Original Paper

Sealant for Gable Top Cartons in Use of Chilled Distribution Mineral Water

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Current sealants for gable top skived cartons consist of laminated LDPE or L-LDPE layer which are different from aseptic liquid packaging because flame sealing process is required. Such sealants often cause off-odor or off-flavor to water which is thought to be a result of the migration of hydrocarbon molecules generated during heat seal or lamination and the adsorption of flavor respectively. To address these problems, this study is focused on polyester sealant which is applicable for flame seal operation. It is known some polyester pellets contain small particles such as talc to promote crystallization. While charcoals, activated carbon, zeolite and TiOx, are not studied much. In this research, these small particles are added into polyester and expected to be plasticizer and/or crystal core when they were laminated together with resins on the paper board. Flame sealing process requires quick crystallization and proper elongation of film. Polyesters which successively varied their adhesion property for flame seal were forwarded to sensory test. They were soaked into mineral water as an inner layer of carton and tested for both electric tongue and sensory test to evaluate correlations. Some of the polyester films were found to be good quality for flame sealing.
Keywords: gable top skived carton, polyester sealant, flavor, charcoal, flame seal, electric tongue, crystallization, elongation

1. INTRODUCTION

Liquid paper packaging for chilled circulation and flexible packaging materials consist of multilayer films[1)] and paper board in order to add various barrier functions such as oxygen, vapor, flavor and scent. Their sealants are mostly laminated or film type polyolefin, which is used as for heat seal with seal bar, hot air and flame. However, polyolefin type sealant includes small molecular weight compounds where off-odor of beverages especially mineral water is occurred. In addition, the adsorption of volatile and hydrophobic compounds in beverages sometimes deteriorates taste [2, 3)]. To address these problems, polyesters are considered to be used as sealant especially for skived gable top cartons. As far as current skived flame sealing process is concerned, only LDPE and L-LDPE are appropriate materials for sealant. Polyester has high specific gravity and are synthesized by condensation polymerization, of which polydispersity is lower than polyolefin's[4)] which alienates wide distribution of molecular weight and good sealability.

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In case of flame sealing process of polyester to polyester adhesion, physical property such as friction, modulus of elasticity in tension, MFR, Tg, etc. are not satisfactory. In order to improve physical property of polyester, this study is focused on the various additives which improve sealability. We found charcoal and activated carbons behave not only as plasticizer but also as crystal core in various polyesters. Films were extruded with resins containing charcoal or activated carbon on OPP film or paper board if MFR at 190 or 210℃ was suitable value for extrusion. Their physical properties were analyzed by DMA, DSC, WAXD, tensile and friction testing devises to predict polyester-polyester adhesion.

Polyester laminated carton boards (Fig.1) were adhered by actual flame seal machine for liquid packaging cartons[5,6] (Fig. 2).

