Physicochemical and Thermal Properties of Phenol–Formaldehyde-Modified Polyphenol Impregnate

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ABSTRACT: Tannin, a natural polymer belonging to the polyphenolic group of compounds, is widely used in the leather industry, specifically as a tanning agent for the conversion of putrescible collagen fibers into leather matrix during the leather-manufacturing process. Unspent tannin poses a serious environmental threat to the public because it has a very high half-life, leading to groundwater pollution when discharged into soil. Attempts have been made to separate tannins through chemical means and recovered tannin needs to be encapsulated for its safe disposal. In the present study the recovered tannin was impregnated in phenol–formaldehyde (PF) resin. Spectroscopic and thermogravimetric (IR, NMR, TGA and DSC) studies revealed that the modified polyphenol was held physically in the impregnate. The impregnated matrix showed resistance to mineral acids, strong alkalis and organic solvents and was tested for its adhesive property on leather sheets. The leather that bonded with PF-modified polyphenol impregnate (PFT) had a 27% increase in peel strength and a 40% increase in lap shear strength as compared to the sample bonded with PF resin. The corrosive resistance result of the PFT resin shows it has potential application as an anticorrosive paint in the paint industry. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1567–1571, 2001

Key words: polyphenol; impregnate; leather adhesive; resin

INTRODUCTION

Along with chromium compounds, the polyphenolic compound tannin is used as a tanning agent during the manufacture of leather for the conversion of putrescible collagen fiber into nonputrescible leather matrix. Tannin fixation on collagen fibers is limited by its molecular weight and pH. Hence, the complete fixation of tannin on the collagen matrix has been a subject of interest because it could reduce its polluting discharge to zero. It has been observed that in an unfixed condition high-molecular-weight tannin slides from the leather matrix, producing tannin in the spent liquor. Unspent tannin discharged in wastewater totals 3.027 g/L. In India nearly 80 t of tannin is discharged each day into surface water bodies and soils. The discharge of tannin into the sea causes an environmental imbalance, which may even severe affect the survival of aquatic organisms.[1]

Tannin is also considered a rich source of pollution because it resists the biodegradative properties of wastewater. Its hydroxylated phenolic compounds are polymerized to oligomeric compounds,[2] both stabilizing the hydrogen bond with the exocellular membranes of the organisms in the wastewater and at the same increasing toxicity to and decreasing the growth of the microorganisms. Tannin inhibits this methanogenic ac-

tivity of anaerobic bacteria involved in wastewater treatment,[3,4] when its concentration exceeds 300–325 mg/L. Tannins are reported to be inhibitory to nitrifying bacteria, which are important for the post-treatment of nitrogenous wastewater.[5–7] Basarban et al. have reported that the decomposition of organic material applied to soil is retarded 1–2% by tannin.[8] Tannins are therefore regarded as an environmental pollutant both because of their high toxicity and their resistance to biological degradation.

Thus, there is a real need for the removal of the unfixed vegetable tannin from the spent tannin liquor so as to improve the removal efficiency of the treatment plant and to conserve the ecosystem. Tannin removed from wastewater requires further treatment prior to disposal. Without this treatment, the tannin would support spore-producing fungi that would ultimately causes allergy and asthma complaints in human beings. Hence, a carrier material has been sought for the encapsulation of the recovered tannin to ensure its safe disposal. Moreover, if a application developed for encapsulating the matrix is commercially viable, tanners would practice the removal of tannin from the spent liquor because it would increase their revenue. That is, if the treatment of tannin-laden wastewater can be shown to be a practicable task, it will be viewed with interest.

The focus of this study was the development of an encapsulating matrix for the recovered tannin and developing its use as a paint pigment for corrosion-resistant applications. Phenol–formaldehyde (PF) resin, which is compatible with polyphenol, was selected as a carrier material for the recovered tannin and for use as a mixture for paint coatings for mild steels.

EXPERIMENTAL

Materials

Phenol (Ranbaxy Fine Chemicals Ltd., New Delhi, India), formaldehyde (E. Merck Ltd., Mumbai, India), oxalic acid (Ranbaxy), and methanol (Ranbaxy) were used as received.

Wastewater from the vegetable tanning process was collected from a tannery in Pallavaram, India (near Chennai). The unfixed tannin was recovered in accordance with the procedure mentioned elsewhere. The recovered tannin was further purified by acetone and was dried at 50°C under vacuum.

Preparation of PF-Recovered Tannin Resin

To a 500-mL flask were added 1 g of recovered tannin along with 130 g of phenol, 13 mL of distilled water, 92.4 g of formaldehyde (37% aqueous solution), and 13 mL of distilled water, and 1 g of oxalic acid was added to the reaction mixture and refluxed. The above-mentioned procedure was adopted in the preparation of PF-recovered tannin resin (PFT).

