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Separation properties of aluminium–plastic laminates in post-consumer Tetra Pak with mixed organic solvent

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Abstract

The separation properties of the aluminium–plastic laminates in postconsumer Tetra Pak structure were studied in this present work. The organic solvent blend of benzene–ethyl alcohol–water was used as the separation reagent. Then triangle coordinate figure analysis was taken to optimize the volume proportion of various components in the separating agent and separation process. And the separation temperature of aluminium–plastic laminates was determined by the separation time, efficiency, and total mass loss of products. The results show that cost-efficient separations perform best with low usage of solvents at certain temperatures, for certain times, and within a certain range of volume proportions of the three components in the solvent agent. It is also found that similar solubility parameters of solvents and polyethylene adhesives (range 26.06–34.85) are a key factor for the separation of the aluminium–plastic laminates. Such multisolvent processes based on the combined-system concept will be vital to applications in the recycling industry.

Keywords

Aluminium–plastic laminates, benzene–alcohol–water, separation, Tetra Pak, triangle coordinate figure

Introduction

Composite aseptic packaging materials, like Tetra Pak, are composed mainly of paper, aluminium, and low-density polyethylene plastics (LDPE); a small amount of printing ink, coatings, and adhesives are also present. The brick-type packaging generally contains 73% fibre, 25% LDPE, 5% aluminium and 2% others (Korkmaz et al., 2009). The aluminium–plastic laminates in the packaging structure are formed by the process of high frequency and hot pressing, which closely bond layers of aluminium and LDPE plastic together (Xie et al., 2009). After being consumed, the aluminium–plastic composite is difficult to be effectively separated and fractionated into elemental components; therefore, much of this kind of liquid packaging are now burnt or embedded in disposable consumer goods, which results in resource waste and environmental pollution (Cui, 2009; Fan et al., 2007; Xie et al., 2009).

At present, the most effective approach to converting these wastes to valuable materials is to separate the laminated packaging composites into several single materials which contain fibres, aluminium, and plastics. With the resource shortage of petroleum and nonferrous metals, the separation and materials respective reusing have high regenerated value. Fibres can be extracted from these postconsumer aseptic packaging by hydraulic dissociation. The reinforced aluminium–plastic laminates can be separated by a variety of recycling approaches (Gente et al., 2003; He, 2010; Johansson and Ackermann, 1995; Kulkarni et al., 2010; Lopes et al., 2006; Zhang et al., 2010, 2012), and separation with solvents has attracted a lot of attention from many researchers. Super-critical water, inorganic acid, and organic solvents as hydrochloric acid, sodium hydroxide, nitric acid, formic acid, acetic acid, single components such as benzene and acetone, and mixed solvent have been brought into practice (Zhang et al., 2012). These approaches with solvent are effective for the separation of aluminium–plastic laminates, along with loss of a large quantity of mass and solvent pollution.

In earlier studies, we found that organic solvents such as methylbenzene and benzene are good separating reagents for aluminium–plastic laminates, but the separation reaction is not complete and there is more loss of polyethylene (PE). In this manuscript, on the basis of law of similarity and solubility, benzene was used as separating reagent, and ethanol and water were added to adjust the solubility of the blended solvents. The mixed

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solvent achieved the separation purpose and reduced mass loss. Furthermore, the benzene–alcohol–water solutions are partly soluble ternary solutions which have an isothermal critical mutually soluble point and exhibit certain critical phenomena. This critical consolute phenomenon can be used to enhance some chemical reactions (Shen and Zheng, 1993; Su et al., 2010; Yang et al., 2005).

However, to our knowledge, there are few reports on this solvent blend application in the separation of aluminium–plastic laminates (Zhang et al., 2010, 2012). The goal of the present study was to investigate the feasibility of benzene–ethyl alcohol–water technologies to recover nonoxidized aluminium without attachment of polymers from laminated wastes.

Materials and methods

Laminated aluminium–plastic composite samples

Laminated composite samples containing aluminium foil used for liquid packaging were received from market and were stored in the dark at room temperature. A model composite material such as Tetra Pak was selected for this research based on the composition and lamination method. After pulp fibres were extracted, the total thickness of the laminated sample was 78 μm.

