

Modification of High Ortho Novolac Resin with Diacids to Improve Its Mechanical Properties

Tülin Banu İyim

Department of Chemical Engineering, Faculty of Engineering, İstanbul University, 34320 Avcılar İstanbul, Turkey

Received 30 October 2006; accepted 21 March 2007

DOI 10.1002/app.26628

Published online 11 June 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To improve the brittleness of high ortho novolac resins, at first, high ortho novolac resins (N) were synthesized and condensation reactions between N and flexible diacids such as adipic acid (DA4) and azelaic acid (DA7) were carried out with different amounts of diacids, in the presence of zinc acetate as catalyst, in toluene as solvent. To characterize the diacid-modified resins (MN), FT-IR analysis, TGA and DSC techniques were used. The morphologies of MN were also investigated. Moldings were prepared from the mixture of MN, fillers, and curing agent

hexamethylenetetramine. Mechanical properties of these moldings were also determined. The results showed that high ortho novolac resin was toughened by the incorporation of flexible diacids in the polymer backbone and these modified resins can be used as a matrix resin of composite materials. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 46–52, 2007

Key words: high ortho novolac; diacid; brittleness; morphology; mechanical properties

INTRODUCTION

The phenolic resins may be considered to be the first polymeric products produced commercially from simple compounds of low molecular weight. Although they are now approaching their centenary, phenolic resins continue to be used for a wide variety of applications such as thermal insulation materials, molding powders, laminating resins, adhesives, binders, surface coatings, impregnants, composite materials, because of its excellent ablative property structural integrity, thermal stability, and solvent resistance.^{1–7} The phenolics are resinous materials produced by condensation of a phenol or mixture of phenols with formaldehyde. The initial phenol–formaldehyde reaction products may be of two types, resols and novolacs.

Resols are formed by reacting phenol with an excess of formaldehyde under alkaline conditions⁸ and often referred to as one-step resins since they can be cured by heat alone and require no crosslinking agent.⁸ Therefore it is very difficult to obtain the blend of these resins with other thermoplastic polymers.¹ Novolacs are prepared under acidic conditions with an excess of phenol with formaldehyde. Unlike resols, novolacs require the addition of a crosslinking agent and heat to achieve cure. Hexamethylenetetramine (HMTA), a common crosslinking agent, is added at levels between 8 and 15%.⁸ When

the hydroxides of alkali and alkaline earth metals are used as catalysts in the preparation of novolac resins, an increasing value of the ortho/para substitution ratio of the hydroxymethylphenols is observed. The catalysts are capable of selective hydroxymethylation of phenol at the ortho-position dependent on the pH value of the reaction mixture and so high ortho novolac resin was synthesized.^{9,10} This type of novolac resin is known to be more reactive than the other phenolic resins and been preferred for the most blends.^{11–13} This resin also has exhibited to be much more rapid curing by means of HMTA than those made by conventional acid-catalyzed condensation.⁸

On the other hand, in general, thermoset resins such as phenolic and epoxy resins are inherently brittle due to their high cross-link density,¹ and consequently, their application has significantly been limited by inherent brittleness.⁴ This problem can be moderated using derivatives of phenol (such as dihydroxydiphenyl ether) in main reaction with formaldehyde¹⁴ or incorporating the elastomeric and/or thermoplastic polymers into phenolics.¹⁵ Materials used as toughening agents of phenolic resin include elastomers such as natural rubber and nitrile butadiene rubber^{16,17}; reactive liquid polymers such as liquid nitrile butadiene¹⁸ and carboxyl-terminated butadiene¹⁹; plastics^{4,20,21} such as polysulfone, polyamid, polyethylene oxide (7–8%), phenoxy resin (12–15%), unsaturated polyester²²; oils such as cashew nut shell liquid,²³ tung oil⁴; and fibers such as glass fibers and aramid fibers.⁴ Resol resin has many reactive hydroxyl groups. This advantage was

Correspondence to: T. B. İyim (tulib@istanbul.edu.tr).

adopted to modify the resol resin by chemical reaction with polyurethane and nitrile rubber.^{16,24} Like the high molecular weight polymers, a small molecule can also be used to improve the brittleness of resol type phenolic resin.¹ Novolac resin is almost unable to crosslink without curing agent which is allowed to modify the novolac resin by melt blending with flexible thermoplastic polymers. In most of the cases, novolac resins were modified blending with thermoplastic homopolymers or copolymers.^{14,25–33}

