



Trade Science Inc.

December 2008

Volume 4 Issue (2-3)

Macromolecules

An Indian Journal

Full Paper

MMALJ, 4(2-3), 2008 [135-138]

Synthesis and characterization of novel polyamide based adhesives

G.Vinod¹, H.Jayadevappa¹, B.S.Sherigara^{1*}, K.Sheshappa Rai²,
T.E.Musturappa¹, M.P.Yashoda³

¹Department of Studies and Research in Industrial Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta-577 451, (INDIA).

²Department of Studies and Research in Polymer Science, University of Mysore, Toobinkere, Mandya, (INDIA)

³Department of Studies and Research in Chemistry, Manipal Institute of Technology, Manipal, (INDIA)

E-mail : bssherigara@rediffmail.com

Received: 21st May, 2008 ; Accepted: 26th May, 2008

ABSTRACT

A new class of polyamides for adhesive application has been synthesized by condensation polymerization method using chemically modified diamines and diacids. The synthesized polymers were characterized by FTIR and ¹H NMR spectroscopic method. Viscosity and thermal studies were carried out by Ubbelohde viscometer and TGA respectively. Results showed that the new polyamide adhesives possess good thermal resistant property. © 2008 Trade Science Inc. - INDIA

KEYWORDS

Adhesive;
Polyamide;
Viscosity;
Thermal resistance.

INTRODUCTION

Polyamide is a generic description for high molecular compounds, which consist of monomers that are linked by amide bonds. To the latter the naturally occurring polypeptides and proteins can be added. In contrast, the members of the group of polyamides are made of one type of monomer. Depending on the kind of, monomer of which they are synthesized, they can be further subdivided into the amino carboxylic acid. Whereas the chemically synthesized perlon, which is produced from aminocaproic acid, is an example of the former, Nylon, which is synthesized from 1,6-hexanediamino and adipic acid, is an example of the latter. Regarding the composition the aminocarboxylic homopolyamides are the simplest polyamides.

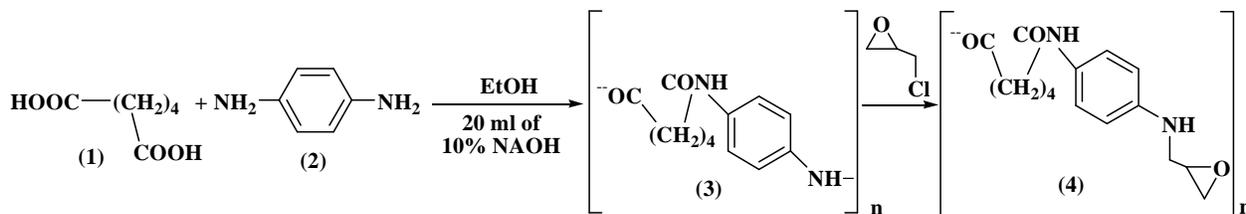
The original polyamides were made using linear diamines^[1,2]. A very novel patent was claimed for a specific type of polyamide that was, made from cyclic diamines, such as piperazine^[4]. Compared to other dim-

mer-based polyamide, these resins were declared to give unique adhesion to polyvinyl chloride (PVC), termed vinyl in the remainder of this paper. Although more than 35years have passed since this discovery^[4], and there have been over 40 patents that involve piperazine-dimer acid polyamide, no model has been proposed to explain this specific adhesion to vinyl. In addition, the only polyamide hot melt adhesives that have been reported to bond to vinyl were made from these secondary diamines. Wholly aromatic polyamide adhesives are one of the most important classes of high performance polymers^[1-17]. The repeating units of these polymers possess one amide (-NHCO-) linking bond between appropriate aromatic nuclei.

EXPERIMENTAL

Synthesis of polyamide diamine in ethanol (50ml) and NaOH (20ml of pH10) were taken in 100ml round bottom flask. The flask was then fitted with a water

Full Paper



SCHEME 1: Synthetic route for the synthesis of polyamide based water soluble adhesives

cooled condenser and then refluxed at 60°C for about 6 hours on oil bath. Then the solvent and water are removed by distillation, viscous resin is remains at the bottom of the flask.

Synthesis of resin

A mixture of polyamide-amine resin was (50% aqueous solution of the resin was prepared by adding 5.3ml of water) taken with of epichlorohydrin and the contents were refluxed for about 6hr at 60°C. After that the excess of epichlorohydrin was removed by distillation. A viscous resin was obtained.

