C	750°C
I3a	3.0	27.4	50.4	62.7	79.7	92.6
I3b	3.2	28.8	51.0	63.0	79.3	94.1
I3c	2.8	25.9	49.3	63.2	75.2	91.9
I3d	3.0	24.0	46.6	61.8	75.9	91.7
I3e	3.5	24.7	48.7	59.9	80.0	92.9
I3f	3.2	28.2	48.2	60.8	76.1	92.6
I3g	3.0	26.1	47.4	62.3	77.4	93.0
I3h	3.2	25.5	49.5	61.0	76.5	93.5

Results and Discussion of Composites

Because of the non-processability of the present insoluble cross-linked polyamide, a novel approach was also conducted to develop this matrix system for processable (~150°C) glass-fibre composites. All the composites prepared were dark brown sheets. The addition polymerization of 5,5-dimethylhydantoin with bisamic acids of compressed composites, from which the polymerization continues towards the inner part of the composites without evaporation of any reaction by-products or solvent molecules. Characteristics of the glass reinforced cross-linked polyamide composites are summarized in **Table-2**. The density values were in the range with respect to the nature of polyamide compounds, chemical resistance to organic solvents and concentrated 1.51M HCL. However treatment with concentrated 6.2 M NaOH changes their thickness a little and the weight by about 1.3%. Examination of the results of mechanical properties **(Table-2)** of cross-linked polyamide composites reveals that all the composites have good mechanical strength.

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References

1. You, J., Chen, C. C., Dou, L., Murase, S., Duan, H. S., Hawks, S. A., Xu, T., Son, H. J., Yu, L., Li, G., Yang, Y. (Oct. 2012), Metal Oxide Nanoparticles as an Electron-Transport Layer in High-Performance and Stable Inverted Polymer Solar Cells. Advance Materials., Vol. 24, No. 38, pp 5267-5272.
2. Koronis, G., Silva, A., Fontul, M. (Jan. 2013), Erratum to Corrigendum to Green composites: A review of adequate materials for automotive applications, Composites Part B: Engineering, Vol. 44, No. 1, pp 120-127.
3. Meenakshi, K. S., Sudhan, E. P. J., Kumar, S. A., Umapathy, M. J. (May 2012), Development of dimethylsiloxane based tetraglycidyl epoxy nanocomposites for high performance, aerospace and advanced engineering applications, Progress in Organic Coatings., Vol. 74, No. 1, pp 19-24.
4. Lee, K. Y., Kumar, B., Seo, J. S., Kim, K. H., Sohn, J. I., Cha, S. N., Choi, D., Wang, Z. L., Kim, S. W. (Mar. 2012) P-Type Polymer-Hybridized High-Performance Piezoelectric Nanogenerators, Nano Letters., Vol. 12, No. 4, pp 1959-1964.
5. Biju, A. C., Victoire, T. A. A., Selvaraj, D. E., (Jul. 2015) Enhancement of Dielectric Properties of Polyamide Enamel Insulation in High Voltage Apparatuses Used in Medical Electronics by Adding Nano Composites of SiO_2 and Al_2O_3 Fillers, Journal of Electronic Engineering and Technology, Vol. 10, No. 4, 30-40.
6. Hummel, D. O., Heimen, K. U., Stenzenberger, H., Siester, H. (Mar 2003), Infrared spectroscopic determination of the kinetic data of the polymerization of aliphatic bismaleimides, Journal of Applied Polymer Science., Vol. 18, No. 7, pp 2015-2024.
7. Serafini, T. T., Delvigs, P., Lightsey, G. R. (Mar. 2003), Thermally stable polyimides from solutions of monomeric reactants, Journal of Applied Polymer Science., Vol. 16, No. 4, pp 905-915.
8. Galanti, A. V. (Mar. 2003), A kinetic study of the polymerization of aliphatic imides, Journal of Applied Polymer Science., Vol. 29, No. 5, pp 1611-1616.
9. Kricheldorf, H. R. (1999) Progress In Polyimide Chemistry, Advances in Polymer Science., Springer, 140.
10. Reghunadhan Nair C. P., Bindu R. L., Ninan K. N. (Feb. 2000) Phenolic resins bearing maleimide groups: Synthesis and characterization, Journal of Polymer Science Part A: Polymer Chemistry, Vol. 38, No. 3, pp 641-652.
11. Bindu R. L., Reghunadhan Nair C. P., Ninan K. N., (Dec. 2001), Thermal characteristics of addition-cure phenolic resins, Polymer Degradation and Stability., Vol. 73, No. 2, pp 251-257.
12. Reghunadhan Nair C. P., Bindu R. L., Ninan K. N., (Sep. 2001), Phenyl ethynyl functional addition cure phenolic resins: Synthesis, characterisation and thermal properties, Journal

of Material Science.,. Vol. 36, No. 17, pp 4151-4157.

13. Mittal, K. L. (1985), Polyamides, synthesis, characterization and applications, Plenum, Newyork.
14. Reyx, D., Campistron, L., Cailluad, C., Villate, M., Cavendon, O. (1995)., Thermal reaction between N-phenylmaleimide and 2-allylphenol as a model for the crosslinking reaction in bismaleimide polymerization with diallylbisphenol A, Macromolecular Chemistry and Physics, Vol. 196, No. 3, pp 775-785.
15. Patel, H. S., Panchal, K. K. (Apr. 2005), Novel Unsaturated Polyester Resins Containing Epoxy Residues, International Journal of Polymeric Materials and Polymeric Biomaterials., Vol. 54, No. 1, pp 1-7.
16. Faghihi, K. (Jan. 2008), Synthesis and Properties of New Polyamides Based on 4-Phenylenediacrylic Acid and Hydantoin Derivatives in the Main Chain, Turkish Journal of Chemistry., 32, No. 2, pp 191-200.
17. Patel, H. S., Panchal, K. K. (Feb. 2007), Novel Unsaturated Polyester Amide Resins Based on Epoxy Resins, Polymer-Plastics Technology and Engineering, Volume 43, No. 4, pp 1177-1185.
18. Faghihi, K., Hajibeygi, M. (Dec. 2003), New polyamides containing azobenzene unites and hydantoin derivatives in main chain: synthesis and characterization, European Polymer Journal., Vol. 39, No. 12, pp 2307-2314.
19. Wagner, E. C., Baizer, M. (1940), 5,5-DIMETHYLHYDANTOIN, [Hydantoin, 5,5-dimethyl-], Organic Synthesis., Vol. 20, pp 42.
20. Patel, H. S., Patel, V. C. (Apr. 2001), Polyimides containing s-triazine ring, European Polymer Journal., Vol. 37, No. 11, pp 2263-2271.