The main aim of this work is to improve the brittleness of high ortho novolac resin (N), which is reactive than other novolac resins. At first, high ortho novolac resin is prepared according to the known procedure.^{9,11} Then, N is modified with a low molecular weight flexible diacid such as adipic and azelaic acids by the reaction between the carboxyl end groups of diacid and methylol groups of the N. N and diacid-modified resins (MN) were characterized using FT-IR spectroscopy. Thermal properties of these resins were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. Moldings were prepared from the mixture of MN, fillers, and curing agent HMTA, and mechanical properties of these moldings were investigated. The morphology (i.e. homogeneity and phase separation) of these modified resins was also investigated.

EXPERIMENTAL

Materials

Phenol (P), formaldehyde (FA) (37% aqueous solution stabilized with 10% methanol), flexible diacids (adipic acid (DA4), azelaic acid (DA7)), and the rest of the materials were all purchased from Merck AG (Darmstadt, Germany). All materials were of synthetic or analytical grade and used as received. The numbers 4 and 7 in the parentheses indicate the number of methylene unit for each diacid.

Preparation of high ortho novolac resin

Polycondensation reaction of FA and P was carried out according to known procedure^{9–11,34} using 0.187 mole ratio of FA/P and at pH = 7. The reaction system was a 500-mL four-necked conventional glass reaction kettle equipped with a mechanical stirrer, heating mantle, reflux condenser, temperature control system, and N₂ inlet. P, FA, and NaOH as catalyst (0.044 mol/L in the total reaction mixture) were added into reaction kettle at room temperature, stirred mechanically, and the temperature was increased to 65°C and kept constant. The reaction was followed by the determination of the free FA amount according to the hydroxylamine hydrochlor-

ide method.³⁵ After 4 h the amount of the free FA was constant and found to be 0.62%. At the end of the reaction, N was purified (excess phenol and water were removed) under vacuum in a rotary evaporator system, then cooled and pulverized mechanically into fine particles, and further dried to constant weight in a vacuum oven at 30°C for 24 h. N was characterized by FT-IR spectroscopy, viscosity molecular weight was determined³⁶ and found to be $M_v = 1350$.

Preparation of the diacid-modified high ortho novolac resins

Diacid-modified high ortho novolac resins (MN) were synthesized by the condensation reaction of N with adipic acid (DA4) or azelaic acid (DA7). Condensation reactions were carried out in a 250-mL four-necked conventional glass reaction kettle equipped with a mechanical stirrer, heating mantle, reflux condenser, and temperature control system. For each 1 g of N, the mol amount of DA4 and DA7 was varied as 0.00035, 0.0007, 0.0014, 0.0028, and 0.0007, respectively. Zinc acetate was used as catalyst (1 wt % of the total reaction mixture) and toluene was used as solvent (10 wt % of the total reaction mixture). Calculated amounts of N, DA4, or DA7, zinc acetate, and toluene were added to the reaction kettle at room temperature and stirred for 15 min, and then the temperature was increased to 110°C and held there until the acid value (AV)³⁷ was constant (~ 4 h). At the end of the reactions, the products were purified under vacuum at 40°C and storage for using in the preparation of moldings. MN were characterized by FT-IR spectroscopy. The feed compositions of the resins and AV changes during the condensation reactions are shown in Tables I and II.

Preparation of the moldings

Moldings were prepared as follows: since it was very hard to prepare homogenous mixture with the soft and sticky resins, MN were dissolved in acetone, and to obtain homogenous mixtures, wood flour was impregnated with this solution. Solvent was removed under vacuum at 30–40°C. Dried sample

TABLE I
The Symbols of MN and the Feeding Composition in the Condensation Reaction

Symbols	N/DA4 or DA7 (g/mol)
NDA4-3.5	1/0.00035
NDA4-7	1/0.0007
NDA4-14	1/0.0014
NDA4-28	1/0.0028
NDA7-7	1/0.0007

TABLE II
The Changes of AV After the Modification Reactions

Symbol of resin	Initial AV (mg KOH/g)	Final AV (mg KOH/g)
NDA4-3.5	38	18
NDA4-7	71	31
NDA4-14	130	28
NDA4-28	223	189
NDA7-7	70	30

was grinded to powder and mixed with HMTA, stearic acid, and calcium oxide according to an industrial formulation.³⁸ The mixtures were molded by Buehler Metaserv for 20 min at 150–160°C under 3000 psi pressure to obtain test pieces in standard dimensions (1 in. length × 0.5 in. diameter).³⁹ One molding was also prepared using N as resins for the comparison the results. Compositions of the moldings were presented in Table III. After storage at ambient temperature conditions for 24 h, mechanical properties of these moldings were determined and presented in Table III.