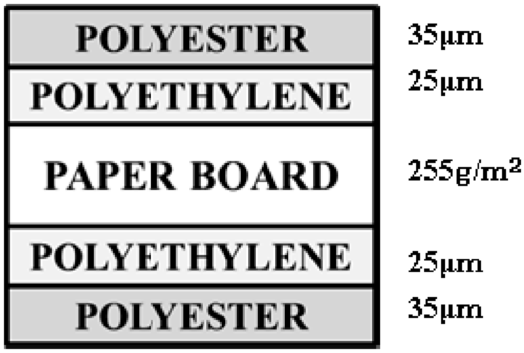

Fig.1　Structure of laminated board

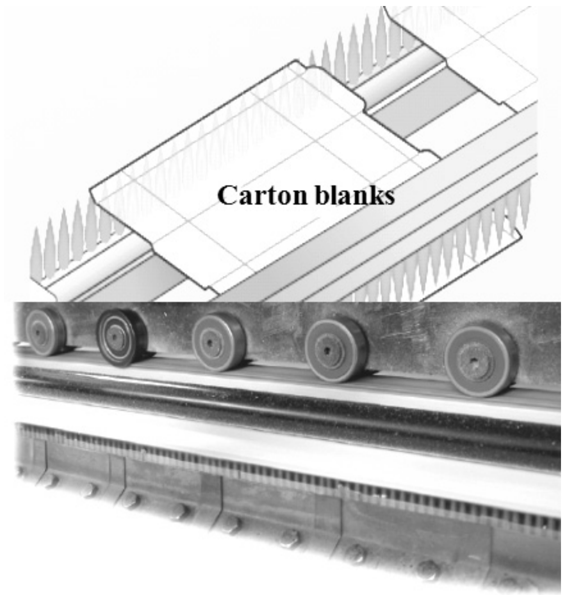

Fig.2　Conceptual diagram of flame seal machine

Then sealing property and quality were examined followed by sensory test and electric tongue which employs similar statistical analysis methods for electric nose and tongue[7,8,9)] together with LDPE as a comparison.

In the case of butylene structure is rich, polyester films tend to be selected as a sealant for mineral water packaging. However, in real operation of flame sealing, physical property of above chosen films also suggest a need for modification of flame seal machine itself.

2. MATERIALS AND METHODS

2.1 Materials

Pellets of LDPE were supplied by TOSOH Ltd. (Tokyo, Japan) and various polyesters VYLON®[10)] and SI173 as amorphous crystallized PET by TOYOBO Ltd. (Osaka, Japan). Liquid paper board (255g/m^2) was obtained from Stora Enso Oyj (Helsinki, Finland). Cider charcoal (6.5μm, d50) was synthesized in our Laboratory. and bamboo charcoal (6.5μm, d50) was obtained by Maruto Ltd.(Shiga, Japan), activated carbon E153 (4μm, d50) by NIHON NORIT Ltd. (Tokyo, Japan), Carbon black by SUMIKA COLOR Ltd. (Osaka, Japan). Zeolite ABSCENTS™ 2000 (4μm, d50) was obtained by UNION SHOWA K.K. (Tokyo, Japan) and TiOx CR-93 by ISK Ltd (Osaka, Japan).

KayastainQ (Nippon Kayaku Ltd., Takasaki, Japan) was used for checking heat seal of polyester and LDPE adhesion and water solution of Acid brilliant scarlet 3R dye (Hodogaya Chemical Ltd., Tokyo, Japan) and surfactant Teepol-eight (TEEPOLservice Ltd., Odawara, Japan) was for pinhole check. PET bottled mineral water Tennen-sui (Suntory Ltd., Osaka, Japan) was used for sensory evaluation as a blank.

2.2 Preparation of testing materials

Masterbatches for extrusion were prepared by double-screw strander (PCM-30, Ikegai Ltd.) and pelletizer (PL-60 Ishinaka Ltd.) by adding additives of 2%-10%(w/w) to various polyesters (VYLON® GM,GA). More than 1wt% of additives in base resin resulted in extreme coloring and inadequate film formation. So the concentration of additives in base resin and masterbatch mixture was decided to be less than 1wt%.

Liquid packaging carton blanks for polyester-polyester flame sealing test were prepared by extruding suitable VYLON® polyesters about 35μm thickness using T-die extruder (L/D=24, dia. 32mm screw, GT32-24A PLABOR) onto 25μm of LDPE (TOSOH P204) pre-coated paper board as a substrate at 200±30℃. Then they were cut and creased by sample cutter (CF 0907, Mimaki) for about 270mL of liquid paper carton blanks. Polyester/LDPE layer does not show serious adhesion problem because of thermal fusion.

Polyester films for physical analysis were casted on to OPP films or uncoated paper by T-die extrusion with a favorable thickness, then peeled off from substrate.

About 300 cm^2 films (30μm thickness) were soaked into 500mL of mineral water at 80℃ for 5 days for human sensory test and electric tongue. Area of the films was calculated by considering inner side contact panel of 500mL of liquid paper cartons.

2.3 Flame sealing test

Laminated carton blanks by various type of polyester were evaluated by flame sealing machine equipped with two burners[5,6] (Fig. 2) by changing operation speed of the test cartons at the same condition of burners. Normal operation speed of mini type juice carton was counted as 1 unit (about 400m/min.). And polyester laminated cartons were calculated by the comparison of LDPE.

