THESIS INFORMATION

Title: Photoresist waste treatment technology research
Major: Environmental Technology for Solid Wastes
Code: 62.85.06.10
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Abstract:

The current strong development of printed wire boards is accompanied with the key application of dry film photoresist (DFR). In place of complicated formation of resistant film from a liquid material, a film is made and applied to the printed wire board (PWB). This technique makes the transfer of photos much easier without complicated equipment and high skills. The most popular negative DFR are acrylates. All amounts of photoresists are removed after printing as waste, i.e. photoresist (PR) waste. In Vietnam, PR is classified as hazardous waste for "toxicity not clearly known". In the USA, the Environmental Protection Agency (EPA) stated that: "PR is subject to hazardous waste treatment as specified in 40 CFR Part 261 Subpart C". EPA made such a decision, suspecting that PR might contain hazardous components produced in the engineering process or the associated galvanizing line. PR is coded F006 in the group of galvanizing waste.

This kind of waste is currently treated by either (1) burning – this always accompanies with air pollution risks; or (2) stabilization and solidification – as a final solution (before landfill). The second is to cover up and chemically and physically isolate the waste, thereby prevent leakage, conversion or solution of pollutants therein. Nevertheless, land-filling sooner or later increases the environmental costs, for instance, land acquisition, costly monitoring, and moreover, it disables the utilization of useful leftover of the waste.

***Subject matters*:** The subject matter of the research is the waste photoresist from the PWB production line with DFR technology from Fujitsu factory (Dong Nai province), where the PR production is large.

Targets:

(i) Study of properties of waste photoresist and mechanical physical properties of monolithic blocks;

(ii) Application of stabilization and solidification technologies to modification of technical resin-rubber towards recycling.

Contents:

An overview of DFR applications and researches into technology changes, waste reduction, liquid waste treatment, photoresist polymer treatment, applications of acrylic polymers in the world and national studies in relation with photoresist and PR treatment.

A research into properties and environmental impacts of PR, solid waste identification of PR in compliance with the EPA procedure in combination with Vietnamese technical standards.

A research into properties of some polymer-photoresist blends, and establishment of the formation mechanism of NR- and NBR-PR blends .

Adjustment of blend compositions and processing parameters for building up a PR recycling technology; Recommendation of an engineering process of 10 ton per month, i.e. capable of treatment of all arising PR; and pilot production of resultant products, including two main groups, namely (i) oil resistant cushions and (ii) waterproof cushions for civil uses.

Methods:

Analyzing and measuring methods: Compositions and properties of PR are determined using ICP, GC/MS, IRS, thermal analyses (TGA, DTA), toxic matters are extracted with TCLP at laboratories of Vietnam Institute for Tropical Technology and Environmental Protection (VITTEP), Institute for Environment and Resources (IER), Analytical Services and Experiments Center (ASE) and Environmental Technology and Management Center (ETM). Scanning electronic microscope (SEM) images of phase morphology and thermal analyses (TGA, DTA) of samples are taken at laboratories of VITTEP and the International Training Material Science Institute (ITIMS) in Hanoi.

Analyses of environmental parameters: moisture, soluble contents of samples and further solidification under infrared, mobile acrylate content (Fedotova method), environmental parameters of leakage (pH, EC, COD, BOD_5, TDS, Kjeldahl nitrogen, ammonium) and bio-toxicity to indicator D. magna are accomplished at laboratories of VITTEP, IER and ETM.

Measurement of physical mechanical properties of blend specimen: properties such as vulcanization, tensile strength, elongation and effects of liquids, Brinell hardness, stability and ageing, abrasion resistance are done at the laboratory of VITTEP and verified at Quatest 3.

Experiment planning: with orthogonal arrays of level 1 and tests for building up mathematical descriptions as background for experiments towards an appropriate blend formula and a processing process.

Environmental economics: comparative advantages are weighed based on flow cash in combination with NPV and IRR in order to evaluate the feasibility of the recommended processing process.

Main outputs:

1. Waste photoresist is a cross-linked product with hydrophilic acrylate resins as principal component and heavy metals contents lower than hazardous levels. Its solid part is inert and stable as a resin in the environment. Its impacts are dependent on the acrylate mobility and content. The research has successfully applied the hazardous waste definition procedure of RCRA (EPA) in combination with technical standards of hazardous waste thresholds, whereby PR is identified as hazardous waste based on tests of its properties (mobile acrylate content of PR is 4 to 5 times as high as the basic value set forth in QCVN 07: 2009 BTNMT).

2. Blends NR and artificial rubber NBR with compatibilizing agent CSTNgAM and cashew oil (HD), respectively demonstrate improvements in physical and mechanical properties and processing properties such as fluidity and phase morphology. Mechanisms of compatibilization in recycling materials are determined as *reactive Compatibilization* in systems of nitrile rubber and *non-reactive compatibilization* in those of natural rubber.

3. The factors with strong effects on properties of samples include: (i) content of PR, (ii) carbon black, (iii) compatibilizing agent, and (iv) moisture of PR. Experimental planning and actual measuring results make it possible to recommend an appropriate rubber blend formula of recycling products as follows: PR 30 part (w/w), carbon black 25 part (w/w) and compatibilizing agent 5 part (w/w) (CSTNgAM for NR blends and cashew oil for NBR blends).

4. Stability of blend samples is shown by good mechanical and physical properties (tensile strength, elongation) for a long time. Samples were still stable after accelerated ageing tests in the air, water (blend NR) and the air, oil (blend NBR) and the ageing coefficients were all higher than 80 %. The abrasion resistance was improved by 10 – 16 %, compared with non-PR samples.

5. The leaching process TCLP 1311 was applied to the utmost conditions of sample cut-off (Vietnam has no regulation and in fact, products will not work under such conditions), and samples were then tested in accordance with QCVN 07 showed that mobile acrylates were fixed (no detection) in the following cases:

- Samples of NR and NBR blends without TTH containing 20 part (w/w) PR and
- Samples of NR and NBR blend with TTH containing 40 part (w/w) PR.

6. It is the first time in Vietnam PR is successfully recycled by addition of NR and NBR as components to improve abrasion resistance and weather durability of

ordinary products in a cost-effective manner. Two main products, namely water-tight O-rings and oil-resisting soles and others such as spring cushions of train knuckle cases, industrial ladder steps have been fabricated in laboratories of VITTEP and Thanh Danh Rubber Manufacturing Co., Ltd., in according to the PR recycling process by means of solidification in elastic polymers with compatibilizing agent CSTNgAM and cashew oil.

Scientific significance:

The researches brought environmental engineering closer to other applied sciences. In the cases, physical and chemical thermodynamic analyses clarify the mechanism of the stabilization and solidification which have been widely used in industrial solid waste treatment.

Practical significance:

Other outputs of the research include the improved management of a solid waste (limitation of risks) and environmental protection with a new environment-friendly solution for PR treatment;

The successful application of blends of rubber, polymers and PR opens a new supply of recycling materials for the large market of technical rubbers, and at the same time, limits environmental risks of waste burning.

Pending matters:

1. Improvement of the dispersion in rubber-PR systems for better properties of resultant blends.

2. Acceleration of PR drying during treatment. In addition, regulations on classification and storage of PR should be established, giving favorable conditions for recycling.

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