Composite separation

Benzene, ethyl alcohol, and water were mixed by volume ratio in glass beakers as reactors. The aluminium–plastic sheets were cut into pieces of size ~3×3 cm. For the reaction, about 100 mL separating reagent and 0.98 g laminated sample were charged into the reactor beaker. Then the reactor was sealed and immersed in a water bath for heating. After slight stirring and heating to a certain temperature, the laminated aluminium–plastic composites were separated. The reaction times 10–300 s and temperatures 20–70°C were investigated in this research. After the desired reaction time, the solid residues plastic and aluminium were taken out and washed with ethyl alcohol or distilled water, respectively, dried in an oven at 60°C for 48 h, cooled to room temperature, and kept in dry conditions until analysis.

Optimization of component proportions in solvent blends with triangle coordinate figure

A triangle coordinate figure can be used to express or optimize the dissolved proportion of each component in the solvent blends (Zhang et al., 2011). The triangle's three vertices each show a component of the solvent blend; the farther from the vertex, the lower mass fraction of that vertex's component in the solvent blend. Inside the triangle, any point represents a tri-component system, whose component composition can be determined by the percentage of each component. By this triangle method, the solvent composition can be accurately determined.

Aluminium–plastic separation and loss rates

In order to investigate the separation and loss of the components of aluminium–plastic laminates, the following formulae were used.

The calculation formula for separation rate of the laminates was:

$$S = \frac{m_1}{m_2} \qquad \textbf{(equation 1)}$$

where m_1 is the total mass of aluminium foil and plastic after separation, and m_2 is the total mass of aluminium foil, plastic, and nonseparated aluminium–plastic sheet after separation.

The calculation formula for loss rate of aluminium–plastic composites in separation was:

$$L = \frac{m_2}{m} \qquad \textbf{(equation 2)}$$

where m is the total mass of the aluminium–plastic composite before separation.

Determination of the solubility parameter of the mixed solvent

The solubility parameters of the solvent blend was calculated as follows (van Krevelen et al., 2009):

$$\delta_n = \sum_{i=1}^{n} r_i \delta_i \qquad \textbf{(equation 3)}$$

where, r_i is the volumetric fraction of composition i and δ_i is the solubility parameter of composition i.

Results and discussion

Structure of the aluminium–plastic composite laminates

The laminated aluminium–plastic composites are composed of four layers – PE2/aluminium/PE1/LDPE – of which LDPE is the layer to be in contact with food (Figure 1) and the aluminium forms the middle layer (10–20 μm thick) with the PE layers on either side. In other words, the aluminium layer plays a role as the carrier of polyester or polyether. The samples were manufactured by the extrusion lamination process, which refers to a method where molten PE is poured between two different films as an adhesive.

During the experiment, it was found that there were different separation characteristics between PE2 and PE1 from aluminium layers. The bonding of PE1 and aluminium, where molten PE1 was used as adhesive, was easy to separate. The PE2 layer was difficult to separate. This may be due to the different adhering mechanisms between the two sides of PE2–aluminium and aluminium–PE1, or other polymers such as ethylene–methacrylic acid random copolymer (EMAA) which are used as adhesive, which may cause a stronger interaction between the PE2 and aluminium layers (Lopes et al., 2007). The separated layers of these materials are shown in Figure 2.

Effect of temperature on aluminium–plastic separation

The solvent blend ratio V was selected (benzene): V (absolute ethyl alcohol): V (water) =30:20:50, the laminates were charged and heated in the range of 20–70°C and the separating reaction time was fixed at 6 min. Temperature was an important factor for the separation of aluminium–plastic laminates by the solvent blend of benzene–ethyl alcohol–water (Figure 3). When the separating temperature was less than 50°C, aluminium and plastic did not separate and the loss rate was close to zero, which indicates stability of PE at room temperature. As the temperature increased to 55°C, 80% of the aluminium and plastic mass were separated within the defined separation time of 6 min. The separation rate of the aluminium–plastic reached 100% within 6 min at 60°C or above. The temperature 65°C is the boiling point of the separation reagent. The loss of mass of total aluminium and plastic occurred at temperatures above 50°C. The higher the temperature, the more total loss rate of the composites occurs. Therefore, 60°C was the optimal separation temperature of the aluminium–plastic composite; at that point, the reaction time is short and the total loss rate is still low.

