Method For Recycling Valuable Materials from Waste LCD Panel

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Abstract

LCDs have replaced CRTs as the main display devices recently. To satisfy the increasing demands, billions of LCDs are manufactured annually. However, as more LCDs are produced and are used, the amount of LCD waste is increasing at an alarming rate. LCD waste can be simply disassembled into a numerous parts, most of which are commonly recycled, but the LCD panels typically are not. Waste LCD panels are generally disposed of in a landfill or by incineration. An increasing number of countries are prohibiting such treatments, because waste LCD panels are potentially hazardous and detrimentally affect health. The development of a new solution that involves the recycling and recovery of waste LCD panels is important.

LCD panels consist of LCs, indium, glasses and other rare metals and organic materials. LCs is stable, non-degenerate and have high unit price. Indium is rare in Earth's crust. Glasses are a kind of alkaline earth boro-aluminosilicate with high purity and stable compositions. These three materials have higher recycling values than other materials in LCD panels. Therefore, this work develops a method for recovering and re-using LCs, indium and glasses from waste LCD panels. The reformulated LC mixture, after it has undergone extraction, purification and blending, is utilized to produce LCD panel again. The recovery rate of indium from waste LCD could reach to 90% by simply leaching and concentrating process. After removing LCs and indium, the glasses are transformed into a high efficiency absorbent for treatment of waste water which is contained some heavy metals such as arsenic or lead by a specific process.

Key words: waste LCD panel, recycle, liquid crystal

Introduction

Liquid crystal display (LCD) is the primary display device in modern life and is appeared in everything and everywhere. The worldwide shipments of large-area (larger than 9-inch) LCD panel are expected to reach 718 million units in 2014.[1] Unfortunately, such a large amounts of LCD product could enter into their end-of-life stage in near future due to the lifespan of a LCD is estimated only of 8-10 year.[2] LCD waste can be simply disassembled into a numerous parts, most of them are commonly recycled, but the LCD panel typically is not. Waste LCD panels are generally disposed of in a landfill or by incineration. An increasing number of countries are prohibiting such treatments, because waste LCD panels are potentially hazardous and detrimentally affect health. The development of a new solution that involves the recycling and recovery of waste LCD panels is important.[2] LCD panel is a sandwich-like structure including 15% plastics (polarizer, color filter, sealant, alignment layer and spacer), 85% glass substrate, 0.01% indium tin oxide (ITO), 0.001% thin film transistor (TFT) and 0.1% liquid crystal (LC), as shown in **Fig 1**.[3-4] Although there is possibly no economical use for recycled plastics and TFT, the other materials could be reused after conducting proper treatments. LCs have a higher recycling value than other materials in LCD panels because they are stable, non-degenerate and have high unit price. Indium (In) is a rare metal with the abundance about 0.1 mg/kg in Earth's crust. Glasses are the mainly components of the LCD panel and need to be recovered from the WEEE. They are a kind of alkaline earth boro-aluminosilicate with high purity and stable compositions. Therefore, this work develops a method for recycling LCs, indium and glass from waste LCD panels.

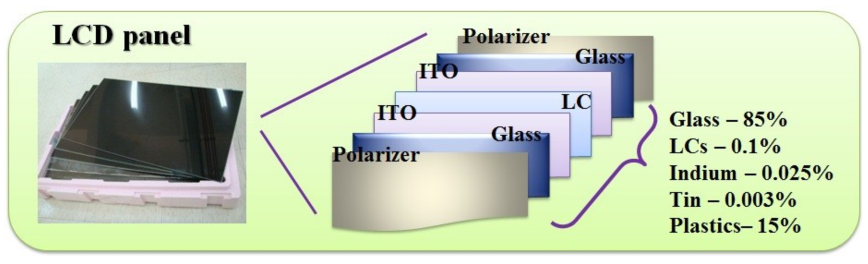

Figure 1 The brief structure of a LCD panel

Integrated approach to waste LCD panel recycling

Four batches (A, B, C, D) of waste LCD panels were collected from a waste electric household appliances treatment factory in Taiwan. Batch D was a TN-type LCD panels and the others were VA-type ones. The procedure used for recovery of LCs, In and glass is illustrated in the flow chart **(Fig. 2)**. Each batch of LCD panels was treated by above procedure respectively. The steps involved are described below.[5-9]

A. Crash process

First, to retrieve LCs that are sandwiched between two pieces of panel glass, the waste LCD panels are broken into pieces of glass with areas of less than 100 cm^2 by using a crusher to expose the LCs.

