

Synthesis and Characterization of Some Novel Copolymer Resins. III

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ABSTRACT: In continuation of our endeavor to develop synthetic resins of improved properties and performance, we report here the synthesis of mixed copolymer resins by the condensation of resorcinol, aniline, and formaldehyde with *ortho*-, *meta*-, and *para*-phenylenediamine separately. The resins were characterized by infrared (IR) and thermogravimetric analysis (TGA). The mixed copolymer resins were found to have superior thermal stability over conventional phenol-CH₂O and resorcinol-CH₂O resins. The solubility behavior of the resins showed that they are resistant to common solvents. However, they are soluble in concentrated H₂SO₄ and HNO₃, but insoluble in concentrated HCl. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 2183–2187, 1998

INTRODUCTION

Phenolic resins, because of their remarkable heat and weather resistance, chemical inertness, dimensional stability, electrical insulation, etc., are perhaps the first category of synthetic polymers to have acquired significant commercial success.^{1–3} This is attributed to their wide industrial applications in the manufacture of commodity articles, machinery, electrical items, electronic parts, toys, sports items, adhesives, writing devices, and optical lithography and as matrix materials in fiber-reinforced plastics for high-strength applications.^{4–12} They also are being used for preparing plywood, particle boards, fiber boards, and paper and fabric laminates which find numerous applications in the building industry.¹³

Currently, we are synthesizing mixed copolymer resins of a template type comprising aromatic amines, aliphatic diamides, thioamides, phenolics, and relevant compounds with formaldehyde and furfural,^{14,15} exhibiting superior properties over conventional phenolic resins for use as matrix materials in natural fiber-reinforced low-cost

lightweight composites. The present article covers an aspect of our research program on such speciality materials.

EXPERIMENTAL

Materials and Methods

Resorcinol, aniline, and *ortho*-, *meta*-, and *para*-phenylenediamine (BDH) were purified by standard methods before use. The formaldehyde (BDH) used as obtained was a 40% solution (formalin). Other reagents like acetone, benzene, toluene, methanol, *n*-propanol, hexane, chloroform, dioxane, DMSO, and DMF were of AR grade and used as obtained.

Synthesis of Copolymer Resins

Resorcinol (37.5 g) and formaldehyde (120 mL) were stirred in a three-necked round-bottomed flask until the mixture was homogeneous. A mixture of 10 g of *o*-phenylenediamine and 20 mL of aniline (1.02 g/mL) were dissolved in 140 mL of 4N HCl in a 500 mL beaker. This solution was then slowly added into the contents in the flask while vigorously stirring the mixture. After 15 min, the mixture was left sitting until a thick slur-

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Table I Composition and General Appearance of the Resins

Name of the Resins	Composition	Percent Yield Color	Structure
R-A- <i>o</i> PDA-F	Resorcinol, aniline, <i>o</i> -phenylenediamine, formaldehyde	80 Brick red	Crystalline
R-A- <i>m</i> PDA-F	Resorcinol, aniline, <i>m</i> -phenylenediamine, formaldehyde	70 Greyish black	Crystalline
R-A- <i>p</i> PDA-F	Resorcinol, aniline, <i>p</i> -phenylenediamine, formaldehyde	75 Dark brown	Crystalline

rylike mass formed. The tarry was then heated to remove the occluded water. The solid was washed with methanol followed by acetone and then dried in a vaccum.