Instruments

FT-IR spectra of the all resins were recorded on a Digilab Excalibur FTS 3000 MX Model (Randolph, MA) in the range of 400–4000 cm⁻¹. To prepare the samples pellets, the samples were diluted with IR grade Merck KBr (sample/KBr = 1/200, w/w).

The mechanical properties (compression strength, elastic modulus, and strain to failure) of the moldings were determined using a universal test machine according to the ASTM D 695. Thermal properties of the N and MN were determined using TGA and DSC techniques.

TGA analysis were carried out with Shimadzu TGA 50A (Japan) thermal analyzer with a heating rate of 5°C/min in air. DSC measurements were carried out with Setaram 131 Model apparatus (France) with a heating rate of 10°C/min in air in a temperature range of 5–250°C. The sample mass was 20 mg. The morphologies of the resins (homogeneity, phase

separation, etc.) were compared from micrographs obtained by Olympus CK2 Invert Microscope (Japan) (3.3 × 10).

RESULTS AND DISCUSSION

In this work, diacid-modified novolac resins (MN) were prepared and some of their mechanical properties were investigated. Firstly, a special type novolac resin having high ortho substitution was prepared by the condensation polymerization of 0.187 mole FA with 1 mol P at pH = 7. After purification, the resin was characterized by FT-IR analysis.

To obtain MN, diacids such as adipic acid (DA4) and azelaic acid (DA7) that have flexible methylene units (4 and 7, respectively) were used to modify N by condensation reaction. The condensation reaction between methylol groups of novolac resin and carboxyl groups of diacid forms ester linkage¹ as shown in Scheme 1.

MN were characterized by using FT-IR spectroscopy and their thermal properties were investigated using TGA and DSC techniques. Moldings were prepared from these MN and their mechanical properties were determined. Morphologies of MN were also investigated.

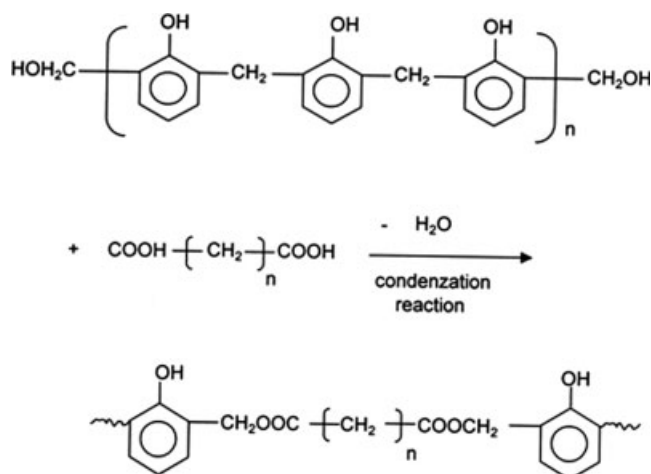
FT-IR spectra of the MN

The overall changes in the structure of the N depending on the modification reaction by diacids DA4 and DA7 were investigated by FT-IR analysis. The FT-IR spectra of the N and MN were presented in Figures 1 and 2. These spectra indicate the reduction of the intensity of the absorption band observed at 1409–1315 cm⁻¹ (max at 1371 cm⁻¹)³⁴ due to the hydroxyl groups of methylol groups in the high ortho novolac resin structure and this absorption band has also shifted to about 1374, 1366, 1363, and 1359 cm⁻¹ depending on the type and amount of the diacid. The changes in the above mentioned bands can be attributed to the change in the methylol con-

TABLE III
Compositions and Mechanical Properties of the Moldings

Symbol of resin and molding	Molding composition wt. (%)				Mechanical properties		
	Resin	Wood flour	HMTA	Additives ^a	Compression strength (MPa)	Elastic modulus (MPa)	Strain to failure (%)
N	44	48.5	5.50	1.76	99	44	3
NDA4-3.5	44	48.5	5.50	1.76	84	14	6
NDA4-7	44	48.5	5.50	1.76	142	21	7
NDA4-14	44	48.5	5.50	1.76	91	10	10
NDA4-28	44	48.5	5.50	1.76	65	18	4
NDA7-7	44	48.5	5.50	1.76	120	21	7

^a Stearic acid 0.88% and calcium oxide 0.88%.