B. Extraction process

These panel fragments with LCs and other cell materials are put into a continued extraction system and are dipped in an organic solvent to dissolve the LCs to generate an extraction liquid. The extraction liquid is cooled to reduce the solubility of the cell materials, which therefore precipitate as solids and are removed by filtering. Then, the filtered extraction liquid is heated to evaporate the organic solvent. The organic solvent vapor is condensed to be stored as a liquid in the system and subsequently be reuse. After it is separated from the solvent, the colored LCs, which contain some impurities, are collected from the extraction system. With optimum extraction parameters, the LCs was totally separated from panel fragments.[5]

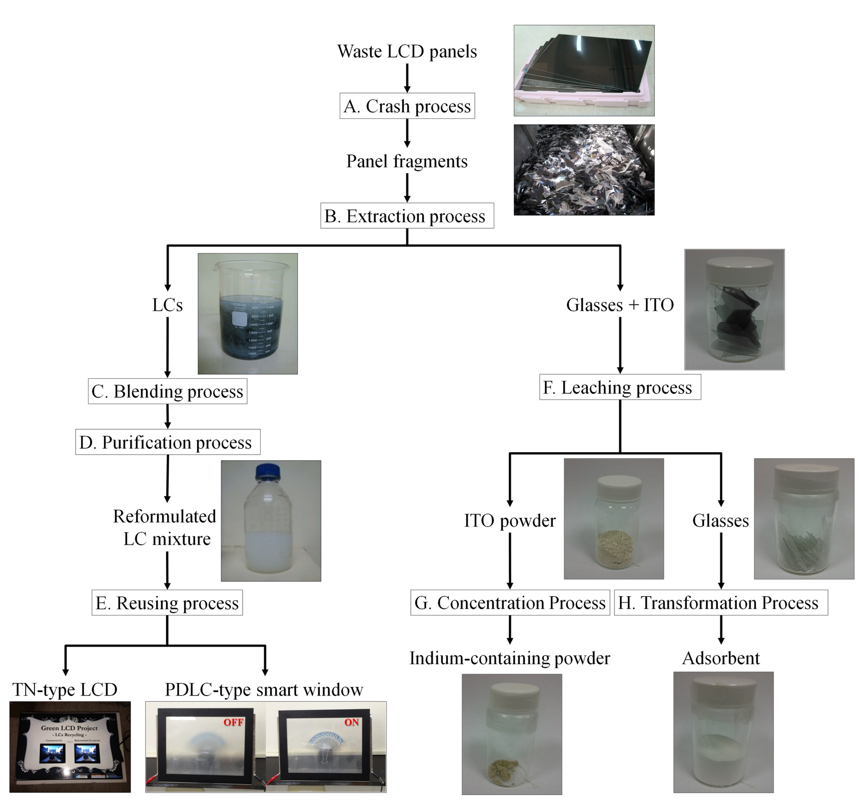

Figure 2 Procedure for recycling LCD

C. Blending process

A salt adsorption method is used to remove most of impurities in the collected LCs, yielding regenerated LCs, which are now whitish (which is the normal color of LCs). Four regenerated LCs with different properties containing three VA-types and one TN-type were retrieved from four batch LCD panels using the above processes respectively. **Table 1** presents the properties of the four regenerated LCs. The formulation is supposed to be close to the commercial LCs. A commercial VA-type LC is selected as a target for reformulating a VA-type LC mixture. Based on the properties of the commercial VA-type LC and the three regenerated VA-type LCs, the weight ratio of the regenerated VA-type LCs to produce the reformulated VA-type LC mixture with the desired properties is determined. The three regenerated VA-type LCs are blended in the above calculated ratios to form the reformulated VA-type LC mixture. **Table 2** presents the properties of the commercial VA-type LC and the regenerated VA-type LC mixture. Even though some properties of the reformulated VA-type LC mixture differ slightly from those of the commercial VA-type LC, they are similar. On the other hand, the regenerated TN-type LCs is blended with a specific polymer and a halogen contained non-ionic surfactant to form as a polymer dispersed liquid crystal (PDLC) emulsion.[10]

D. Purification process

To satisfy the purity requirements of the commercial VA-type LCs, the electrophoresis method is used to purify the reformulated VA-type LC mixture. After the residue impurities has been removed, the resistivity and moisture content of the reformulated VA-type LC mixture are found to meet the requirements and the other properties are unchanged, as presented in **Table 2**. Therefore, the above recycling process yield a reformulated VA-type LC mixture with high purity and properties identical to the commercial VA-type LC.

