Original Research

Materials Separation from Waste Liquid Crystal Displays Using Combined Physical Methods

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Received: 2 December 2011
Accepted: 16 July 2012

Abstract

With the liquid crystal displays (LCDs) being widely used in televisions, notebooks, and mobile phones, etc., large quantities of LCDs are entering into their end-of-life stage for treatment. If not treated properly, a loss of resources and undesirable impacts on the environment and human health can occur. In order to treat the waste LCDs in an efficient and environmentally friendly way, a combined process of physical methods was proposed to separate and recover materials from waste LCDs in the present study. On the basis of primary disassembly, two key processes (including liquid crystals removal and the recovery of polarizer and glass) were studied. Liquid crystals were removed from the panel glass by dissolving in isopropyl alcohol solution (16.7 vol.%) assisted with ultrasound. Recovery of polarizer and glass was achieved through mechanical crushing and gravity concentration. Results show that approximately 100 wt.% of liquid crystals were removed after dissolving for 45 min at 60ºC. Up to 79.7 wt.% of polarizer was separated from glass and its average content in the recovered product was 90.3 wt.%.

Keywords: waste liquid crystal display, material separation, liquid crystal removal, polarizer, glass

Introduction

Due to the characteristics of low energy consumption, no electromagnetic radiation, small volume, and lightweight etc., liquid crystal displays (LCD) have aroused worldwide attention ever since they were introduced for commercial use. Associated with technological innovation and production cost reduction in the past few decades, LCDs have gradually become the leading display in the market and been widely used in televisions, notebooks, mobile phones, pocket calculators, measuring and control instruments, computer monitors, digital cameras, etc. Statistics show that LCDs accounted for almost 90% of the global market for flat displays in 2006, and the number was still increasing in the following years [1]. Since an LCD typically has a lifespan of 3-5 years and has been on the market for several years, large quantities of LCDs are entering into their end-of-life stage for treatment.

Waste LCD is non-homogeneous and complex in terms of the materials and components. An LCD monitor is comprised of a front frame, the LCD panel, plastic housing, film set, back frame, backlight assembly, power supply and controller, a rear cover, and a base/stand. The detailed subassemblies of an LCD monitor are shown in Fig. 1. As the key unit, an LCD panel is the main part of waste LCDs after primary dismantling. According to the material flow analysis conducted by Lee and Cooper, the amount of waste LCD panels from portables, PC flat screens, and TV flat screens were estimated at 2.5×10^4 tons (maximum) in 2009, accounting for about 10% of the total waste LCD mass in America [2].

The LCD panel mainly consists of two plates of glass with a liquid crystal mixture sandwiched in. The outer sides of the glass are attached with polarizer and the inner side is

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Table 1. Major hazardous components in waste LCDs.

Materials and components	Description	Biological toxicity
Liquid crystals	Liquid crystal mixture containing benzene, cyano-group, F, Cl, Br, etc.	Potentially harmful to the environment and human health
Backlight assembly	Mercury is used	Harmful to kidneys, liver, nervous system, and the hematological system; carcinogenic
Plastic housing and frames	Brominated flame retardants such as PBDE and PBB	Harmful to the brain, kidneys, liver, nervous system, endocrine, and reproductive system; carcinogenic
Power supply and controller	Arsenic (As) and heavy metals such as lead, cadmium, and chromium	Harmful to the liver, kidneys, skeleton, nervous system, and hematological system

coated with functional films and a transparent conductive electrode that contains indium-tin oxide (ITO). Usually, the glass accounts for about 85 wt.% of the LCD panel and polarizer almost 15 wt.%. The indium content is approximately 102 mg/kg of the ITO glass [3, 4] and the liquid crystal mixture accounts for about 0.1 wt.% of the LCD panel. Although minor in weight, the constituents of liquid crystals are complex, which usually contains about 10-25 compounds. The liquid crystals are aromatic-based polymers with benzene, cyano-group, fluorine (F), bromine (Br), and chlorine (Cl), etc., which are potentially harmful to the ecosystem and human health.