2.4 Evaluation of physical character

For DMA, DVA-200S (IT Keisoku Ltd.) was used. Test pieces were prepared to 0.5mm-1mm thickness and 5mm width, then adjusted to 40mm length. Measurement condition were 2℃/min. of heat rate, 1Hz of frequency and 1L/min. of N_2 purge.

For tensile test to calculate young's modulus, SIMADZU Ltd. EZ test was used. Test pieces were prepared about 50μm thickness and 5mm width then adjusted to 10mm length. Pulling rate was 20mm/min..

GM400 and charcoal containing film sample were analyzed by (wide-angle) X-ray diffractometer equipped with Ni filter, of which radiation source and output were CuKα and 40kVx40mA (RINT2000 RIGAKU Ltd.). Equatorial scan was conducted 2θ (10~40°) for comparing crystallinity.

Coefficient of dynamic friction (μ') was measured on the surface of laminated film based on JIS K7125 compliance.

For DSC (DSC220 SEIKO INSTRUMENT) analyses, 5mg of each film sample was once heated up to 250℃ then cooled down to below -100 ℃, then heated up to 250℃ again to detect Tc1 peak for relative comparison of crystallization speed.

MFR was measured by using TOYOSEIKI MI F-F01 at 170℃ and /or 190℃ only when Tm of polyester resins was high enough to measure.

2.5 Evaluation of electric tongue and sensory test

Human sensory test was conducted among extract of films soaked in mineral water (shown in testing material) by employing basically triangle test and pair test[11]. 7 samples were tested. For human sensory test, scores of the samples were determined from 1 to 10 where 10 is perfect score and 1 is the lowest. In this test, score of PET bottled mineral water was 9. Scores of each tested samples are shown in Table 4.

For electric tongue, αASTREE (Alpha M.O.S Japan K.K.) was employed. The 8 sensors which have own response rate were used to examine response value[12]. Then the principal component analysis (PCA) was applied as a statistical methods based on the sensor response. Principal component (PC1) and secondary component (PC2) were determined as the total of contribution rate so as to be more than 97%. In this experiment PC1 was 92% and PC2 was 8% which means only two sensors were enough to evaluate PCA (Fig.6). Each weight center of the sample was calculated by software and plotted as euclidean distance from blank and plotted in Fig.7. Correlation between human sensory test and electric tongue was calculated by PLS and plotted together with coefficient of correlation in Fig.8.

3. RESULT AND DISCUSSION

3.1 Property of extruded resins and flame seal testing

Polyester resins were chosen from VYLON® with the difference in melting temperature (Tm), glass-transition temperature (Tg) and MFR with additives to control physical property. These polyesters include butanediol and/or ethylene glycol as raw materials. For example GM400 consists of 35% of ethylene glycol and remaining component is mostly butanediol showing partly PBT properties. GA1310 consists of 100% butanediol showing PBT properties. As for crystallization, GA1310 is much faster but flavor barrier is lower. In addition, PBT has better properties of bend performance and water resistance than those of PET [13]).

Resins were chosen by Tm in between 107-179℃. In case Tg is below 0℃, severe adhesion to metals and plastics were found in ambient temperature, also low Tm caused high MFR and poor formation of films. For polyester extrusion, MFR and Tg are found to be key factors which are same as polyolefin. Physical properties of extruded resin are shown in Table 1.

Both sides polyester laminated boards shown in Fig. 1 were processed to tens of carton blanks by using sample cutter then tested for flame sealer shown in Fig. 2 to check polyester-polyester adhesion.