The mixed copolymer resins with *meta*- and *para*-phenylenediamine were separately prepared following the same procedure as adopted for *o*-phenylenediamine. In all these cases, the resins

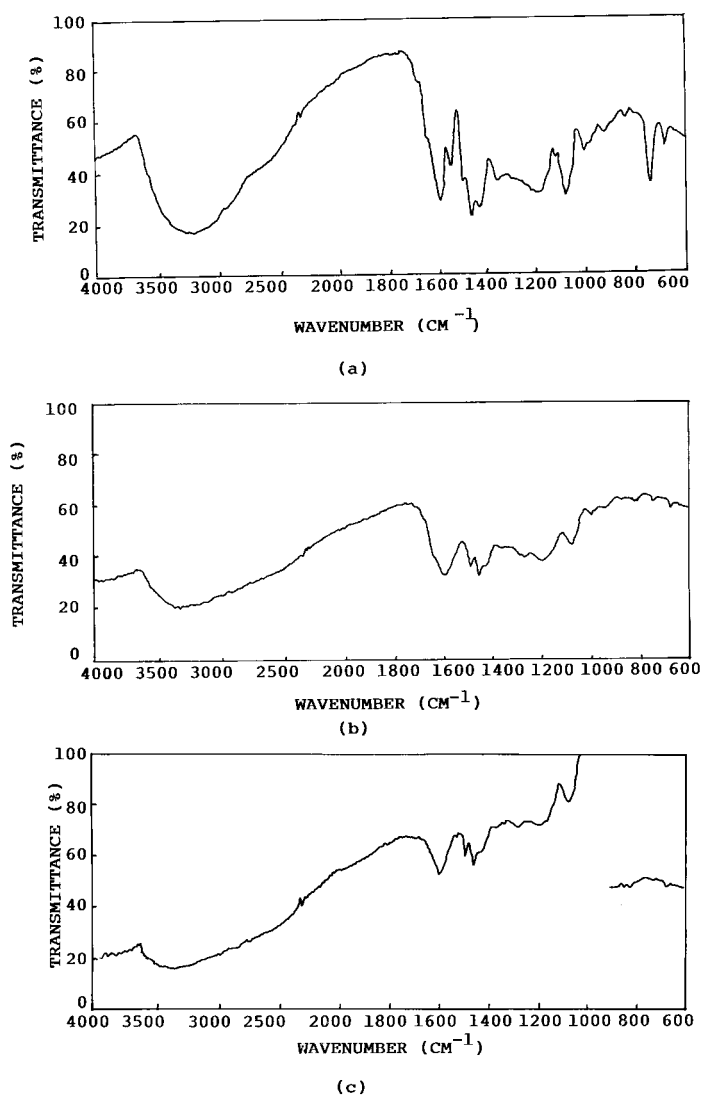


Figure 1 IR spectra of copolymer resins: (a) R-A-*o*PDA-F; (b) R-A-*m*PDA-F; (c) R-A-*p*PDA-F.

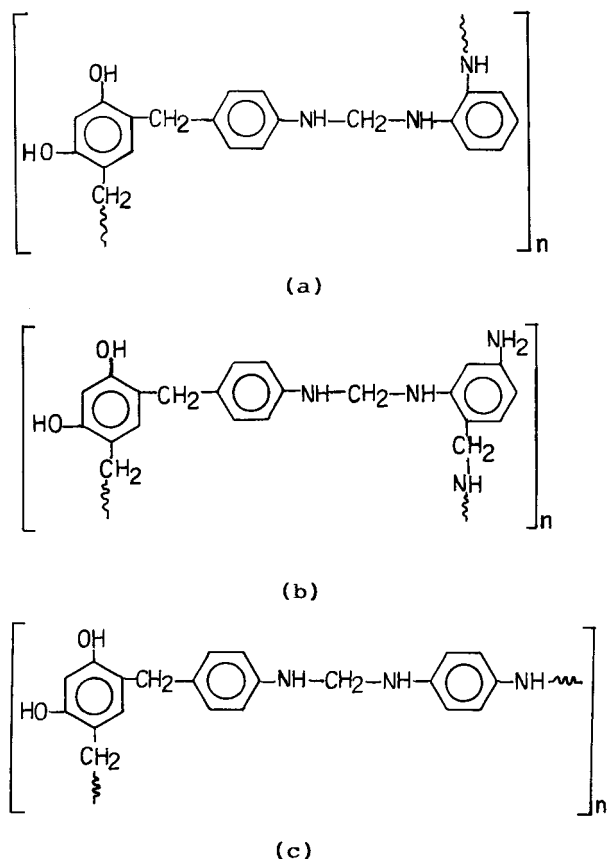


Figure 2 Structure of copolymer resins: (a) R-A-oPDA-F; (b) R-A-mPDA-F; (c) R-A-pPDA-F.

were precipitated out after 15 min of mixing the components.