From the above description, it can be noted that waste LCD is important not only in terms of its quantity but also its toxicity. Many of the materials contained in waste LCDs are highly toxic. If not treated properly, they will have serious impact on the environment and human health. Major categories of hazardous materials and components contained in LCDs are listed in Table 1. On the other hand, materials such as plastic, glass, and metals have a relatively high residual value and could be recycled using proper technologies [5-9]. Recovery of these valuable materials will contribute to avoiding resource-wasting and to obtain economic benefits. Therefore, treatment of waste LCDs is of great importance not only for material recovery but also for removal of hazardous pollutants.

In the practice of waste LCD recycling, thermal treatment has been studied and developed for material separation and recovery. For example, a two-phase thermal process was used to recover glass and metal oxides from the LCD panel [10]. During the process, liquid crystals were first heated to evaporate and discharged by gases. Then with a further increase in temperature, polarizer and other coating films were incinerated. After the thermal treatment, glass and metal oxide could be obtained in residues. In the study of Li et al. [11], based on the difference of thermal stabilities between polarizer and glass, polarizer was successfully removed from glass substrates by the method of thermal shock. Martin [12] reported a method of combusting LCD plastic films to supply energy for glass recovery. The thermal method offers many advantages for waste LCD treatment, such as easy realization and high efficiency. However, certain undesirable air pollutants, such as polycyclic aromatic hydrocarbons (PAHs), tend to occur during the thermal treating process of waste LCD scraps [1, 13]. On the other hand, incineration of the polarizer is a kind of resource wasting. In view of the negative impacts on the environment and resource recycling, a more eco-friendly and efficient method is needed for the treatment of waste LCDs.

Compared with the thermal treatment, the physical method has better environmental property and easy operability. It has drawn much attention during the recycling of waste electric and electronic equipment for full material recovery. In the present study, a combined process of physical methods was proposed to partition materials from waste LCDs, aiming to fully reclaim material from waste LCDs and facilitate the treatment of hazardous substances. In this process, components of the waste LCDs were first disassembled by manual operation. Then the material separation from LCD panel was carefully studied, which includes liquid crystal removal and recovery of the polarizer and glass.

Experimental Procedures

Materials

Fourteen-inch LCD monitors from desktop computers were used as the experimental materials in this study. The chemical reagent of sodium dodecylbenzene sulfonate (SDBS) and isopropyl alcohol is analytical-grade and was supplied by the Sino-pharm Chemical Reagent Co., Ltd

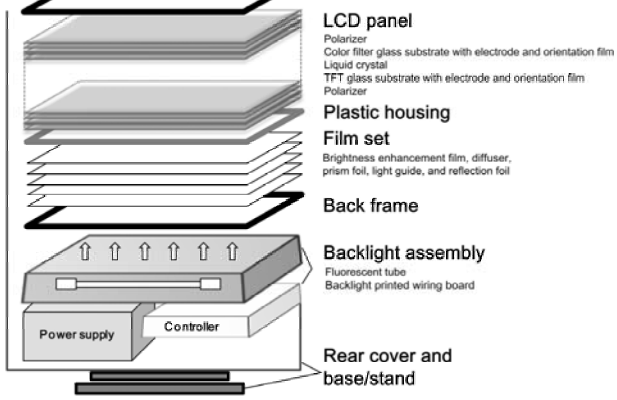

Fig. 1. Subassemblies of LCD monitor.

(shanghai, China). Saturated potassium carbonate (K_2CO_3) solution was used as separation fluid to separate polarizer and glass. The water used during the whole study was de-ionized.

Procedures

Component Partition from Waste LCD

Based on the structural and component features of waste LCD, a detailed strategy of material separation was designed as shown in Fig. 2.

Firstly, the waste LCD monitor was disassembled by manual operation inside a ventilation cabinet, and the disassembled components were classified as plastic, metals, printed circuit boards (PCBs), backlights, and LCD panels (Fig. 3).