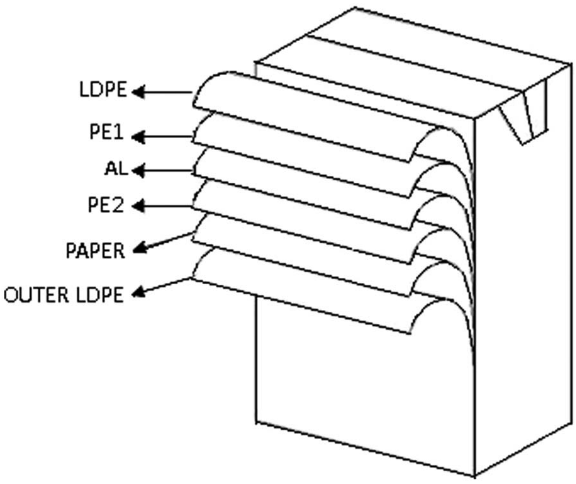

Figure 1. Schematic structure of Tetra Pak.

Optimum solvent ratio

The optimum solvent ratio was investigated for selected proportions of the three components in the solvent blend. As seen in Figure 4, the vertex coordinates 1, 56 and 66 indicate 100% content each of benzene, absolute ethyl alcohol, and water, the vertex coordinates 5, 47, and 54 and 13, 39, and 43 indicate volume fractions where a single component is in the majority to different extents, respectively, the vertex coordinates on the sides, 16, 21, and 61, indicate pairwise mixing, and point 0 in the centre indicates equal proportions of each component. These 13 vertex coordinates were chosen as the solvent ratios to be investigated first (Table 1).

The aluminium–plastic separation effects were investigated at the temperature of 60°C. With the points 1, 5, and 16, which contained 0 or 10% water, the laminate of LDPE–aluminium, adhering to PE1, achieved completely separating in a short time, while aluminium–PE2 did not separate after any length of time. With the points 56, 61, and 66, which contained 0% benzene, no layers separated. With the points 39, 43, 47, and 54, the content of benzene was too low to make the plastic swell and separate. Only with points 13 and 0 were the aluminium–plastic composites completely separated.

It can be inferred that points 13 and 0 and the surrounding triangle area indicate the optimum range of separating agent volume proportions (Figure 5): 30–60% benzene, 20–50% ethyl alcohol, and 20–50% water. This study next tested this range of volume proportions of the solvent blends (Table 2). All of the investigated solvent blends could separate the aluminium–plastic laminates effectively (separation rate 100%). The separating time was kept to within 6 min, and was decreased with increasing proportion of benzene; however, with increasing proportion of benzene the total loss rate increased (from 2.54 to 3.82%). The mass losses were mainly because of the plastic and adhesives partly dissolving. These results show that most of the constituents in aluminium–plastic laminates (above 96%) can be recovered by this organic solvent separation approach.

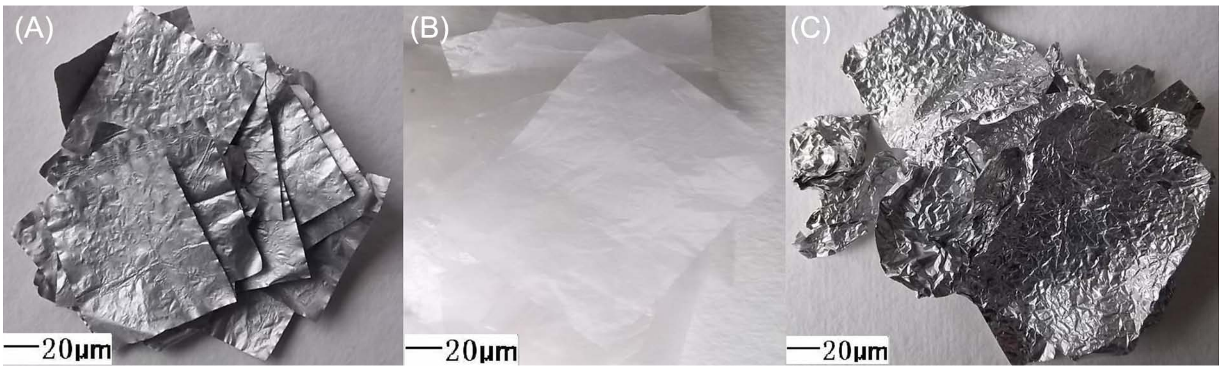

Figure 2. Images of the separated layers: (A) separated Al-PE laminates, (B) separated PE, (C) separated aluminum layer.