Instruments

Infrared (IR) spectra of the samples were recorded on a Hitachi 270-50 spectrometer, with potassium bromide pellets. Magnetic measurements were done at room temperature using Gouy's method, by employing $Hg[Co(SCN_4)]$ for calibration purposes, corrected for diamagnetism by Pascal's constant. Thermogravimetric analysis (TGA) of the samples was performed on a Mettler 3000 TA thermal analyzer at a heating rate of 20°C/min. Differential scanning calorimetry (DSC) of the samples were run on a DuPont 2000 thermal analyzer, with a rate of heating of 10°C/min. Viscosity measurements were made by a Brooke field digital-type viscometer (model RVDV 1+). The developed product was tested for corrosion resistance over mild steel. The mild steel was cleaned by mechanical buffing and with dilution with HCl, followed by steam for 30 min; it was then dried. Peel strength and sheer strength were measured on an Instron Corp. Series IX (automated materials testing system 1.04) according to standard procedures designated as ASTM D-1002 and ASTM D-1876, respectively. Leather specimens were scrubbed with emery paper and then PF and PFT resins were applied on the leather to test its adhesive nature.

RESULTS AND DISCUSSION

PFT was prepared from a phenol, formaldehyde, and tannin mixture using oxalic acid as a catalyst by adopting the same procedure followed for novolac resin. PFT resin was soluble in chloroform, isopropyl alcohol, toluene, acetone, THF, and dimethyl sulfoxide (DMSO).

The formation of PF and PFT resins were confirmed by IR spectroscopy. Physicochemical characterization of the PFT and PF resins was carried out by specific gravity and viscometry methods. The initial rise in the specific gravity value may

be due to the unfolding of molecules and development of crosslinks. Hence, volume occupied by unit weight of polymer becomes very high. On adding tannin, crosslinking is reduced, so the unanchored long-chain molecules are mobile and refold themselves, contributing less volume per unit weight of the polymer. On exceeding 0.77% the addition of recovered tannin hampers the growth of polymeric chains, possible leading to random orientation with increased volume and consequently decreased specific gravity.

Characterization of Resins

The IR spectra of the PF and PFT resins exhibit absorption because of the OH, CO, and phenyl ring. The IR frequency of the PFT resin shows a broad band in the region of 3500–3000 cm^{-1}, which may be a result of the intra- and intermolecular hydrogen-bonded phenolic —OH stretching vibration. The strong bands at 1600 and 1500 cm^{-1} may be due to the C=C stretching vibration of the aromatic ring, and the medium intense band at 1360 cm^{-1} results from the C—*O vibration of the hydrogen bonded ring system.

Physical Properties

Specific gravity and viscosity of the polymer were used as a tool to determine the extent of polymerization. Specific gravity of the polymer indicates the packing nature of the recovered tannin molucule. The recovered tannin materials are being encapsulated in such away that release of the tannin molecules to the solvent matrix is prevented when the resin is made to contact with the liquid phase. Specific gravity of the adduct rose smoothly until reaching a maximum of 1.7 at 0.77% of recovered tannin in the PFT adduct; thereafter it decreased slowly, for a ratio of 1.4%.

The specific gravity results are well supported by the viscosity measurements. The viscosity of the PFT resinous solution showed a maximum of 1040 centipoise at 0.77% tannin in the adduct, followed by a gradual decrease in viscosity. This initial viscosity rise may be due to the accommodation of tannin molecules in the PF matrix for the development of the compact structure of the adduct. The smooth decrease in viscosity confirms the free molecular mobility from the broken chain length on interaction with the added tannin, forming a low-molecular-weight product. Thus the amount of tannin in the PFT resin was fixed as 0.7%, and other testing was done.
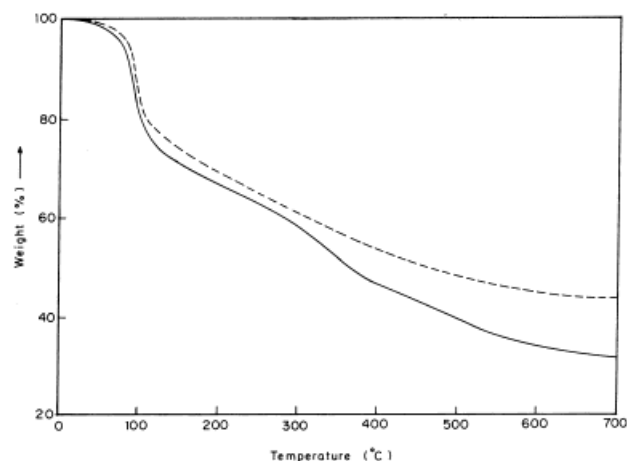
Figure 1 Thermogravimetric analysis (TGA) curves in nitrogen for (- - - -) RT and ($|$) PF–RT resin.