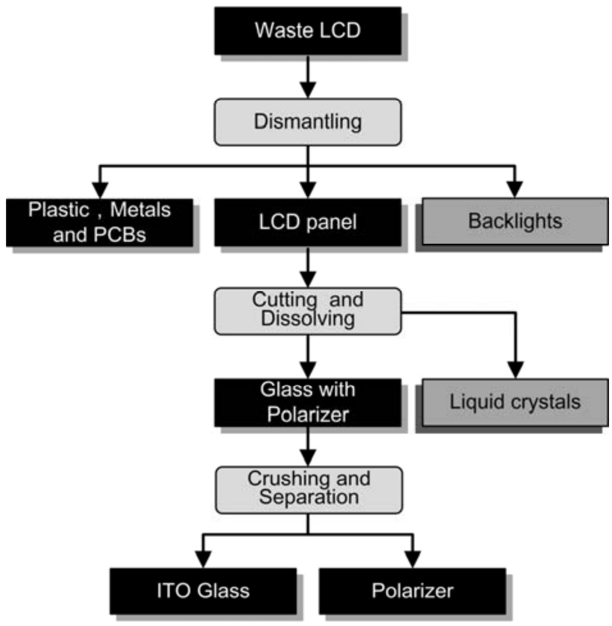

Fig. 2. The whole process designed for material separation from waste LCD in this study.

The plastic, metals, and PCBs could be recycled by existing technology. The backlights, because they contain toxic mercury, should be disposed of by qualified companies. The LCD panel needs further separation to remove the liquid crystals and to reclaim the polarizer and glass. The process of liquid crystals removal, and recovery of the polarizer and glass from the LCD panel is the focal point of this study.

Removal of Liquid Crystals

The disassembled LCD panel was cut into small pieces (about 2 cm×2 cm) and then immersed in a solution to remove the liquid crystals with the assistance of ultrasound. During the process, the dissolving solution was sampled at different time intervals (0, 5, 10, 15, 20, 25, and 30 min) and analyzed by ultraviolet spectrophotometer to evaluate removal efficiency. After the process finished, the panel glass was collected by filtration. The filtrate that the liquid crystals dissolved in needs effective disposal to eliminate its eco-toxicity before discharge.

Separation of Polarizer and Glass

Considering the density difference between polarizer and glass, gravity concentration, a density-based separation method, was introduced in this study to separate polarizer and glass. The saturated K_2CO_3 solution was used as separation fluid because its density (1.8 $g\cdot cm^{-3}$, 20ºC) is exactly in-between the densities of polarizer and glass, whose densities are respectively 1.42 $g\cdot cm^{-3}$ and 2.3 $g\cdot cm^{-3}$. The separation procedures are as follows.

The panel glass (without liquid crystals) was crushed by a hammer mill (Continuous feeding grinder DF-15) to liberate polarizer. Then the pulverized particles were sieved into fractions of different size ranges. The fractions with certain granularity were put into the saturated K_2CO_3 solution for the separation of polarizer and glass. To effectively separate the polarizer and glass, the suspension was stirred

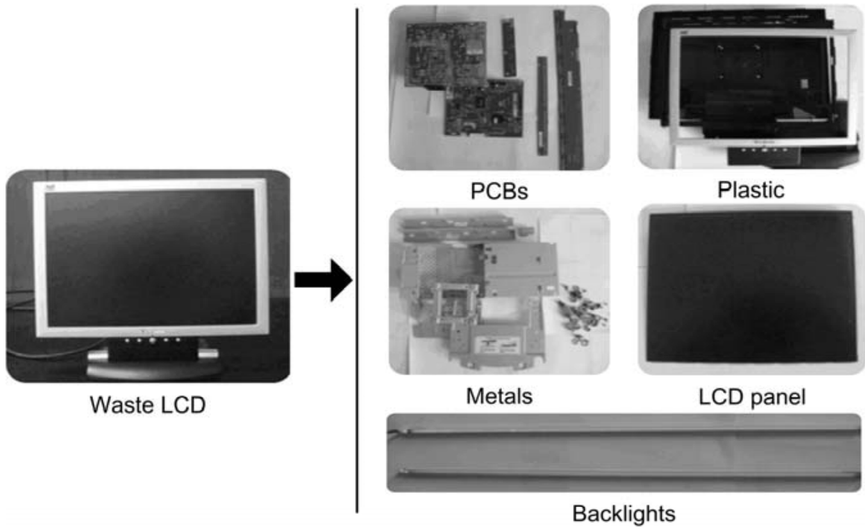

Fig. 3. Disassembled materials from waste LCDs.

for about 5 min and then kept standing for 15 min to separate into layers. The upper layer, consisting mainly of polarizer, was light product and materials obtained from the bottom were defined as heavy product.