Table 1 Physical properties of various resins and films with required output unit of flame seal

Resins	Composition (wt%)	Observation of Film Character	Young's Modulus (MPa)	Mn ($x10^3$)	Specific Gravity	Tg ℃	Tm ℃	MFR(g/10min) (170℃)	(190℃)	Flameseal Minimal Output Ratio*
PE	-	-	**83.6 (n=3)**	17	0.92	-50	110	-	7	-
GM900	-	Excess adhesion	-	25	1.26	-15	112	37	-	-
GM913	-	Excess adhesion	149.7 (n-4)	35	1.15	-70	126	10	-	1.2~1.3
GM920	-	Excess adhesion	105.2 (n=3)	30	1.15	-60	107	55	-	-
GA3410	-	-	**71.9 (n=3)**	25	1.25	0	122	-	-	1.3~1.5
+TiOx	1	Modulus decrease	46.5 (n=4)	-	-	-	-	-	-	-
GA1310	-	-	**242.2 (n=3)**	20	1.29	27	179	-	-	>2.1
+TiOx	1	Modulus decrease	154.8 (n=3)	-				-	-	-
GM400	-	-	**216.1 (n=2)**	25	1.3	19	143	-	46	1.5
+TiOx	1	Modulus decrease	178.4 (n=2)	-	-	-	-	-	-	-
+cider charcoal	1	Modulus decrease	109.9 (n=3)	-	-	-	-	-	-	-
+bamboo charcoal	1	Modulus decrease	108.1 (n=3)	-	-	-	-	-	-	-
GM400+GA1310	80:20	Good film form	163.9 (n=4)	-	-	-	-	-	-	1.5~2.1
GM400+GA1310	50:50	Good film form	182.7 (n=4)	-	-	-	-	-	-	>1.8
GA2310	-	-	140.6 (n=3)	20	1.29	26	136	7	39	1.7~1.8
+activated carbon	1	Modulus decrease	143.2 (n=3)	-	-	-	-	-	-	1.5~1.8

*StoraEnso's juice carton=1(unit)

Adhesion of polyester and LDPE were examined by staining these portions by KayastainQ, which elucidated thermal fusion.

Polyester laminated carton blanks were applied to flame sealer equipped with two burners used for real carton production in the factory. Seal and pinhole check were judged by soaking adhesion portion into mixture of Scarlet 3R dye and Teepole water solution in one minute and then peeled off adhesion site. Then adhesion energy was calculated from the unit of operation speed. Tested carton blanks were operated by relatively low speed, which means high energy were required as shown in Table 1. As observed during extrusion, low Tg resins adhered strongly to cartons and metals, which disturbs operation of flame sealer. On the other hand, high Tg showed poor adhesion.

It seemed carbon additives were of help to reduce the flame energy (discussed latter section). As a result, mixture of GA1310 (80%) and GM400 (20%) were the best selection from the flame sealing point of view.

3.2 Relation between storage elastic modulus (E') and Tg

To analyze adhesion properties, E' of polyester films and films with additives at 50 and 100℃ (listed in Table 2) were plotted against local maximal value of tanδ as Tg measured by DMA (Fig.4). Arrowed line in Fig.3 shows E' of GM400 at 50 and 100℃. Most of the flame sealable polyesters showed around 10^8 Pa at 50℃ and also maximal value of tan δ at about 30℃, which indicates both value may be the regulatory factor for flame seal adhesion. In fact Tg is lower than ambient temperature, films become sticky and E' is higher than 10^8 Pa, no adhesion is expected.