Element Detection

Lassaigne's test¹⁶ for nitrogen was found to be positive for all the copolymer resins, confirming the entanglement of nitrogen.

Characterization

Infrared spectra of the copolymer resins were recorded with a Perkin-Elmer 237 spectrophotometer using a nujol mull or KBr pellets. Thermogravimetric analysis of the copolymer resins was done in a nitrogen atmosphere at a heating rate of 10°C per min using a DuPont 9900 thermal analyzer.

Solubility

The solubility of the copolymer resins at room temperature was determined in solvents like acetone, benzene, toluene, methanol, *n*-propanol, hexane, chloroform, dioxane, DMSO, and DMF. A

known amount (1%) of the resin was put into a test tube containing a fixed volume of the solvent. The dissolution of the resins was followed for 15 days. All the resins were insoluble in the above solvents. The solubility of the resins in mineral acids was also tested. The resins were soluble in concentrated HNO₃ and H₂SO₄, but insoluble in concentrated HCl. The results are directives of the suitability of these resins to be used as matrix materials in fiber-reinforced plastics for marine and industrial applications.

RESULTS AND DISCUSSION

The composition and general appearance of the resins are presented in Table I.

Infrared Spectra

The IR spectra of the copolymer resins are shown in Figure 1(a-c). The possible assignments of the peaks were analyzed to ascertain the probable structure of the copolymer resins.

R-A-oPDA-F Copolymer Resin

Bands [Fig. 1(a)] at 3600–2700, 1590, 1550, 1465, 1430/1080, 1355, 1210–1170, 1005/925, 840/745, and 685 cm⁻¹ due to O—H/N—H stretching, aromatic C—C stretching/N—H bending, N—H bending in secondary amine, alkane —CH₂— bending, aliphatic C—N vibration, phenolic C—O stretching, phenolic O—H bending, aromatic C—C stretching, and C—H bending of an aromatic substitution type with two and four adjacent H-atom and C—H/N—H rocking vibrations, respectively, support the resin structure as shown in Figure 2(a).

R-A-mPDA-F Copolymer Resin

Bands [Fig. 1(b)] at 3600–2800, 1600, 1495/1005, 1460, 1290–1260, 1220–1180, 1080, 880/840, and 685 cm⁻¹ due to O—H/N—H stretching, aromatic C—C stretching/N—H bending, aromatic C—C stretching, alkane —CH₂— bending, aromatic C—N vibration of primary amine, phenolic O—H bending, aliphatic C—N vibration, and C—H bending of an aromatic substitution type with two and one adjacent H-atom and C—H/N—H rocking vibrations, respectively, support the resin structure as shown in Figure 2(b).

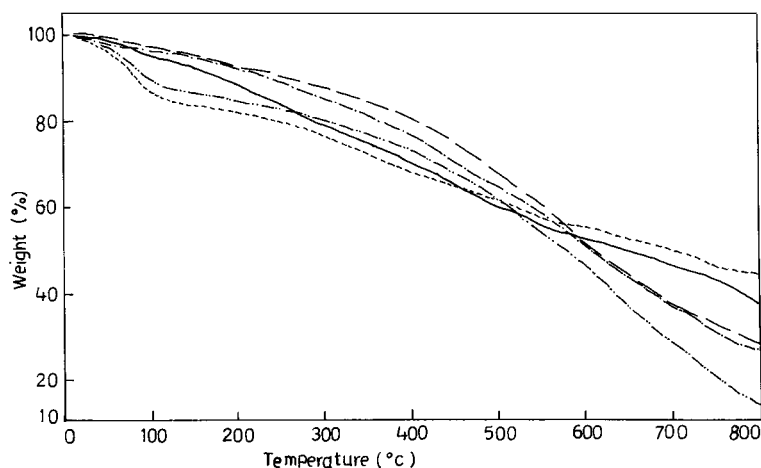


Figure 3 Primary thermograms of copolymer resins: (—) R-F; (---) R-A-F; (-·-·-) R-A-oPDA-F; (-·-·-·-) R-A-mPDA-F; (-----) R-A-pPDA-F.