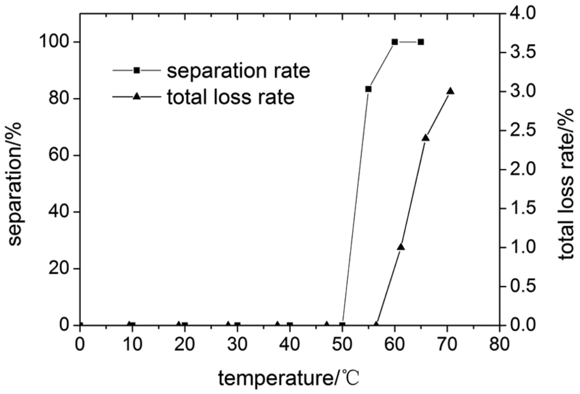

Figure 3. Effect of temperature on aluminium–plastic separation and loss.

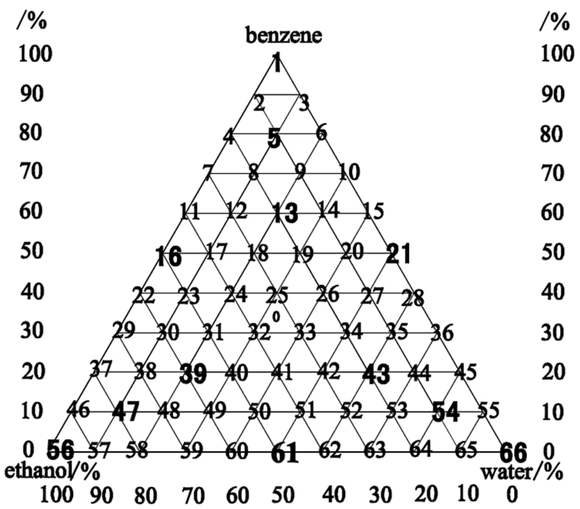

Figure 4. Triangle coordinate figure showing the positions of selected solvent ratios.

Compared with separation with methanoic acid, for which separation rate reaches 100% in 25 min at 60°C with 4 mol L^{-1} methanoic acid and the loss rate of aluminium was 4.73% (Zhang et al., 2008), a benzene–alcohol–water solvent exhibits more effective separation. Considering the lower organic solvent usage and less total loss rate, at the separating temperature 60°C and time 5.85 min, the optimum proportions of a separation solvent are 30:20:50 benzene–alcohol-water. The feasible range of separation components in solvent blends is 30–60% benzene, 20–50% ethyl alcohol, and 20–50% water.

Analysis of separation actions

Generally, plastic can be dissolved in benzene or swelled in a certain concentration range. When PE swell occurs, the bonding forces between aluminium and plastics are reduced, and separation is achieved. Also, ethanol is soluble in benzene and also can be mixed with water in any proportion, and adding ethanol to a mixture of benzene and water promotes the mixing rate of benzene and water by emulsification, and there exists a critical mutually soluble point in the partly soluble ternary solutions.

The reason why solvent blends that consist of benzene, ethanol, and water can separate aluminium–plastic composites may be attributed to the similarity law, and similar solubility parameters of solvents and PE adhesives are a quite important factor (Hansen, 1999). The solubility parameters are a way to judge whether or not chemicals will dissolve into each other. According to Hansen theory, intermolecular forces contain London forces (δ_d), polar forces (δ_p), and hydrogen bonds (δ_n). These force values of the three components of separation solvent are shown in Table 3 with also force values of PE and EMAA.

It can be seen from Table 3, the solubility parameter δ_i of PE is smaller than that of benzene, while EMAA has a higher

Table 1. Separation effects of solvent ratios first selected from the triangle coordinate figure.