Analytical Methods

Liquid Crystal Removal

The absorbency of dissolving solution was analyzed to determine the effect of liquid crystal removal, because the change of absorbance follows Lamber-Beer's law, which means that absorbency of solution varies proportionally with solute concentration. During the process of liquid crystal removal, the liquid crystals dissolved into the solution would lead to absorbency increase of the dissolving solution. The absorbency of the solution was analyzed with an ultraviolet spectrophotometer (UV-2802, Unico) at 210 nm in the present study. All quantitative data reported were the average values of the analytical results of three samples with standard deviation less than 10%.

Separation Efficiency of Polarizer and Glass

In order to evaluate the separation efficiency of polarizer and glass, recovery rate (η) of polarizer was introduced in the present study, which is defined as the ratio of recovered polarizer to its original content in the feed (Eq. 1).

$$\eta = \frac{\beta(\alpha - \theta) \times 100\%}{\alpha(\beta - \theta)} \quad (1)$$

...where α, β, and θ is the weight percentage of polarizer in the feed, the light product, and the heavy product, respectively.

The polarizer content in different products was determined using a thermal method. Polarizer is organic material that begins to decompose at temperatures higher than 220ºC. By contrast, the panel glass has good thermal stability and no chemical changes occur at temperatures lower than 600ºC [11]. Based on the thermal stability difference of polarizer and glass, samples were put into a furnace and heated to 550ºC, through which the polarizer could be removed by decomposition or incineration so that the weight loss was defined as polarizer content. To ensure the complete removal of polarizer, the samples were maintained at 550°C for 2 h under air conditioning. All quantitative data reported were the average values of the analytical results of three samples with the standard deviation less than 2.5 %.

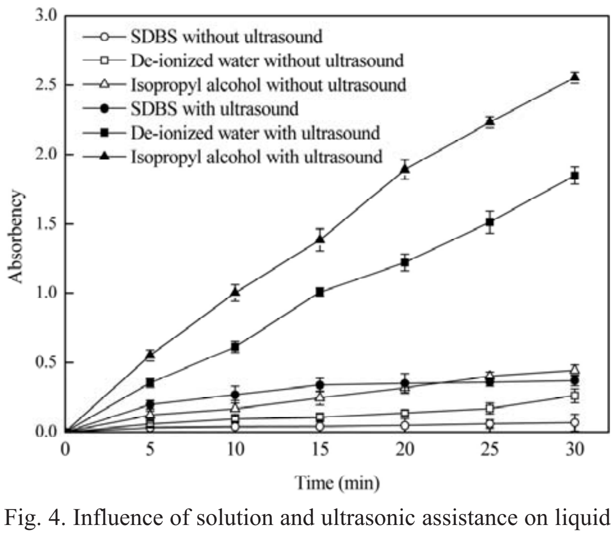

Fig. 4. Influence of solution and ultrasonic assistance on liquid crystal removal.

Results and Discussion

Liquid Crystals Removal from Glass Substrate

Effect of Dissolving Solution on Liquid Crystal Removal

In order to assess the influence of dissolving solution on the removal effect of liquid crystals, different types of aqueous solution, including de-ionized water, SDBS (0.06 $mol \cdot l^{-1}$), and isopropyl alcohol (16.7 vol.%) was investigated.