Characterization

Infrared spectra of the prepared polymers were recorded using Perkin-Elmer infrared spectrophotometer, ¹H NMR.

Spectral charectarization of compound (4)

IR (KBr) cm⁻¹; 3031(C-H, Ar-H); 3376(N-H); 1639 (C=O); ¹H NMR (DMSO d₆), δ 6.9 (d, 2H, Ar-H, J=8.05), 7.3 (d, 1H, Ar-H, J=7.65), 2.54 (m, 4H, CH₂), 1.12 (m, 4H, CH₂), 2.9 (m, 2H, CH), 4.00 (s, 1H, N-H, J=4.08).

Polymer characterization

Viscosity

Intrinsic viscosity measurements were carried out on 0.5% solutions of the adhesive polymer in DMAc at 30°C using Ubbelohde viscometer. Energy correction. Flow times were measured at five different concentrations of the polymer sample. All the plots obtained were linear. The intrinsic viscosity was determined by usual extrapolation of η_{sp}/C to zero concentration and expressed in deciliter per gram (dl g⁻¹).

Solubility

Solubility of the polymers in various amide solvents

like, DMF, DMAc and DMSO was determined at room temperature (25°C). It was performed by gradual addition of the polymer to the solvent till saturation. The maximum solubilities of the polymers were calculated as percent weight of the polymer per hundred ml. of solvent (% wt/v).

Thermogravimetric analysis

Thermogravimetric analysis (TG) curves were recorded on a Shimadzu TGA-50 H in air and nitrogen atmospheres at a heating rate of 10°C min⁻¹ and a heating range from 27°C temperature to 400°C. The samples weights ranged from 3 to 5 mg and the gas flow rate was 30 ml min⁻¹.

RESULTS AND DISCUSSION

Polymer characterization

Viscosity

TABLE represents the intrinsic viscosity values for the prepared polyamides. The values reflect the high molecular weight of the polymers. It can be noted that the intrinsic viscosity of the polymers (in DMAc at 30°C) increase in paralinkages and ranges between 0.73 and 4.83 dl g⁻¹ when the paraphenylene rings content increases from 0 to 100 mol%. This indicates that the polymers chain rigidity increases as a function of their para-linkages. The polymer with all meta-linkages has the lowest intrinsic viscosity, whereas that with all para-linkages has the highest one. The polymers with various proportions of meta-to-paralinkages have intermediate intrinsic viscosities. The higher intrinsic viscosity value of wholly p-oriented type of polymer can be attributed to the higher rigidity, much interchain hydrogen bonding, associated with higher chain symmetry and efficiency. This observation seems to support the results which were previously reported^[5,8,9].

Flow time for solvent (water)=43sec

Concentration, C(g/dl)	Flow time, t (sec)	t/to= η_r	$\eta_r-1=\eta_{sp}$	η_{sp}/C (dl/g)	$\ln \eta_r$	$\ln \eta_r/C$ (dl/g)
0.2716	91.5	2.1287	1.1287	4.156	0.7556	2.782
0.1940	75.28	1.7509	0.7509	3.870	0.5601	2.887
0.1509	67.26	1.5644	0.5644	3.740	0.4475	2.996
0.1235	62.26	1.4481	0.4481	3.629	0.3702	2.998
0.1045	59.00	1.3722	0.3722	3.562	0.3164	3.028