Scheme 1 The condensation reaction between novolac resin and diacids.

tent of the novolac resin due to the modification reactions.

On the other hand, absorption peak at 1691 cm^{-1} due to the carbonyl stretching vibration of carboxyl groups in the adipic acid⁴⁰ has shifted to a higher frequency about 1728, 1702, 1697, 1696, 1695 cm^{-1} , depending on the type and amount of the modification compounds. Also, the appearance of new small absorption bands or shoulders at about 1180 and 1280 cm^{-1} (ester C—O stretching vibration) is attrib-

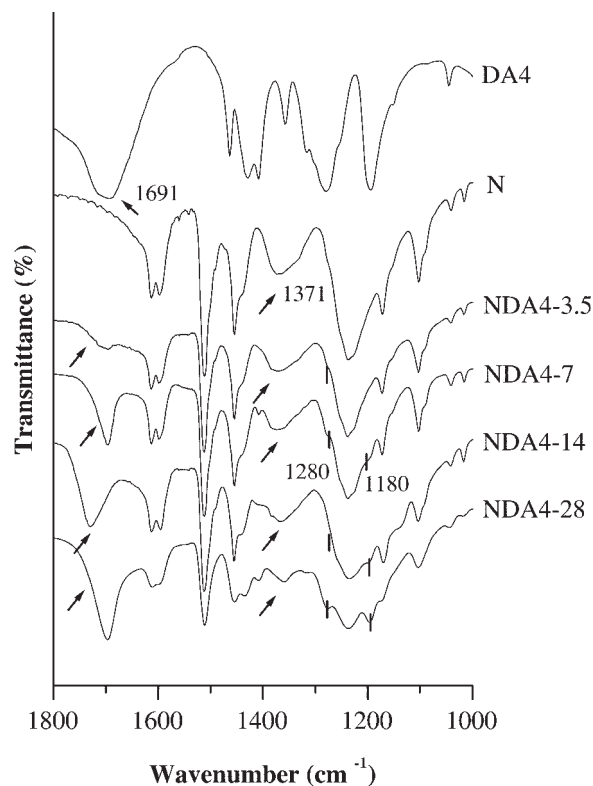


Figure 1 The FT-IR spectra of DA4, N, and MN.

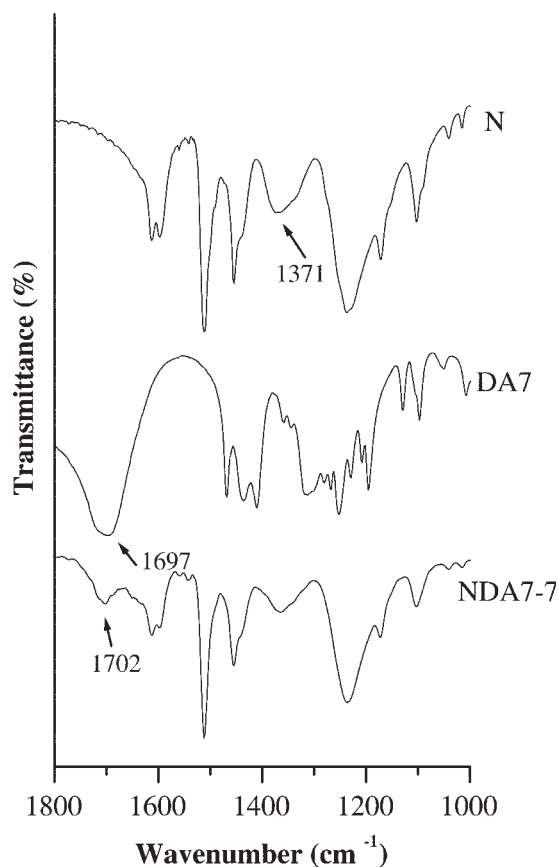


Figure 2 The FT-IR spectra of N, DA7, and NDA7-7.

uted to the formation of ester linkage⁴¹ in the MN structure. The intensities of these absorption bands change depending on the amount of the diacids.

Thermal properties of MN

Thermal properties of N and some MN were investigated by TGA and DSC techniques. All TGA and DTG thermograms were shown in Figure 3 and the results determined from TGA data were also presented in Table IV.