Point mark[a]	Volume of solvent			Aluminium–plastic separation rate (%)		Separation time (s)	Loss rate (%)
	Benzene (%)	Alcohol (%)	Water (%)	LDPE–aluminium	Aluminium–PE2		
1	100	0	0	100	0	10	1.03
5	80	10	10	100	0	14	0.87
13	60	20	20	100	100	295	5.69
16	50	50	0	100	0	20	0.59
21	50	0	50	ND	ND	–	–
0	33.33	33.33	33.33	100	100	312	3.65
39	20	60	20	0	0	–	–
43	20	20	60	0	0	–	–
47	10	80	10	0	0	–	–
54	10	10	80	0	0	–	–
56	0	100	0	0	0	–	–
61	0	50	50	0	0	–	–
66	0	0	100	0	0	–	–

[a]See Figure 1.
ND: not done, because the components did not mix uniformly and so could not meet the requirements of the separating agent.

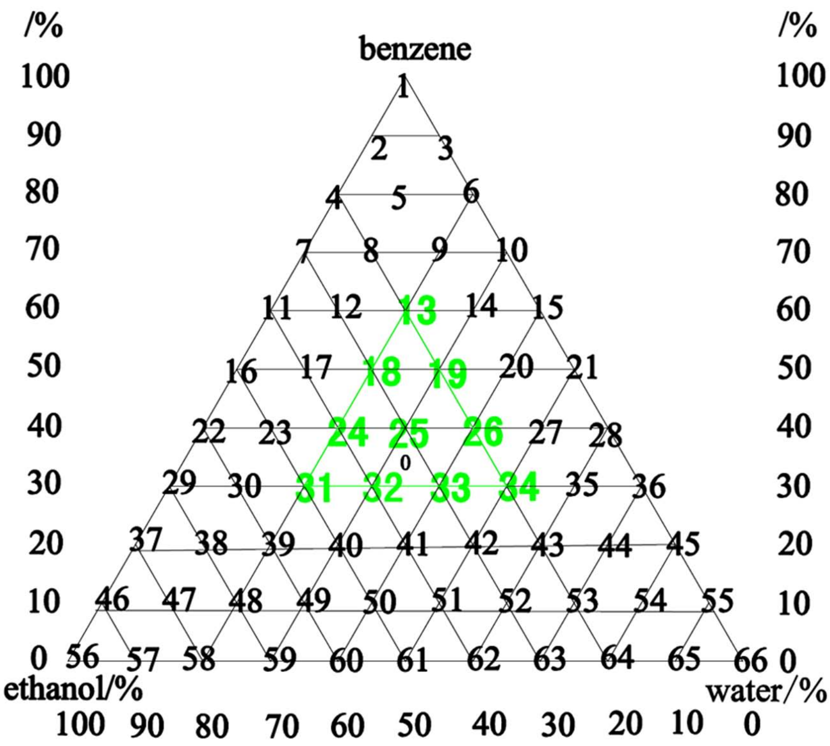

Figure 5. The optimum separation area in the triangle coordinate figure.

Table 2. Separation effects of solvent ratios in the optimum area of the triangle coordinate figure.

Point mark[a]	Benzene (%)	Alcohol (%)	Water (%)	Aluminium–plastic separation rate (%)	Separation time (s)	Separation loss rate (%)
13	60	20	20	100	293	3.82
18	50	30	20	100	307	3.36
19	50	20	30	100	310	3.35
24	40	40	20	100	329	2.91
25	40	30	30	100	325	2.89
26	40	20	40	100	339	2.86
31	30	50	20	100	353	2.69
32	30	40	30	100	338	2.64
33	30	30	40	100	341	2.58
34	30	20	50	100	351	2.54

[a]See Figure 1.

Table 3. Solubility parameter of polymers and solvent blends.

	δ_d	δ_p	δ_h	δ_i	Range of proportion (%)	Range of solubility parameter (δ_n)
Benzene	18.4	0	2	18.7	30–60	26.06–34.85
Alcohol	15.8	8.8	19.4	26.2	20–50	
Water	15.6	16	42.3	48	20–50	
Range of mixing proportion	–	–	–	16.35	–	–
Range of solubility parameter of mixture solvent	–	–	–	26	–	–

Only the intermolecular London force of PE and EMAA were considered in this work.

solubility parameter. That may be why the aluminium–PE1 layer separated easily and the PE2–aluminium layer, which may bonded with EMAA, proved difficult to separate. When the three solvents were blended together with certain volume proportions, the solubility parameter of the mixture solvent was in a broad range so that it could be in good contact with the polymer and separate the aluminium–plastic laminate.