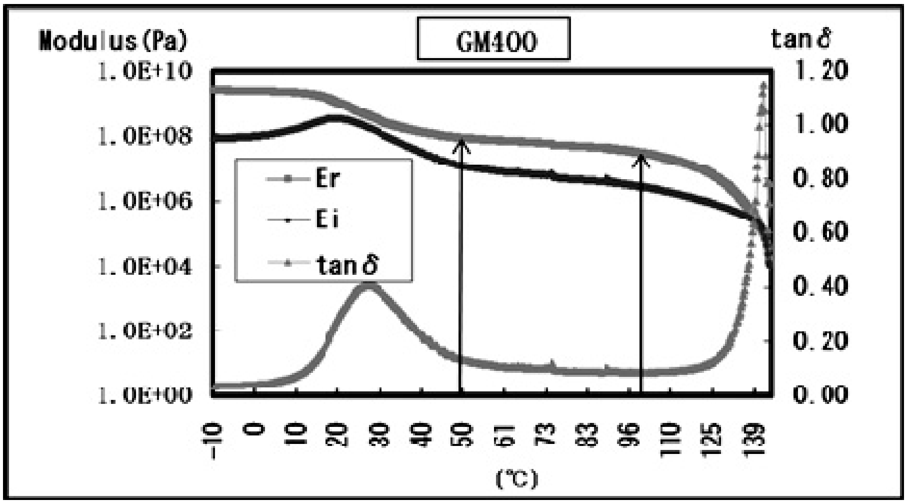

Fig.3 Storage elastic modulus at 50 and 100℃ of GM400

Table 2 Storage elastic modulus at 50 and 100℃ and local maximal value of tanδ

(Pa x10^5)

Description		GM913	GM900	GA3410	GM400+bamboo	GM400+cider	GM400	GM:GA=8:2	GA2310	GM:GA=5:5	GA2310+carbon	GA1310	LDPE
Number		i	ii	iii	iv	v	vi	vii	viii	ix	x	xi	Ref
Modulus(E')	50℃	159.0	295.0	341.0	70.0	976.0	868.0	1200.0	735.0	1380.0	493.0	2180.0	938.0
	100℃	63.4	33.9	54.2	409.0	409.0	312.0	352.0	247.0	433.0	225.0	ND	57.7
tanδ TEMP	(℃)	-43.8	-16.1	5.6	25.3	25.4	27.3	28.1	32.1	34.1	36.1	44.2	*68.1*

On the other hand, LDPE showed maximal value of tanδ at 68℃ and E' was almost 10^8 Pa at 50℃ and E' at 100℃ was much lower than above mentioned polyesters because of melting temperature is around 110℃. We do not have clear explanation why the maximal value of tanδ at 68℃ of LDPE appears.

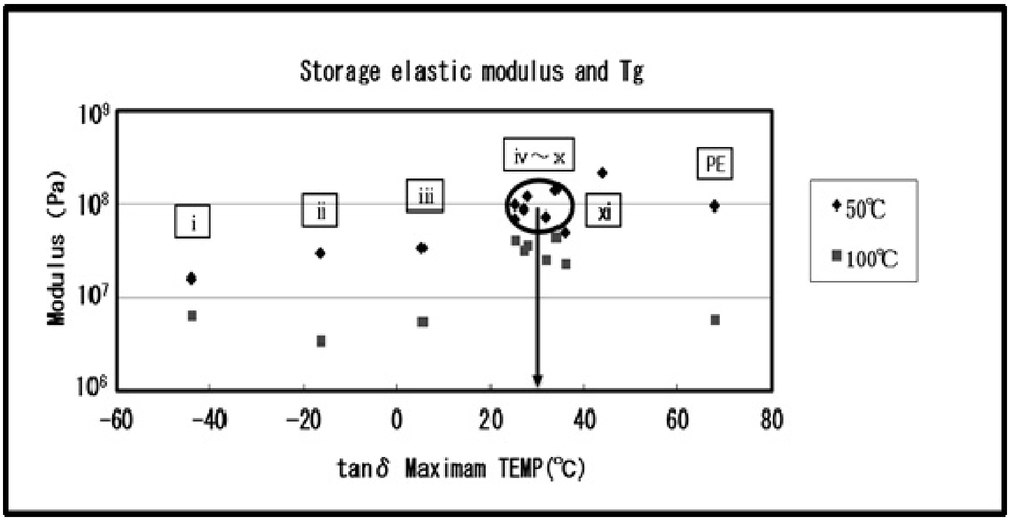

Fig.4 Plot of local maximal value of tanδ as Tg versus Modulus

3.3 Effect of additives to physical properties of polyesters

LDPE has generally low young's modulus compared to polyesters in extrusion grade. In case young's modulus is so high, folded cartons sometimes show peel off along crease or pinholes because of the low elongation of layer. It was observed that addition of 1wt% charcoals or TiOx to GM400 and GA2310 etc. had potential to lower young's modulus (Table 1).