Table 1 Properties of four regenerated LCs

Test items	A	B	C	D
Float Viscosity (η, cps)	17	19	32	18
Clearing Point (Tc, °C)	80.6	72.0	103.0	86.2
Birefringence (Δn)	0.091	0.082	0.105	0.092
Dielectric Anisotropy (Δε)	-2.6	-2.8	-3.6	10.0

Table 2 Properties of commercial LC and reformulated LC mixture

Test items	Commercial LC	Reformulated LC mixture	Purified reformulated LC mixture
Float Viscosity (η, cps)	25	22	22
Clearing Point (Tc, °C)	91.4	81.6	81.6
Resistivity (Ω-cm)	> 1.0E+13	5.4E+12	> 2.0E+14
Moisture Content (ppm)	< 100	77.8	48.4
Birefringence (Δn)	0.090	0.089	0.089
Dielectric Anisotropy (Δε)	-3.1	-3.0	-3.0

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E. Reusing process

The highly pure reformulated VA-type LC mixture is used to produce 100 pieces of 10” VA-type LCD panels by Innolux Corporation (INX), of which 95% of LCD panels passed the light-on test. The feasibility evaluation of the LCD panels that are filled with the reformulated VA-type LC mixture is judged by INX according to their new material evaluation criteria. However, these testing data were considered to be confidential business information, INX just commented that the reformulated VA-type LC mixture has passed the evaluation test and can be reused to fabricate LCD panels. On the other hand, the PDLC emulsion contained regenerated TN-type LCs is used to produce a composite film by Display Technology Center (*DTC*) of industrial technology research institute (ITRI). The composite film is made by coating the PDLC emulsion to an electrically conductive substrate such as a PET substrate with an ITO layer and heating to remove the solvent. Then, the PDLC composite film can be directly utilized in large-size LCD, banners and smart windows for buildings or cars.

F. Leaching process

The panel fragments without LCs are further leached with 2 M NaOH solution to collect the ITO. The ITO film in LCD panel was covered by LCs originally. Because LCs has been extracted, ITO film contact with NaOH solution directly and is easier to lift-off. Over 80% ITO film was separated from panel fragments and precipitated in solution with the parameters. (60 min leach time, 25ºC temperature, 2 M NaOH solution of reusable leach agent, 1:1 liquid-solid ratio) The ITO powder containing 2% - 3% In was collected after filtering the NaOH solution, as shown in **Table 3**. In which, the concentration of In in ITO powder (C1) was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the In content (C0) in LCD panel was about 250 mg kg^{-1}.[4] The recovery rate was calculated by using C1 divided by C0.

Table 3 Recovery of In from panel fragments

Weight of LCD panel (Kg)	In content in LCD (g)	Weight of ITO powder (g)	In content in ITO powder weight /conc. (g / %)	Recovery rate (%)
5	1.25	30.7	1.18 / 3.85	94.6
10	2.50	74.6	2.19 / 2.93	87.4
100	25.0	750	20.5 / 2.73	81.9
200	50.0	1169	43.4 / 3.71	86.7

G. Concentration process

Some organic materials containing in ITO powder are removed by heating to 600ºC for 30 min. Adding proper amounts of 7N nitric acid into the ITO powder to dissolve In. After filtering, the concentration of In in nitric acid raise to about 10%. In spite such acidic solution with percentage level of In could be sold to refining plant. Using NaOH to adjustment the pH value of nitric acid to 7.4, the In-containing powder with the concentration of In at 38.9% precipitate and have higher acquisition price. Cementation and electrorefining method can further be applied to purify the In-containing powder and collect high purity In metal. In with a purity of 99.995% (4N5) can be reused to fabricate ITO target.[11]

H. Transformation process

After removing most of the cell materials, the glasses with some polarizer and TFT are collected. Theses glasses are alkali-free and composed of SiO_2, Al_2O_3, B_2O_3, and alkaline earth oxides and are similar to some absorbent such as aluminum silicate, zeolite and so on. A modification agent consists of alkali salt and alkaline earth salt with specific ratio is added into the glasses and the mixtures are mixed by a V-mixer. The structural conformation of the glasses change after the mixtures are melted at 800ºC -1500ºC and some microporous are created on their surface, as shown in **Fig.3**. The surface area of the modified glasses increase and more asymmetric charges and reactive sites for ion exchange form during the melting process. The polarizers are completely burned and convert to carbon dioxide and water during melting. Meanwhile the TFT, which consists of metal oxides, are doped into glass structure.