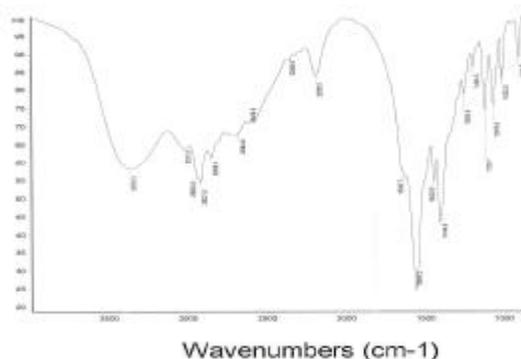


Figure 1: IR spectra of newly synthesized water soluble adhesive (polymer) 4

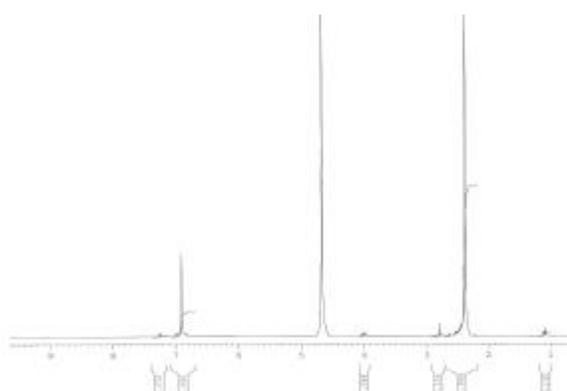


Figure 1: IR spectra of newly synthesized water soluble adhesive (polymer) 4

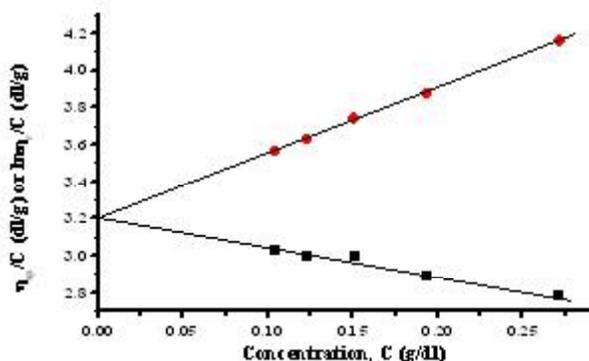


Figure 3: Plots of η_{sp}/C versus C and η_r/C versus C for adhesive sample

Solubility

All the investigated polymers were found to be highly soluble in several organic polar solvents such as DMAc, DMSO and DMF at room temperature. In general, high solubility is a desired requirement for polymer processing. The higher solubility of polyamide in comparison to Kevlar (polyterephthalamide) is due to their weaker intermolecular forces relative to interaction with the solvents^[37,38].

The maximum solubility (wt/%) of these polymers at 25°C are listed. Regardless of the nature of the solvent used, it can be noted that polymer with all paralinkages appears to be less soluble relative to other polymers containing different proportions of metalinkages and forms very high viscous solutions even at lower concentrations, however, at higher concentrations these solutions appear as gels. An increase in, meta-phenylene moieties content of the polymers from 0 to 100 mol % resulted in an increase in its solubility from 22 to 72 wt/v% in DMAc. This behavior provides additional evidence for the increased rigidity, packing effi-

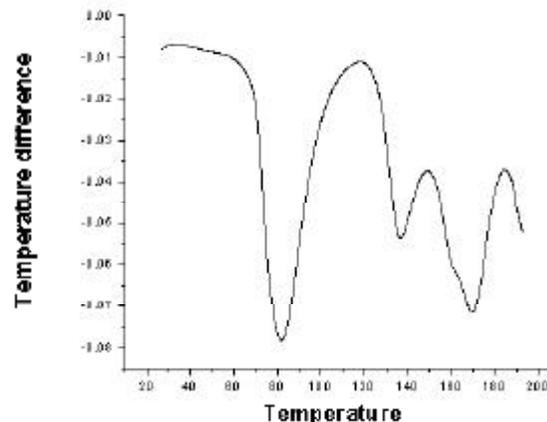
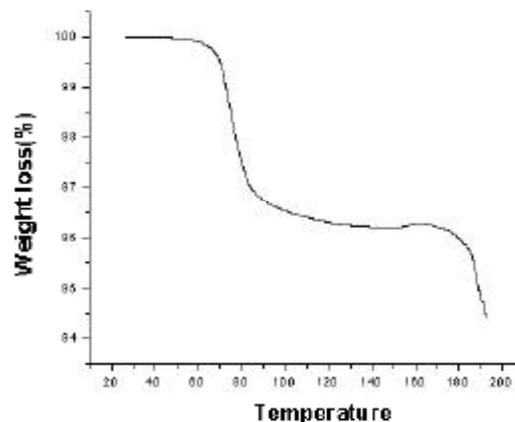


Figure 4: TGA spectra for weight loss and temperature difference of synthesized water soluble adhesive

Full Paper

ciency and hydrogen bonding of wholly p-oriented type of polymer. This conclusion would seem to be supported by the observation made earlier by Satre et al.^[9].