Fig. 4 depicts the absorbance variation of different solutions with the operation time under conditions with or without ultrasonic assistance. From Fig.4 it can be noted that each solution has different absorbance after reacting for the same time. It illustrates the different dissolution abilities of liquid crystals. The isopropyl alcohol solution had a much higher absorbency than the de-ionized water and SDBS, illustrating the better removal effectiveness of liquid crystals. The phenomenon was probably related to the chemical properties of liquid crystals and isopropyl alcohol. Liquid crystals are organic matters that are insoluble in ordinary aqueous systems but are easily dissolved in organic medium. Isopropyl alcohol, with hydrophilic and hydrophobic groups, is amphoteric and soluble both in water and in organic solvents. The dissolution of isopropyl alcohol in water creates an organic-aqueous solvent mixture in which the liquid crystals could be easily dissolved.

Effect of Ultrasonic Assistance on Liquid Crystal Removal

With the aim to improve the removal efficiency of liquid crystals, ultrasound was introduced to enhance the removal effect of liquid crystals. Ultrasonic waves of 40 kHz were used in our study since they are effective for contamination removal and widely used for surface cleaning in the manufacturing industry.

Fig. 4 also depicts the influence of ultrasonic irradiation on liquid crystal removal. As shown in Fig. 4, the absorbency of each solution had a significant increase with ultrasonic assistance, demonstrating that more liquid crystals had been transferred from glass substrates to the solution. The ultrasonic irradiation in water could bring about the formation and collapse of small gas bubbles. During the collapse, a local reaction site of several thousand degrees and several hundred atmospheres is produced due to the quasi-adiabatic collapse [14-16]. This process is known as cavitation, which is accompanied by the generation of shockwave, impact, and shear force, etc. Such a physical process is expected to occur on the surface of glass substrates, which enhanced the removal effect of liquid crystals.

One thing that needs to be mentioned is that the promotion effect of ultrasound to each solution varies a lot. The improvement to isopropyl alcohol and de-ionized water was more significant than SDBS in comparison. The phenomenon could be explained by low cavitation intensity in the SDBS solution. Usually, cavitation is regarded as the main mechanism of ultrasound cleaning and it is related to aqueous surface tension. The presence of SDBS in water will cause the reduction of water surface tension, which is adverse to the occurrence of cavitation [15].

Effect of Temperature on Liquid Crystal Removal

Aiming to optimize operating conditions, the influence of temperature on the removal effect of liquid crystals was assessed. The absorbency of isopropyl alcohol solution at 30ºC, 45ºC, and 60ºC was evaluated and results are shown in Fig. 5. It was observed from the results that the absorbency of isopropyl alcohol isopropyl solution increased with temperature rising. It indicates that high temperature contributes to achieving better dissolving effect. Nevertheless, high temperature usually results in high energy consumption. Considering the energy consumption and dissolving efficiency of liquid crystals, the operating temperature was recommended as 60ºC.

Based on the above analysis, the optimal operating condition of liquid crystal removal in the present study was recommended as: isopropyl alcohol solution (16.7 vol.%) as dissolution medium assisted by ultrasound at a constant temperature of 60ºC.

To evaluate the removal rate of liquid crystals, the absorbency of isopropyl alcohol solution under the recommended condition was studied and the results were shown

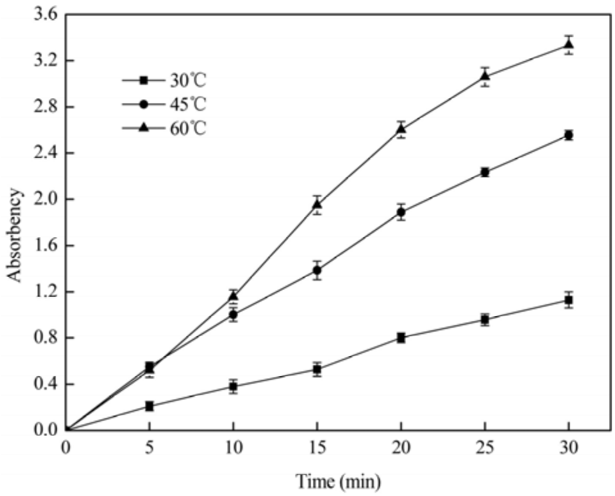

Fig. 5. Influence of temperature on liquid crystal removal.

