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Electrochemical and mechanical studies on influence of curing agents on performance of epoxy tank linings

Akshay Kumar Guin[1], B.P. Mallik, Subrahmanya Shreepathi*

Asian Paints Research and Technology Centre, Plot No. C3 – B/1, Thane Belapur Road, Navi Mumbai 400703, India

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ABSTRACT

Effect of different curing agents on the mechanical, chemical resistance and anticorrosive properties of tank linings based on phenolic + novolac epoxies has been studied. Proportion of two epoxies was chosen by monitoring the processing viscosity of the coating. Parts of hardener required for 100 g of the above resin (phr) was scrutinized using differential scanning calorimetry and flexibility measurements. As a result, five coatings were finalized and their mechanical properties were investigated by dynamic mechanical analyzer. Anticorrosive properties of these coatings were studied using electrochemical impedance measurements and neutral salt spray exposure test. Chemical resistance of these coatings was investigated by monitoring the weight change of the coating during immersion. Coatings cured with modified cycloaliphatic amine (amine value = 350), in spite of lower cross-link density, exhibited superior anticorrosive properties and reasonably good chemical resistance. Electrochemical impedance results correlated fairly well with actual solvent resistance property of the coating.

1. Introduction

In the present industry dominant world, variety of corrosive liquids such as acids, alkalis and petrochemicals have to be stored and transported in a safer way by tanker trucks or cargo containers. Unfortunately, steel and concrete, the most economical and predominantly used materials in metal finishing industry are susceptible to corrosive attack [1]. Organic coatings or polymeric linings are widely used in metal finishing industries to protect steel or concrete against corrosion. Such coatings or linings must be capable of resisting: (i) different chemicals, (ii) thermal variations and (iii) physical abuse [2,3]. Performance of these coatings and linings is of utmost importance in order to maintain purity of chemicals stored and to prevent accidents and environmental damage due to corrosion. Wide range of organic coatings and linings are available in the market [3]. Key properties of the tank lining system such as chemical resistance, mechanical strength and adhesion basically come from the polymer used to manufacture that coating.

Epoxy resins are polymer of choice for tank linings because of their higher electrical resistance, hardness, toughness and chemical resistance [4]. Traditionally, three types of epoxies are used: diglycidyl ether of Bisphenol A, Bisphenol F and novolac resins. They differ in molecular weight, viscosity and functionality [5]. Chemical structure of epoxy coating strongly influences their chemical resistance properties. A summary of chemical structure and applications of each of the above epoxies has been described elsewhere [5]. Selecting the suitable epoxy resins or combinations thereof is the first step to design a tank lining that sets some limits on performance. Bisphenol A is known for toughness, adhesion and wear resistance, whereas, bisphenol F imparts chemical resistance. Lower viscosity of bisphenol F comes as an added advantage to design tank linings. Compared to bisphenol A and F, novolacs provide excellent chemical resistance and heat resistance [5].

The next step is to choose right curing agent that significantly enhance the performance property [5,6]. Aliphatic, cycloaliphatic and aromatic amines and polyamides are the generic class of curing agents that are used to react with epoxies. There are good numbers of modified amines available for use such as amidoamine and polyamide adduct. These are used as sole curatives or in combination. A generic comparison of epoxy curing agent types for low temperature cure and chemical resistance is effectively tabulated in the article by O'Donoghue et al. [7]. Modified aliphatic amine mannich base and polyamide show excellent water resistance but moderate to poor solvent resistance whereas aromatic amine exhibits good water resistance, excellent acid resistance but moderate solvent resistance.

* Corresponding author. Tel.: +91 22 39153508; fax: +91 22 3915 3650.
E-mail addresses: subrahmanya.shreepathi@asianpaints.com, s_udupa@rediffmail.com (S. Shreepathi).
[1] Present address: Research and Development Division, Tata Steel Limited, Jamshedpur 831001, India.

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The field experience reveals that many coatings inside oil storage tank or vessel, with time, develop coating defects such as blistering, cracking and delamination resulting into major unseen damage to the substrate [2]. In addition, coating failures are expensive, hazardous and complicated to repair. Therefore, today's choice of coating material and application process is still open to improvement [8]. There are multiple reasons for coating failure. In the case of a chemical storage tank, the chemical can either soften the coating leading to reduced mechanical strength or react with the moisture or coating to form aggressive species [9]. On the other hand, in crude storage tanks, saline solutions with bacterial sludge and soluble sulfur materials cause corrosion due to very low pH environment. Hence, one has to properly choose the tank lining depending on the service environment. Thus, there is no single coating that can be defined as perfect tank lining [2].

Storage tanks depending upon their service environments are usually opened for inspection at periodic intervals (generally 3–5 years or more). Internal lining is then critically examined and necessary rehabilitation requirements are decided. This exercise is an expensive task and hence there is a growing need to extend the lead time of inspection, maintenance and service life of the lining. Therefore, the biggest challenge in developing a tank lining product is selecting reliable characterization techniques and establishing a correlation between more quantitative analytical methods and qualitative chemical immersion tests.