Thermal stability

TG were performed on the polymers evaluated in this work in order to examine the influence of their structural differences on their degradation behaviour under the purely thermal and thermo-oxidative conditions. These experiments were carried out in nitrogen and in air and the thermogram thus obtained are shown in figures 2 and 3 respectively. Important parameters characteristic of these degradation processes are summarized in TABLE. It can be noted from these results that in both degradation atmospheres all polymers showed a characteristic similar thermal behaviour and their weight losses could be observed in three distinctive stages. First, a small weight loss (1-3 wt.% based on the original polymer weight) occurred at 80-130°C and assigned to evaporation of adsorbed water from the surface of the polymer sample. Second, a significant loss (11-13.5).

CONCLUSIONS

Several easily processed new wholly aromatic polyamides of high molecular weights have successfully been synthesized as highly viscous film forming solutions. They were structurally characterized by various para-to meta-phenylene moieties contents. These polymers exhibited some desirable properties which mark them as promising candidates for corresponding engineering applications and perhaps also for some new ones. Polymer properties were strongly affected by their structural differences. Substitution of para-phenylene units for meta-phenylene ones within these polymers greatly affected their physical, thermal and mechanical properties. In general, it was found that an increase in para-phenylene rings content leads to polymers of a higher thermal stability in inert as well as in oxidative atmosphere, of higher tensile strength and of higher intrinsic viscosity.

These properties indicate the regularity of supermolecular packing occurred within the bulk of the polymer in addition to the collinear arrangement of the para-phenylene units which permits the establishment of stronger interchain hydrogen bonding. The latter would also increase the rigidity of the polymer. On the other hand, polymer solubility and moisture regain are remarkably

enhanced as a function of para-phenylene rings in the chains of the polymer by the more flexibilizing metaphenylene units. Thus, it should become possible to prepare materials with the most favorable properties required for any given engineering application or desired processing conditions by carefully designing relative ratios of the two types of these aromatic units during the polymer synthesis.

REFERENCES

- [1] D.W.Peeran; 'Encyclopedia of Polymer Science and Technology', New York, Wiley, 597 (1969).
- [2] R.W.Johnson, J.M.Valdespino, R.L.Gordon, G.E. Miller, R.W.Kight; 'Encyclopedia of Polymer Science and Technology', New York, Wiley, 11, 476 (1985).
- [3] N.J.Whippany; Anonymous.Adhesives, Skeist Incorporated, 6, 965 (1993).
- [4] D.W.Peeran, L.R.Vertnick; Polyamide Composition, US Patent.
- [5] B.M.Culberston, R.J.Murphy; Polym Sci.Polym. Lett., 5, 807 (1967).
- [6] P.R.Dvornic; Bull.Soc.Chim.Beograd., 49, 589 (1984).
- [7] N.A.Mohamed; Polym Degrad Stab., 44, 33 (1994).
- [8] J.Preston, W.B.Black, W.L.Hofferbert (Jr.); J. Macromol.Sci.Chem., 7, 45 (1973).
- [9] J.Preston, W.B.Black, W.L.Hofferbert (Jr.); J. Macromol Sci.Chem., 7, 67 (1973).
- [10] W.B.Black, J.Preston, H.S.Morgan, G.Raumann, M.R.Liyquist; J.Macromol.Sci.Chem., 7, 137 (1973).
- [11] R.McKinney Jr, J.H.Rhodes; Macromolecules, 4, 633 (1971).
- [12] P.R.Divornic; Polym.Sci.Polym.Chem., 24, 1133 (1986).
- [13] M.D.Stare, N.D.Ghatge, M.P.S.Ramani; J.Appl. Polym.Sci., 41, 697 (1990).
- [14] P.R.Dvornic; J.Appl.Polym.Sci., 42, 957 (1991).
- [15] M.D.Stare, N.D.Ghatge; Desalination, 91, 121 (1993).
- [16] K.Nakamae, N.A.Mohamed; J.Appl.Polym.Sci., Appl.Polym.Symp., 52, 307 (1993).
- [17] N.A.Mohamed; Polymer, 38, 4705 (1997).
- [18] N.A.Mohamed, K.Nakamae; Polymer, 34, 3940 (1993).
- [19] N.A.Mohamed; Eur.Polym.J., 34, 387 (1998).
- [20] P.R.Dvornic; Macromolecules, 17, 1348 (1984).
- [21] W.B.Black, J.Preston; 'High-Modulus Wholly Aromatic Fibers', New York, Dekker, 203, 281-295 (1973).