In several previous articles,^{34,42} the thermal oxidative degradation of phenolic resins was reported and it was mentioned that the phenolic resins mainly degrade in three recognizable steps: preliminary, middle, and a final oxidative degradation. All MN that are produced in this study by the modification reaction with diacids exhibit more or less the same thermal oxidative degradation stability. In addition, NDA4-7 has a higher thermal stability up to 220°C than the others. The modification by the diacids did not greatly change the thermal stability of N. As expected, the thermal stability of the polymer decreases due to the introduction of C—O—C bond of ester linkages as a weak bond in the polymer structure.

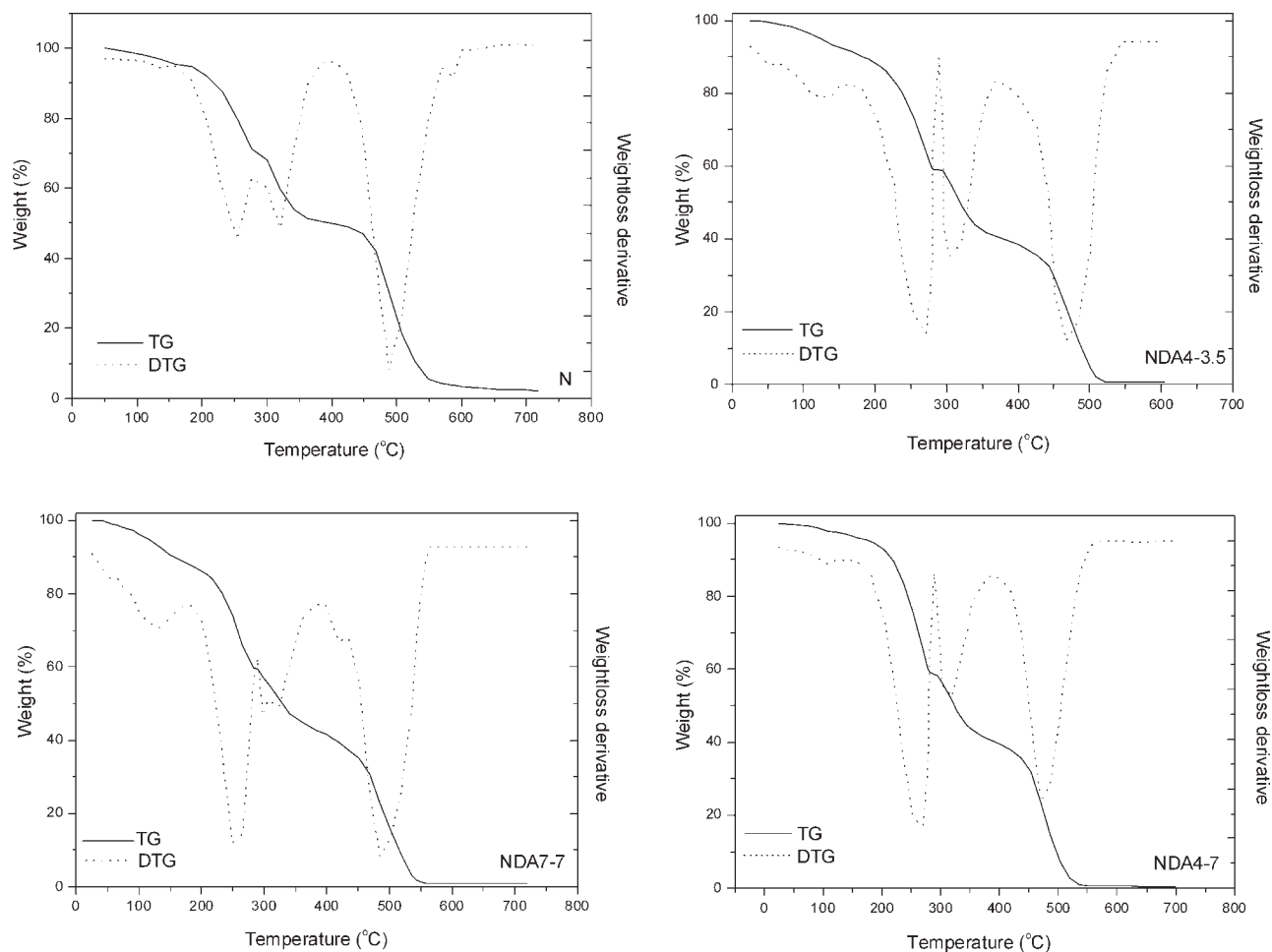


Figure 3 The TGA curves of N and MN.