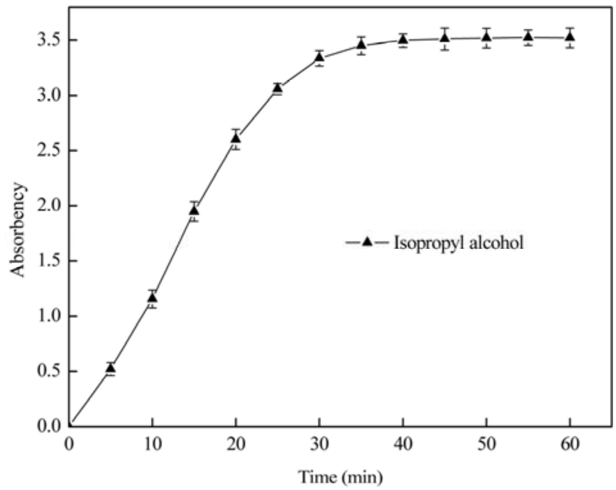

Fig. 6. The absorbency of isopropyl alcohol solution at 60ºC.

in Fig. 6. It was observed from Fig. 6 that the absorbency increased rapidly in the first 35 min and then maintained stability once it had reached 3.52. Since the absorbency of solution indicates the amount of dissolved liquid crystals, the maximum absorbency of 3.52 was regarded as 100% liquid crystals moved from glass substrates into solution. Therefore, the removal rate of liquid crystals was calculated on that basis. According to the result, assisted by ultrasound, approximately 100 wt.% of liquid crystals were transferred from glass substrates into the isopropyl alcohol solution after reacting for 45 min at 60ºC.

Polarizer Separation from Panel Glass

Effect of Mechanical Crushing on Polarizer Separation

Considering the different mechanical strengths of glass and polarizer, the effect of mechanical crushing on the separation of polarizer and glass was investigated. In order to analyze the effect of mechanical crushing, the size distribution of the crushed product and material content in each size range was studied. The experimental results are shown in Fig. 7.

From the size distribution, it can be noted that the large proportion (29.3 wt.%) of the LCD panels were crushed to particles with size smaller than 0.097 mm. Material content in each grade shows that glass mainly concentrated in particles with size smaller than 0.200 mm, whose weight percentage was higher than 94.7 wt.%. Consequently, polarizer is mainly rich in large particles and its content in the mixture shows an increase along with the particle size increasing. It was only 10.4 wt.% in the grade of 0.200-0.300 mm and then increased to 57.8 wt.% in the grade of 0.600-3.00 mm. Totally, there were up to 83.8 wt.% of polarizer concentrating in particles with size larger than 0.200 mm. The result relates to the difference of mechanical strength between glass and polarizer. Glass is inorganic and brittle, and it could be easily crushed into fine particles ($d<0.200$ mm). However, polarizer is organic with good strength and

Table 2. Recovery effeciency of polarizer with saturated K_2CO_3 solution.

Diameter (mm)	Polarizer content			Recovery rate* (%)
	Feed material α (wt %)	Light product β (wt %)	Heavy product θ (wt %)	
0.200-0.300	10.4	74.5	2.91	74.9
0.300-0.355	14.3	76.5	2.15	87.8
0.355-0.600	15.9	79.6	1.34	93.0
0.600-3.00	57.8	92.0	1.90	98.7

*The standard deviation was 1.5%, 0.5%, 0.6%, and 0.3%, respectively.

tenacity and is difficult to comminute. Therefore, polarizer tends to accumulate in large particles while glass in small particles. According to particle size, polarizer and glass could obtain primary separation.

Effect of Gravity Concentration on Polarizer Separation

Although primarily separated by mechanical crushing, smashed materials with size larger than 0.200 mm still need further separation to recover the polarizer and glass. Table 2 shows the recovery rate of polarizer and its content in recovered product after separation by the saturated K_2CO_3 solution.