Thermal Studies

The thermal curves of both recovered tannin and PFT are shown in Figures 1. The decomposition of these systems essentially occurs in three stages. The first stage covers the postcuring, thermal reforming, and preliminary oxidation steps. The second stage depends mainly on the stripping of the ring, chain cleavage, and elimination of volatile fractions. In the third stage oxidative degradation takes place at markedly higher temperatures.

TGA curves of recovered tannin show these three stages. The first stage corresponds to the elimination of water, in which a nearly 19% weight loss has occurred, while in the second stage, the decomposition temperature range of 125–300°C could be the result of the partial breakdown of the intermolecular bonding and the 16% weight loss that has already occurred. The third stage occurs in the temperature range of 300–600°C, which may be due to the fragmentation of the intramolecular forces, and the molecule as a whole is decomposed with 20% weight loss. The char yield was nearly 50%, which accounts for the elements present in the wastewater.

The TGA trace of PFT impregnate shows its three stages of decomposition. In the initial stage of decomposition, a nearly 22% weight loss occurred, which may be because of the loss of water molecules that had been bound with hydroxyl groups present in tannin and in the voids. A nearly 45% decomposition takes place in the temperature range of 125–500°C. The char yield was 32%, an intermediate between PF and tannin.

Table I Corrosion Resistance of PF and PFT over Mild Steel

| Sl. No. | Medium | Corrosion Resistance | |
		PF Coating	PFT Coating
1	0.5% HCl	Unstable	Stable
2	1% HCl	Unstable	Stable
3	5% NaCl	Unstable	Stable
4	0.5% NaOH	Unstable	Stable

Mechanical Properties

The adhesive property of PF and PFT resins were tested on a leather matrix. The peel strength of PF and PFT is 0.4226 and 0.6018 N/mm^2, respectively. The lap shear strength for PF and PFT is 0.591 and 1.040 N/mm^2, respectively.

Coatings

The corrosion resistance of PF and PFT resins was test by applying the resins to mild steel. It was found that the PF resins lost weight drastically and peeled off when exposed to mild alkali (NaOH) and acids (HCl, H_2SO_4). Patches were identified on the surface of the metal on treating the steel plates with 1 : 10 phenanthroline.

The PFT resin, however, showed very good alkali and acid resistance (Table I), revealing that the presence of tannin in the matrix has improved the adhesive nature of the resin. This may be explained by the probability of developing a cage-like structure through the formation of intramolecular hydrogen bonding being restricted because of steric hindrance of the tannin molecules. The free hydroxyl group in a tannin molecule forms bonding with the peptide linkage of the leather matrix

The PFT adduct showed magnetic moment corresponding to the tetravalent chromium complex. Therefore, the polydented complex PFT resin molecules coated on steel exhibit an exchange of electrons between the metal matrix and the coated resin. causing the coating to remain adherent and coherent when coated on steel (Table II).

CONCLUSION

PF and PFT resins were synthesized and characterized, and specific gravity and viscosity measurements were done. The optimum ratio of PF to tannin was investigated. The thermal studies of the resins indicate that PF exhibits better thermal stability than does PFT. The adhesive property of the impregnate suggests its potential use in the leather garment industry. The PFT resins showed potential application in the paint industry as a good anticorrosive paint, as it has resistance to strong acids, alkalis, and organic solvents. The magnetic moment measurement confirmed the tetragonal geometry of the PFT resin. The scheme developed to encapsulate the recovered tannin in the spent liquor is an environmen-

Table II Comparison of Corrosion Resistance Behavior of PF and PFT Resins

Sl No.	Medium		PF	PFT
1	0.5% HCl	IW of the metal	13.8648	13.2192
		FW of the metal	13.8432	13.1469
		Change in weight loss	0.0272	0.0723
2	1% HCl	IW of the metal	13.8648	13.2192
		FW of the metal	12.8214	13.1917
		Change in weight loss	0.0819	0.0275
3	2% HCl	IW of the metal	13.8648	13.2192
		FW of the metal	12.7111	12.9313
		Change in weight loss	0.1922	0.2879
4	5% NaCl	IW of the metal	13.8648	13.2192
		FW of the metal	12.7004	12.9956
		Change in weight loss	0.2029	0.2236
5	0.5% NaOH	IW of the metal	13.8648	13.2192
		FW of the metal	12.1161	12.5607
		Change in weight loss	0.7864	0.6585

IW, initial weight of the metal; FW, weight of the metal after treatment.

tally sound method for the disposal of bioresistant organic chemicals.

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