Figure 4 shows the DSC curves of the N and some MN. As seen from the figure, T_g of N was appeared at 74°C. Also at the DSC curve of the NDA4-14, at about 149°C an endothermic peak was appeared. This peak was attributed to the melting of crystallized unreacted adipic acid and confirms a phase separation.

Morphology of the MN

The morphologies of the resins (homogeneity, phase separation, etc.) were compared from micrographs.

TABLE IV
Thermal Properties of the N and MN

Symbol of resin	T , 10% (°C) ^a	T , 30% (°C) ^b	T , 50% (°C) ^c	Final degradation temp. (°C)
N	220	280	380	625
NDA4-3.5	180	260	320	525
NDA4-7	220	260	325	550
NDA7-7	150	260	330	550

^a The temperature where 10% weight loss occurred.

^b The temperature where 30% weight loss occurred.

^c The temperature where 50% weight loss occurred.

Micrographs [Fig. 5(a–e)] show that N has homogeneous appearance. In case of NDA4-3.5, NDA4-7, and NDA7-7, the appearance of the samples are almost homogeneous. However, NDA4-14 exhibits a phase separation due to the high amount of DA4,

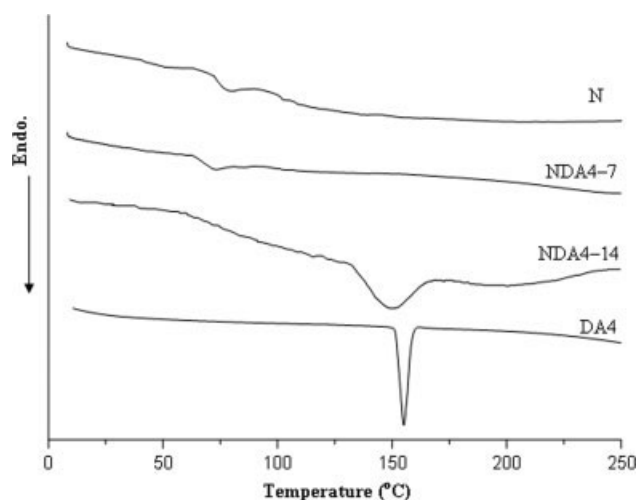


Figure 4 The DSC curves of DA4, N, and MN.

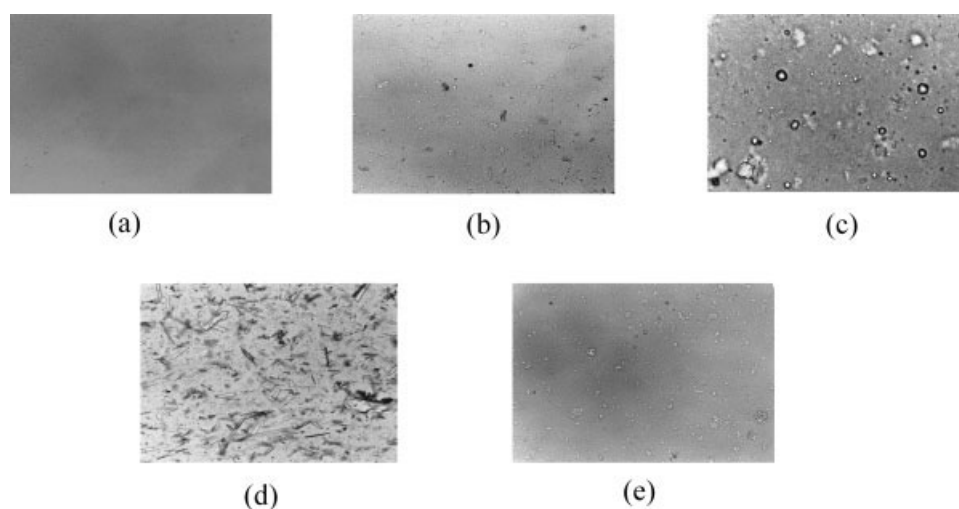


Figure 5 The micrographs of N and MN. (a) N, (b) NDA4-3.5, (c) NDA4-7, (d) NDA4-14, (e) NDA7-7.

and the appearance became heterogeneous. This heterogeneity may probably be the crystalline phase of the unreacted DA4. Mechanical properties (Table III) and DSC curves of NDA4-14 (Fig. 4) also confirmed this matter. Thus it is concluded that the optimum DA4 content for the modification is 0.0007 mol.