Polyester GM400(80%)+GA1310(20%) which includes 1wt% of zeolite and LDPE co-extruded two layer film (16μm each) showed much higher elongation (376%) compared to that of solid ones (279%) on maximum stress. The above polyester and LDPE co-extrusion showed stable film formation where the proper melt tension of LDPE facilitated two layer formations. As zeolite does not have thick color, application to extruder is much realistic than charcoals.

According to the DSC analysis of GM400 shown in Table 3, initiation temperature of crystallization became lower than original one (Tc1) and also half width calculated by peak height/baseline showed higher value if charcoals or carbons were added (Fig.5), indicating charcoals and carbons act as crystal core and simultaneously plasticizer. WAXD also detected high crystallinity, which may result in lower coefficient of dynamic friction (μ'), even LDPE is still low (0.16).

Mixture of GA1310 and GM400 were analyzed with zeolite. Table 3 shows Tg as detected by DMA, Tc1, peak height/baseline calculated by DSC, and coefficient of dynamic friction. Zeolite promoted crystallization rate, but Tg did not change to lower side, which implies charcoal and carbons are better additives if color is not considered. TiOx wears manufacturing machine such as cutter. So, analysis is not focused on TiOx.

Table 3 Effect of additives on physical properties of films

Methods	DMA	DSC		WAXD	-
Measurement Items	Tg (℃)	Tc1 (℃)	Peak Height/Baseline	Crystallinity ratio	μ'
GA1310	44	45.9	1.7	-	0.22
GM400(80%) + GA1310(20%)	32	68.5	1.2	-	0.30
+Zeolite	41	60.9	1.6	-	0.30
GM400	28	70.3	0.5	1.0	0.43
+Charcoal (bamboo)	25	63.8	0.8	-	0.29
+Charcoal (cider)	25	62.8	0.8	4.0	0.29
+Carbon black	ND	63.1	1.0	-	ND

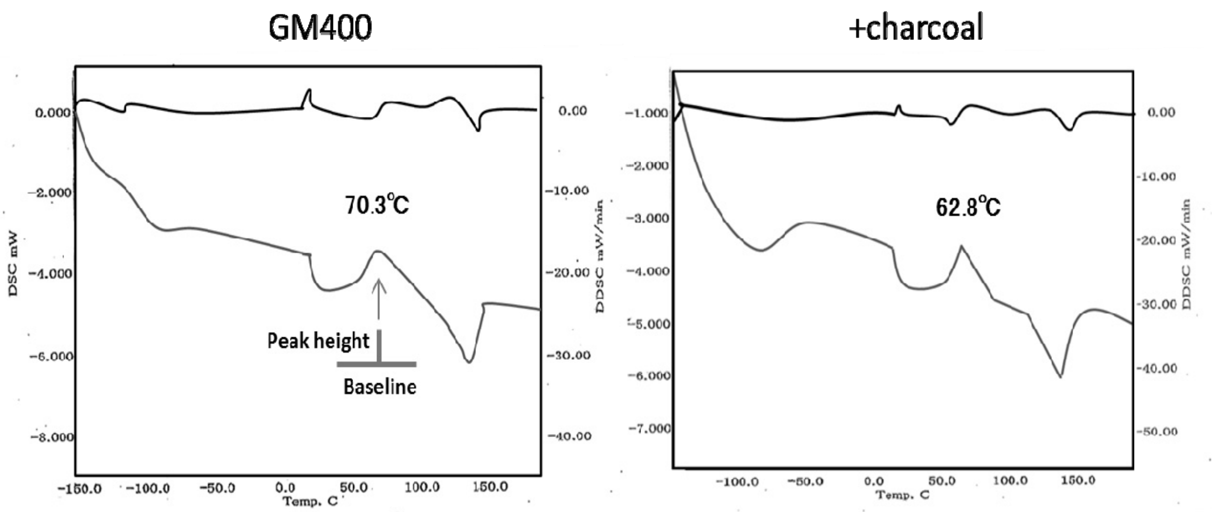

Fig.5 DSC chart of GM400 and charcoal added one

3.4 Human sensory test and electric tongue

Five polyesters and LDPE films together with PET bottled mineral water were analyzed to determine correlation among them. GM400 (with/without 1wt% cider charcoal or zeolite), GA1310 and mixture of each polyester together with amorphous polyester SI173 which can be extruded by the same setting temperature of LPDE as reference (Tg78℃, Softening temperature185℃ respectively) were evaluated by sensory test and electric tongue.