R-A-pPDA-F Copolymer Resin

Bands [Fig. 1(c)] at 3700–2700, 1600, 1525, 1495, 1465, 1350, 1300–1270, 1210–1180, 1080, 850/830, and 680 cm^{-1} due to O–H/N–H stretching, aromatic C–C stretching/N–H bending, N–H bending in secondary amine, aromatic C–C stretching, alkane –CH₂– bending, phenolic C–O stretching, aromatic C–N vibration in secondary amine, phenolic O–H bending, aliphatic C–N vibration, and C–H bending of an aromatic substitution type with two adjacent H-atom and C–H/N–H rocking vibrations, respectively, support the resin structure as shown in Figure 2(c).

Thermogravimetric Analysis (TGA)

Thermogravimetry is one of the important techniques for elucidating the structure of the polymeric resins through the evaluation of their thermal stability.^{17–22} The primary thermograms of the mixed copolymer resins along with resorcinol–CH₂O (R–F) and resorcinol–aniline–

CH₂O (R–A–F) resins are shown in Figure 3. From the thermograms, it can be seen that aniline doping increases the thermal stability of the R–F resin up to 600°C. The depletion of the stability of the R–A–F resin compared to that of R–F beyond 600°C may perhaps be due to the easing of the fission of the C–N bond in the former and formation of charred material in the latter. The low thermal efficiency of the R–A–oPDA–F copolymer in comparison to R–A–F and the high value to R–F is indicative of a branched structure as shown in Figure 2(a).

It can also be seen that the thermal stability of R–A–mPDA–F is lower than that of R–A–oPDA–F and may perhaps be attributed to the high extent of branching in the structural network of the former. The facile cleavage of C–N linkage over C–C linkage leads to an easy loss of branches and thus supports the structure of the copolymer resin [Fig. 2(b)]. The R–A–pPDA–F copolymer resin is expected to have large units of C–N linkage in a linear fashion as shown in Figure 2(c), compared to the R–A–oPDA–F and R–

Table II Thermal Data of the Resins

Resins	Decomposition Percentage at Various Temperatures (T_D) in °C							
	100	200	300	400	500	600	700	800
R–F	5	12	20	30	42	50	55	64
R–A–F	7	8	13	20	33	50	63	72
R–A–oPDA–F	4	8	15	24	36	50	63	74
R–A–mPDA–F	12	19	20	27	38	55	72	86
R–A–pPDA–F	14	18	24	32	39	45	51	57

Table III Order (n) and Activation Energy (E) in kJ/mol of the Resins According to Freeman-Caroll Equation

Resin	n	E
R-F	1.20	3.80
R-A-F	1.04	3.50
R-A- <i>o</i> PDA-F	1.28	4.45
R-A- <i>m</i> PDA-F	1.30	5.34
R-A- <i>p</i> PDA-F	1.30	3.65

A-*m*PDA-F copolymer resins, and the molecular mass ought to be higher than the latter two. The nature of the primary thermogram of the R-A-*p*PDA-F copolymer resin indicates its earlier decomposition in comparison to the other two and is undoubtedly attributed to the large C—N units in it. Significant thermal stability beyond 600°C is attributed to its high molecular mass.

The decomposition percentage of the copolymer resins at various temperatures (T_D) are computed in Table II. From the table, it can be seen that at $T_D = 600^\circ\text{C}$ a 50% weight loss is observed for all the resins. Beyond 800°C, 60–80% weight loss is observed.