The fact that the separation effect increased with increase of benzene in the solvent blend suggests that London forces play an important role in separation. The total loss rate increasing with benzene increase suggested that the aluminium–plastic laminate are damaged during the solvent reaction; which were damaged, aluminium or PE, needs to be identified. Also, the decrease of loss with increase of water in the blend suggests that hydrogen bonds have positive functions on mass retention.

In conclusion, aluminium–plastic laminates can be separated effectively within a short time. The recovered aluminium and plastics can be cleaned by ethanol solution to remove residual benzene, and then the residual ethanol can be cleaned with water. The waste mixture liquid can be recycled and reused by phase equilibrium and distillation of benzene and ethanol, which has little negative effect to the environment.

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Declaration of conflicting interests

The authors declare that there is no conflict of interest.

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References

Cui ZW. (2009) The research of the recycling of liquid packaging paper box. *Shanghai Paper Making* 40: 62–67.

Fan FJ, Yang ZP and Shi FX. (2007) Discussion on recovery and reuse of Tetra pak package. *Journal of Agricultural Mechanization Research* 9: 221–223.

Gente V, Marca FL, Lucci F, et al. (2003) Electrical separation of plastics coming from special waste. *Waste Management* 23: 951–958.

Hansen CM. (1999) Hansen solubility parameters: A User's Handbook. CRC Press, chapter 11, pp 204–206.

He QH. (2010) Study on the separation of aluminum and plastic from aluminum-plastic composite membrane in the alkali-alcohol system. *Guangzhou Chemical Industry* 38: 141–142.

Johansson H and Ackermann PW. (1995) *Method of recovering individual component parts from packaging material waste*. US patent 5421526.

Korkmaz A, Yanik J, Brebu M, et al. (2009) Pyrolysis of the Tetra Pak. *Waste Management* 29: 2836–2841.

Kulkarni AK, Daneshvarhosseini S and Yoshida H. (2010) Effective recovery of pure aluminum from waste composite laminates by sub- and supercritical water. *The Journal of Supercritical Fluids* 32: 1–6.

Lopes CMA and Felisberti MI. (2006) Composite of low-density polyethylene and aluminum obtained from the recycling of postconsumer aseptic packaging. *Journal of Applied Polymer Science* 5: 3183–3191.

Lopes CMA, Goncalves MDC and Felisberti MI. (2007) Blends of poly (ethylene terephthalate) and low density polyethylene containing aluminum: a material obtained from packaging recycling. *Journal of Applied Polymer Science* 106: 2524–2535.

Shen WG and Zheng GK. (1993) Critical phenomena of solution. *Acta Physica et Chimica Sinica* 9: 137–144.

Su YH, Hu HY and Duan AH. (2010) Separation and purification of benzene–ethanol–water waste liquid. *Journal of Yunnan Normal University*. 40: 59–62.

van Krevelen DW and Nijenhuis KTE. (2009) *Properties of polymers*, 4th edn. Elsevier Press.

Xie MH, Li L and Huang ZC. (2009) Life cycle assessment of environmental impacts of Al-PE-Pa laminated packaging and waste treatments. *Research of Environmental Sciences* 22: 1299–1304.

Yang T, Zhou CS and Zhu X. (2005) The critical behavior of benzene–water-ethanol ternary solutions. *Acta Physica et Chimica Sinica* 21: 439–442.

Zhang JF, Yan DH, Huang ZC, et al. (2008) Research on the wet process conditions of the separation of aluminum and plastic in post-consumer aseptic packages. *Research of Environmental Sciences* 21: 99–104.

Zhang JF and Yan DH. (2010) Research on the effect of separation reagent concentration and reaction temperature on Al-PE wet separation technics. *Chinese Journal of Environmental Engineering* 4: 665–670.

Zhang DX, Liu F and Zhang GS. (2011) Rapid screen formulation for 5% hexaconazole suspension concentrate using triangle-coordinate figure. *Scientia Agrici;tira Sinica* 44: 2469–2475.

Zhang SF, Mei XX and Zhang LL. (2012) Research progress of separations technology of aluminum-plastic in aseptic composite packaging. *China Pulp & Paper* 31: 65–68.