An important physical parameter on which chemical resistance of a polymer depends on is its cross-link density. Therefore higher functional epoxies such as Novolacs perform better as tank liners compared to traditional epoxies such as bisphenols. The additional epoxy functionality brings in extra cross-linking making the lining more resistive to many chemicals. There are many ways by which change in cross-linking density of polymer can be tracked. One easiest and widely used qualitative test in the industry is MEK rub test. On the other hand, T_g of the polymer, which is measured by differential scanning calorimetry (DSC), provides semi-quantitative information on cross-link density of the polymer. For example, for a given set of monomers, increase in T_g represents increased cross-linking. However, the most reliable and appreciated tool to understand cross-linking of polymers is by dynamic mechanical analysis [10–13].

The present work focuses on use of more dependable analytical tools such as DMA to study the effect of different types of hardeners on final properties of tank lining. DSC and flexibility measurements were used to scrutinize the ratio of epoxy to curing agent. Anticorrosive properties of the coating were assessed by electrochemical impedance analysis (EIS) and neutral salt spray tests. Chemical resistance of the tank linings was evaluated using traditional weight change during chemical immersion. An attempt was made to correlate cross-link density, anticorrosive properties and chemical resistance.

2. Experimental

2.1. Materials and reagents

Mixture of epoxy novolac resin (average functionality = 2.8, epoxy equivalent weight = 172–179, Dow epoxy) and Bisphenol F epoxy (epoxy equivalent weight = 165–175, Aditya Birla Chemicals) were used as base resin. Several hardeners used in the present study were of commercial grade whose source and key parameters are given in Table 1. Commercial names of the hardeners are not used to avoid the product promotion that may arise out of this work. Cycloaliphatic amines (CAA 16 and CAA 22) listed in Table 1 were used as sole curing agents as well as in combination with CAA 24. On the other hand, aromatic amines were only used in combination (MAA 41, MAA 42 and CAA 24). All other ingredients used to process the paint were also of commercial grade and used without further purification. The chemicals and reagents used for testing were of analytical reagent grade and used as purchased.

2.2. Optimizing the ratio of novolac epoxy to bisphenol F epoxy

Novolac epoxies, because of the higher functionality, produce highly cross-linked dense networks and therefore, are the polymers of choice for tank linings [4]. Unfortunately, their use in coatings is limited due to very high viscosity that creates several processing issues. Novolacs, therefore, are used in combination with phenolic epoxies (bisphenol A or F) and identifying the right ratio of novolac-to-bisphenol F epoxy is the key step in designing tank lining. In this study, best possible combination of Novolac epoxy to bishenol F epoxy was identified by taking different ratio of two epoxies and monitoring their processing viscosities. The desired processing viscosity was achieved at a ratio of 40:60 (novolac:bisphenol F) and hence this ratio was chosen for all further experiments.

2.3. Processing epoxy tank linings

Base component of the two-pack (2 K) coating were processed using a custom built table-top high speed disperser. Pigment volume concentration of the coating was fixed at 27%. Rutile grade TiO_2 (11%), silica (28%) and barytes (14%) were used as pigment and fillers. Small quantity of epoxy resin (Bisphenol-F + Novolac) was taken in a 1 L metal container and additives such as dispersant, wetting agent, defoamer and rheology modifier were added to it. All the pigments and extenders were added slowly into the container by running the high speed disperser at 300 rpm. The speed was then increased to 2000 rpm and the paint mixing was continued for 30 min. Remaining resin and solvent were added to the container once the finish of 3.5 on Hegmann scale was achieved and the mixing was continued for another 10 min. In the end, the paint was cooled to room temperature and stored for further use. Curing agents were used as it is without further modification. In the case of hardener blends, equal weight proportions of individual curing agents were stirred slowly for 10 min to get homogenous mixture.

2.4. Optimizing the ratio of epoxy resin to hardener

Many a times, mixing epoxy resin and hardener in stoichiometric ratio does not produce the desired results [4]. Coating formulators, while optimizing the performance of tank lining for immersion use, generally focus on epoxy coating with higher T_g [14]. It is well established that resistance of the tank lining to solvent or other chemical improves with increased T_g. On the other hand, the metallic storage tanks undergo thermal expansion and contraction during their service life and therefore the tank lining shall also have certain flexibility to accommodate the environmental stresses. Flexibility of coating is generally found in the specification of tank lining [15]. Therefore it is necessary to identify the correct ratio of epoxy resin to hardener (generally called as phr meaning parts hardener per hundred grams of epoxy resin) depending on the desired film properties. For the present study, highest possible T_g at which coating passes at least ¼ inches of flexibility (flexibility on conical mandrel as per ASTM D522) was taken as desired film properties. Accordingly, T_g and flexibility of the coating was measured for different hardeners at four different phr levels (Table 2) to identify the right phr. It is evident from Table 2 that all the hardeners and their combination used in the present study passed the flexibility test up to 80–90 phr. CAA 16, blend of CAA 16 + CAA 24 and MAA 41 + MAA 42 + CAA 24 had passed the flexibility test up to 90 phr whereas CAA 22 and its blend with CAA 24 passed ¼ inch flexibility up to 80 phr. Hence, for CAA 16, blend of CAA 16 + CAA 24 and MAA 41 + MAA 42 + CAA 24, further