Again, as compared with simple phenol-CH₂O (P-F) and aniline-CH₂O (A-F) resins, the mixed copolymer resins are much more stable. At $T_D = 600^\circ\text{C}$, P-F and A-F have an 80% weight loss, whereas the present resins have a 50% weight loss.

From the residual weight of the resins (Table II), the value of $\Delta \log dw/dt$ and $\Delta \log w$ are evaluated, from which the Freeman-Caroll equation^{23,24} at constant $\Delta(1/T)$ is plotted, which yields a linear plot. From the slopes and intercepts of the linear plots, the value of the order of the reaction (n) and activation energy (E) are calculated and presented in Table III.

CONCLUSION

It is possible to synthesize mixed copolymer resins of better thermal stability and inertness to organic solvents and some mineral acids over that of conventional phenolic resins. The importance of the technique is that of their room-temperature synthesis within a very short time. This research was aimed at large-scale production of these resins for use as matrix materials in developing

lightweight low-cost natural fiber-reinforced composites.

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REFERENCES

1. L. H. Backeland, *J. Ind. Eng. Chem.*, **1**, 149 (1909).
2. L. H. Backeland, U.S. Pat. 939,966 (1909); 94285 (1909).
3. L. H. Backeland, *J. Ind. Eng. Chem.*, **6**, 506 (1913).
4. R. T. Conley, *Am. Chem. Soc. Div. Org. Coat. Plast. Chem. Pap.*, **26**, 138 (1966).
5. *Mod. Plast.*, **51**, 40 (1974).
6. R. G. Weatherhead, Ed., *Fiber-reinforced Resin Synthesis*, FRP Technology, Applied Science, London, 1980.
7. A. Kumar, U. K. Phukar, A. K. Kulshrestha, and S. K. Gupta, *Polymer*, **23**, 215 (1982).
8. E. Fitzer and R. Gadoor, *Am. Chem. Soc. Bull.*, **65**, 326 (1986).
9. D. W. Meker, *Carbon*, **24**, 551 (1987).
10. F. A. Vollenbrock and E. J. Spiert, *Adv. Polym. Sci.*, **84**, 85 (1988).
11. S. R. Turner and R. C. Daly, *J. Chem. Ed.*, **65**, 332 (1988).
12. M. S. Chetan, R. S. Ghadge, C. R. Rajan, V. G. Gunjekar, and S. Ponrathnam, *J. Appl. Polym. Sci.*, **60**, 685 (1993).
13. I. K. Verma and V. Choudhary, in *Proceedings of the Workshop on Polymer Composites as Substitutes for Conventional Building Materials*, New Delhi, 1988, p. 2-5-1.
14. R. K. Samal, B. K. Senapati, and R. Debi, *J. Polym. Mater.*, **13**, 169 (1996).
15. R. K. Samal, B. K. Senapati, and T. B. Behuray, *J. Appl. Polym. Sci.*, **62**, 655 (1996).
16. A. I. Vogel, *Text Book of Practical Organic Chemistry*, 3rd ed., Orient Longman, New Delhi, 1985, p. 1039.
17. H. L. Freeman, *U.S. Dept. Conf. Off. Ser. Ber. Rept.*, **24**, 145182 (1959).
18. C. Ouchi and H. Honda, *Fuel*, **38**, 429 (1959).
19. C. B. Murphy, *Mod. Plast.*, **37**(12), 125 (1960).
20. J. J. Millane, *Plastics (Lond.)*, **29**, 81 (1964).
21. W. W. Wendlandt, *Thermal Methods of Analysis*, Interscience, New York, 1964.
22. D. W. Levi, L. Reich, and H. T. Lee, *Polym. Eng. Sci.*, **5**, 135 (1965).
23. B. Carroll and E. S. Freeman, *J. Phys. Chem.*, **62**, 394 (1958).
24. E. S. Freeman and D. S. Anderson, *J. Polym. Sci.*, **54**, 253 (1961).