Table 4 shows specimens and tested score of each film. According to the human sensory test result, GM400 and mixture of GM400 and GA1310 maintained good taste. Zeolite or charcoal added samples did not imply improvement unexpectedly and LDPE was the worst score among them.

Table 4 Samples for human sensory test and scores

Sample(#)	Sample	Score
i	Blank (PET bottled Mineral Water)	9
ii	LDPE	1
iii	GM400	6
iv	GM400 (80%) + GA1310 (20%)	6
v	GM400 with 1wt(%) of zeolite	7
vi	GM400 with 1wt(%) of cider charcoal	5
vii	Ref. Polyester SI173	7

Electric tongue was then used for analysis. It elucidated the shortest euclidean distance from Blank was mixture of GM400 and GA1310 (Fig.7). Additives did not effect to shorten euclidean distance. This result may indicate electric tongue recognizes the existence of additives rather than taste as human feels.

Fig.6 shows PCA plotting of PC1 and PC2, only two semiconductor sensors responded well to calculate contribution rate, of which total contribution rate was 100%. The most of the samples were related to PC1. Blank (i) and mixture of GM400 and GA1310 (iv) occupied almost the same territory, which implied similar directional quality.

Correlation between human sensory test scores and those predicted by electric tongue were analyzed and plotted by PLS statistical methods. Fig.8 indicated electric tongue was able to distinguish category of material and with/without additives easily, but as human sensory test did not reflect significant difference whether additives were included or not, coefficient of correlation was 0.634. Therefore, electric tongue may be suitable for detecting foreign element which human may not notice.