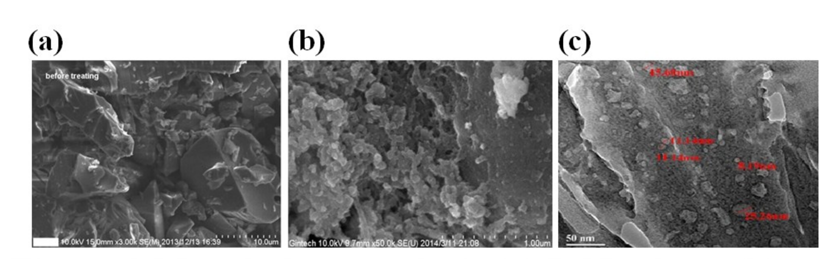

Figure 3 Morphology analysis (a) LCD glass; (b) and (c) modified glass

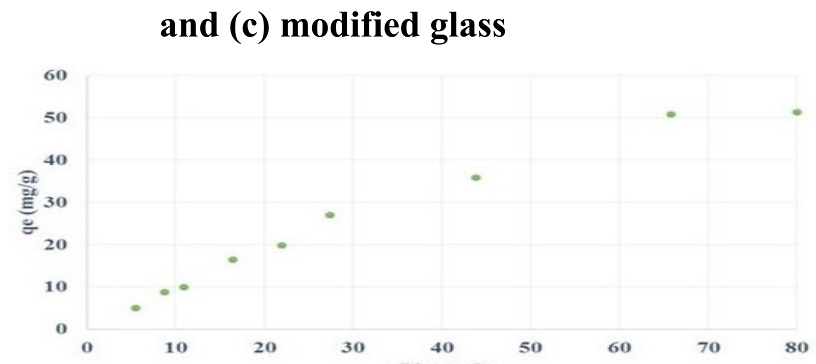

Figure 4 The adsorption study of Pb

Table 4 The metal removal ability test

Elements	Conc. before adsorption (mg L^{-1})	Conc. after adsorption (mg L^{-1})	Removal rate (%)
As	109	28.2	74.2
Pb	111	33.1	70.0

To test the metal removal ability of above material an adsorption experiment is carried out by stirring 10 g of the modified glasses in 200 mL of two metals solution at 25 ◦C. The homemade, pH 2.7, nitric acid solution contained arsenic (As) and lead (Pb) and the initial concentration of the metals are 109 mg L^{-1} and 111 mg L^{-1}, respectively. Adsorbent–solution mixtures are stirred at 180 rpm for 30 min and then filter to collect the final solutions. The concentrations of As and Pb in the final solution are 28.2 mg L^{-1} and 33.1 mg L^{-1}, and the removal rate are 74.2% and 70%, respectively (**Table 4**).

The adsorption study of Pb is carried out by batch equilibrium experiments. A known weight (~0.1 g) of the modified glass is taken in a 250 mL vial and is equilibrated with100 mL of aqueous solutions of different concentrations of Pb for 24 h at 25ºC . The concentration of Pb in the solution before and after equilibrium is determined using the ICP-AES. The maximum adsorption per unit mass of Pb is 50.2 mg g^{-1} according to the Langmuir adsorption model, as shown in **Fig.4**.[12]

Conclusion

An environmentally friendly process has been developed for recycling LCs, indium and glasses from the waste LCD panel. LCs in wasted LCD panel can be extracted, blended and purified to form a reformulated LC mixture with the properties and purity of commercial LCs. The product yield is approximately 95% and INX, the LCD manufacture in Taiwan, confirms the feasibility of reusing the reformulated LC mixture in LCD panels. And these LCs also can be applied to fabricate the PDLC-type smart window. Indium was recovered at 82% or above from waste LCD panel by using 2 M NaOH solution as leach agent. Through a concentration process, the final indium-containing powder contains 38.9% indium. LCD glasses were succeeded in transformed into an adsorbent by adding a modified agent and melting at a specific temperature. The removal rate of As and Pb in the nitric acid solution is 74.2% and 70%, respectively. The maximum adsorption per unit mass of Pb was 50.2 mg g^{-1} according to the Langmuir adsorption model. The modified glasses have chance to apply to deal with the waste water which is contained heavy metals as an environmental purification material.

Currently, around 8000 tons of waste LCD panels are buried in Taiwan every year. The proposed recycling approach for disposing waste LCD panels can solve the growing environmental problem that is caused by them and support sustainable management of materials.

Acknowledgements

This work was supported by the Industrial Technology Research Institute and the Environmental Protection Administration of the Executive Yuan, R.O.C..

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