From the table, it can be observed that the polarizer obtained efficient accumulation after gravity concentration. Its content in the light product had a remarkable increase, which respectively reached up to 74.5 wt.%, 76.5 wt.%, 79.6 wt.%, and 92.0 wt.% in the size range of 0.200-0.300 mm, 0.300-0.355 mm, 0.355-0.600 mm, and 0.600-3.00 mm. In comparison with the feed, the polarizer content was increased by 6.16, 4.35, 4.01, and 0.59 times, respectively, in the size range of 0.200-0.300 mm, 0.300-0.355 mm, 0.355-0.600 mm, and 0.600-3.00 mm.

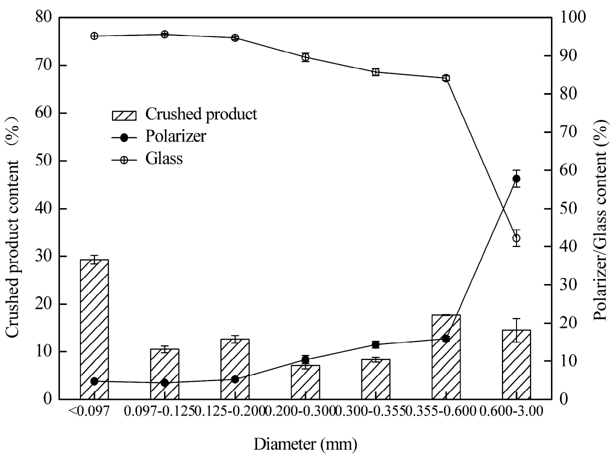

Fig. 7. Size distribution and material content in crushed product.

Eventually, 79.7 wt.% of polarizer was separated from glass and its average content in the recovered product was 90.3 wt.%.

In addition, it should be noted that the recovery rate of polarizer decreased along with particle size decrease. It was 98.7 wt.% for the size range of 0.600-3.00 mm and then decreased to 74.9 wt.% for the size fraction of 0.200-0.300 mm. Likewise, the polarizer content in light product also decreased, along with particle size decrease. These results are probably due to the agglomeration phenomenon, which tends to occur with small particles in fluids. The agglomerates composed of polarizer and glass occurred during the separation process and are difficult to break down, which correspondingly led to low separation efficiency. Therefore, within the range of experiments performed, large particles are conducive to material recovery using the gravity concentration method.

Conclusions

In our study, a combined process of physical methods for material separation and recovery from waste LCDs was proposed. In the process, waste LCD was first disassembled by manual operation, through which it was dismantled to plastic, metals, printed circuit boards backlights, and LCD panels. Then a further material separation and recovery from the LCD panel was conducted, including liquid crystal removal by solution dissolving assisted with ultrasonic irradiation, the recovery of polarizer and glass by mechanical crushing, and gravity concentration.

Experiment results show that the liquid crystals could be effectively removed from the panel glass by dissolving in isopropyl alcohol solution (16.7 vol.%) with the assistance of ultrasonic irradiation. Assisted with the ultrasound (f=40 kHz, P=50W), approximately 100 wt.% of liquid crystals were removed from panel glass to the solution after dissolving for 45 min at constant temperature of 60ºC.

The polarizer and glass could be efficiently separated by mechanical crushing and gravity concentration. With mechanical crushing, polarizer and glass obtained a primary separation based on particle size, with 83.8 wt.% of polarizer concentrating in the particles with size larger than 0.200 mm. Then through the gravity concentration with saturated K_2CO_3 solution, the polarizer achieved a further accumulation. Eventually, 79.7 wt.% of polarizer was separated from the glass and its average content in the recovered product was 90.3 wt.%.

The obtained glass powder with ITO could be further studied to recover the indium. Under the current situation, indium was usually extracted from glass by solvent extraction [11, 17-19]. However, due to the low content of indium in the glass and the large amount of acid in use, recovery of indium by solvent extraction usually is accompanied by low efficiency, instrument corrosion, and secondary pollution. A more efficient, economically feasible, and environmental friendly technique is needed for indium recovery from waste LCDs.

Acknowledgements

The authors gratefully acknowledge financial support from the Key Research Project of Shanghai, in China (10dz1205200) and the National Key Technology R&D Program of China (2008BAC46B02).

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