Mechanical properties of the moldings

To investigate the effects of the diacid content and chain length on the mechanical properties of the N, mechanical properties of the moldings, i.e., compression strength, elastic modulus, and strain to failure % were determined from stress-strain data. The compositions and the mechanical properties of the moldings prepared from modified novolac resins are given in Table III. Modification of N with flexible diacids causes a softening and thus the moldings prepared from MN have higher strain to failure values and lower elastic modulus than the moldings prepared from N. Increasing the mole amount of diacid from 0.00035 to 0.0007 mole/1 g N increases the compression strength, but after this amount (0.0007 mole), increasing the mole amount of diacid causes a decrease in the compression strength. The higher the diacid amount bigger than 0.0007 mole, the lower the compression strength value, according to this situation it can be said that the optimum diacid mole amount is 0.0007 mole for the modification.

Similarly, in case of modification with DA4, increasing the mole amount of diacid against 1 g N from 0.00035 to 0.0014 mole increases the strain to failure values (6.7 and 10%, respectively). But in morphology test results section, it was shown that increasing the mole amount of diacid to 0.0014 mole causes a phase separation and heterogeneous morphology [Fig. 5(d)], and thus it was concluded that the optimum diacid mole amount is 0.0007.

As seen from Table III, NDA4-7 and NDA7-7 have somewhat similar properties. Also, in the group of NDA4 moldings, NDA4-28 mold has the lowest strain to failure value since increasing the mole amount of diacid above 0.0014 mole causes a phase separation and so it is reasonable to obtain decreased strain to failure and compression values. Thus, according to all results it was concluded that the mechanical properties of modified resins were significantly dependent on the diacid content. The brittleness of high ortho novolac resin could be improved by the incorporation of flexible diacids with small molecular weight in the polymer structure.

CONCLUSION

In this work, diacid-modified high ortho novolac resins have been prepared by the condensation reactions of high ortho novolac resin with flexible diacids such as adipic or azelaic acid. These modified resins were characterized by FT-IR spectroscopy and thermal properties of these resins were determined by DSC and TGA techniques. The morphologies of these resins were also investigated. The moldings were prepared using modified resins and their mechanical properties (such as compression strength, elastic modulus, and strain to failure) were also investigated.

Diacid-modified resins prepared in this work are flexible than high ortho novolac resin. The highest compression strength, elastic modulus, and homogeneous morphology were observed for the moldings prepared from NDA4-7 in which 0.0007 mol DA4 was used.

The mechanical properties of modified high ortho novolac were significantly dependent on diacid content. According to the morphology and mechanical test results, the optimum diacid content for the mod-

ification reactions was found to be 0.0007 mol. The thermal resistance of high ortho novolac resins cannot significantly be improved by the modification diacids. However, the brittleness of high ortho novolac resin could be improved by the incorporation of flexible diacids with small molecular weight in polymer structure. These modified high ortho novolac resins can be used as a matrix resin of composite materials.

The author kindly thanks Serkan Emik for his help in FT-IR analysis, and also Professor Dr. Serhat Pabuccuoğlu for his help in micrographs, Dr. Gülin Selda Pozan for her help in thermogravimetric analysis, and Aykut M. Eroğlu for his help in mechanical properties tests.