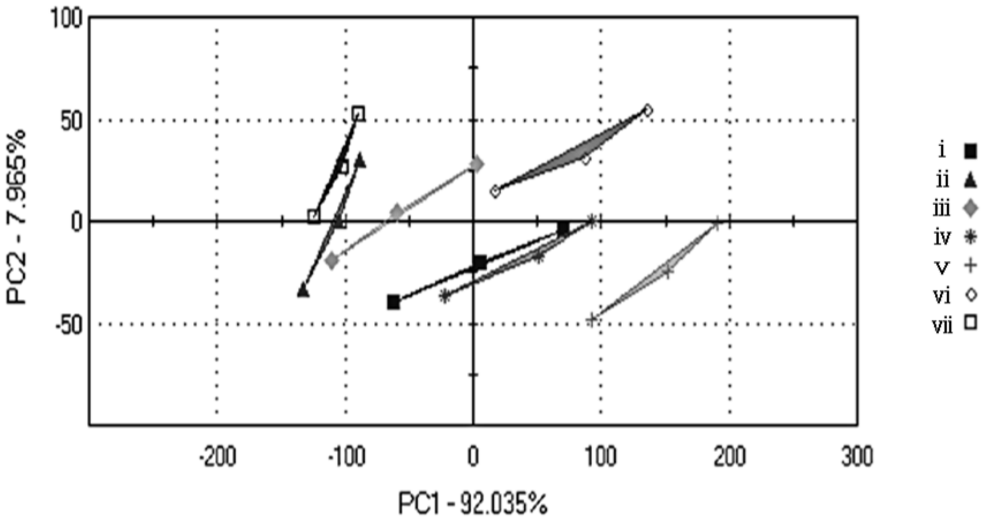

Fig.6 Score plot from the PCA of the electric tongue

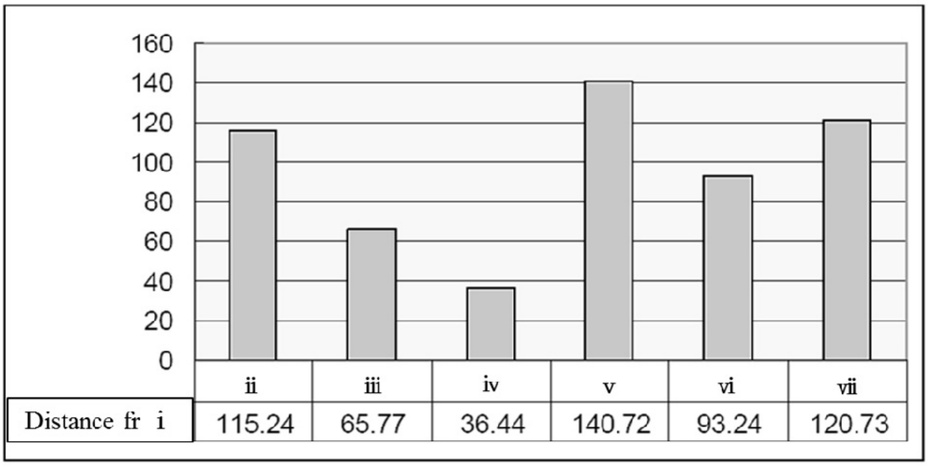

Fig.7 Euclidean center distance from bottled mineral water

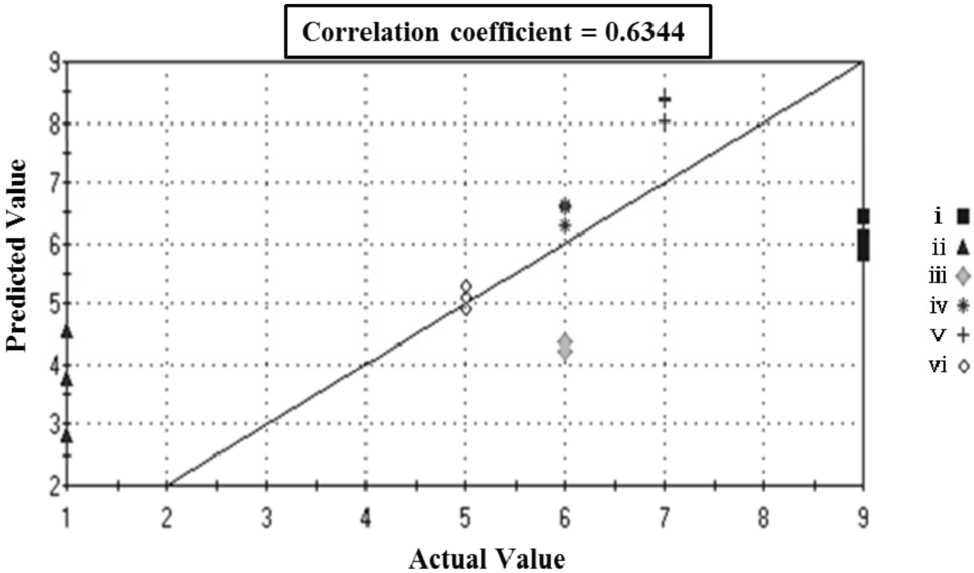

Fig.8 Correlation of human sensory test and electric tongue loaded by PLS

4. CONCLUSIONS

Polyesters are well known as flavors protect materials, which are not expected as polyolefins to be used for sealant of liquid packaging. In this research, various types of polyesters which were laminated both sides of paperboards were tested for flame sealing process. Laminated films with high Tg more than 35℃ rarely adhered. On the other hand, flame sealing operation was not unstable when Tg was less than 35℃ and storage elastic modulus at 50℃ by DMA was 10^8 Pa. In addition, lower value of young's modulus and dynamic frictions were required for carton production process.

Additives such as charcoals, TiOx and zeolite behaved as plasticizer and crystal core and were found to be a key factor for improving polyester physical property.

Both human sensory test and electric tongue elucidated superior property of some polyester in term of flavor protection.

In conclusion, to achieve realistic flame seal operation of gable top cartons especially for chilled distribution, polyester sealant may be developed from material design and additives to control physical properties for production process.

Acknowledgements

We thank Alpha M.O.S Japan KK and other companies for advice of this research.

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(Received 31January 2013)
(Accepted 26August 2013)