References

- Choi, M. H.; Byun, H. Y.; Chung, I. J. *Polymer* 2002, 43, 4437.
- Choi, M. H.; Chung, I. J.; Lee, J. D. *Chem Mater* 2000, 12, 2977.
- Choi, M. H.; Jeon, B. H.; Chung, I. J. *Polymer* 2000, 41, 3243.
- Ma, H.; Wei, G.; Liu, Y.; Zhang, X.; Gao, J.; Huang, F.; Tan, B.; Song, Z.; Qiao, J. *Polymer* 2005, 46, 10568.
- Cherian, A. B.; Varghese, L. A.; Thachil, E. T. *Eur Polym J* 2007, 43, 1460.
- Chiang, C.; Ma, C. M. *Polym Degrad Stab* 2004, 83, 207.
- Zhang, Y.; Lee, S.; Yoonessi, M.; Liang, K.; Pittman, U. *Polym* 2006, 47, 2984.
- Hiltz, J. A.; Kuzak, S. G.; Waitkus, P. A. *J Appl Polym Sci* 2001, 79, 385.
- Peer, H. G. *Rec Trav Chim Part I* 1959, 78, 631.
- Peer, H. G. *Rec Trav Chim Part II* 1960, 78, 851.
- Shepard, F.; Dannels, B. F. U.S. Pat. 3,398,122 (1968).
- Eastmond, G.; Ledwith, A.; Russo, S.; Sigwalt, P. In *Comprehensive Polymer Science*, Vol. 5; Pergamon: New York, 1989; p 632.
- Shipp, D. A.; Solomon, D. *Polymer* 1997, 38, 4229.
- Takase, Y.; Nishi, M.; Yamagishi, T.; Nakamoto, Y. *Polym Prepr (54th SPSJ Annual Meeting, Japan)* 2005, 54, 397.
- Kim, B. S.; Nakamura, G. I.; Inoque, T. *J Appl Polym Sci* 1998, 68, 1829.
- Achary, P. S.; Ramaswamy, R. *J Appl Polym Sci* 1998, 69, 1187.
- Kaynak, C.; Çagatay, O. *Polym Test* 2006, 25, 296.
- Camino, G.; Alba, E.; Buonficio, P. *J Appl Polym Sci* 2001, 82, 1346.
- Gouri, C.; Nair, C. P.; Ramaswamy, R. *J Appl Polym Sci* 1999, 74, 2321.
- Carter, J. T. *Plast Rubber Compos Process Appl* 1991, 16, 157.
- Wu, H.; Ma, C. C.; Lin, J. *J Appl Polym Sci* 1997, 63, 911.
- Cherian, A. B.; Thachil, E. T. *J Appl Polym Sci* 2006, 100, 457.
- Wang, R.; Chen, L.; Sun, M.; Liu, J. In *International SAMPE Symposium and Exhibition Proceedings – Materials and Processing Technology, USA, 2004; Vol. 49, p 3500.*
- Sathiyalekshmi, K. *Bull Mater Sci* 1993, 16, 137.
- Wu, H. D.; Lee, M. S.; Wu, Y. D.; Su, Y. F.; Ma, C. M. *J Appl Polym Sci* 1996, 62, 227.
- Matsumoto, A.; Hasegawa, K.; Fukuda, A.; Otsuki, K. *J Appl Polym Sci* 1992, 44, 205.
- Chu, P. P.; Wu, H. D. *Polymer* 2000, 41, 101.
- Ma, C. M.; Wu, H. D.; Lee, C. T. *J Polym Sci Part B: Polym Phys* 1998, 36, 1721.
- Zhong, Z.; Guo, Q. *J Polym Sci Part B: Polym Phys* 1999, 37, 2726.
- Wu, H. D.; Chu, P. P.; Ma, C. C. *Polymer* 1998, 39, 703.
- Kwei, T. K. *J Polym Sci Polym Lett Ed* 1984, 22, 307.
- Ma, C. M.; Wu, H. D.; Chu, P. P.; Tseng, H. T. *Macromolecules* 1997, 30, 5443.
- Goswami, S.; Nad, S.; Chakrabarty, D. *J Appl Polym Sci* 2005, 97, 2407.
- Tuğtepe, M.; Özgümüş, S. *J Appl Polym Sci* 1990, 39, 83.
- D'Alelio, G. F. *Experimental Plastics and Synthetic Resins*; Wiley: New York, 1955; p 163.
- Kamide, K.; Miyakawa, Y. *Macromol Chem* 1978, 179, 359.
- Welcher, F. J. *Standard Methods of Chemical Analysis, Part B*; D. Van Nostrand Company, Inc.: Princeton, 1963; p 1653.
- Othmer, K. In *Encyclopedia of Chemical Technology*, 2nd ed.; Wiley: New York, 1968; Vol. 15, p 200.
- ASTM. *Book of ASTM Standards Compressive Properties of Rigid Plastics*; ASTM, USA, 1969; Vol. 35, p 259.
- Bellamy, L. J. *The Infra-Red Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: London, 1975; p 183.
- Bellamy, L. J. *The Infra-Red Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: London, 1975; p 217.
- Lochte, H. W.; Strauss, E. L.; Conley, R. T. *J Appl Polym Sci* 1965, 9, 2799.