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Predictive Testing of Seafood Cans and Pouches by Electrochemical Impedance Spectroscopy

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Studies were conducted to evaluate the performance of retortable pouches and coated food cans using Electrochemical Impedance Spectroscopy (EIS). New unused retortable pouches and tin free steel cans were compared with the corresponding processed seafood cans for impedance. The pore resistance (Rp) of lids of tin free steel cans was reduced significantly on storage compared to the body which implies that the former was more susceptible for corrosion and deterioration. Processed retort pouches were superior to cans after two years of storage, which follows equivalent circuit RC. See-through pouches have about 2% reduction in pore resistance after thirteen months compared to the unused pouches The results reveal that EIS studies can be used for predicting the quality of cans and pouches.

Key words : Seafood, cans, retortable pouches, electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is extensively used for testing of performance of paint coatings on metal substrates and it helps to understand the delamination, stability of the coating etc.(Armstrong *et al.*, 1995). In an AC circuit, apart from resistance, the current is impeded by inductors and capacitors. The equation E=IZ is used to determine the impedance, where Z is called impedance (Autolab 2001). In an electrochemical cell, slow electrode kinetics, slow preceding chemical reaction and diffusion can all impede the flow of electrons and can be considered analogous to resistors, capacitors and inductors. The relative electrical permitivity (ε_r) of water is 80 at 20°C and that of an organic coating is 4 - 8 at 20°C. The capacitance of coated substrate changes as it absorbs water; EIS can be used to measure that change. EIS was considered a method of choice for evaluating the behaviour of polymer coated metals in contact with aqueous electrolyte systems. This paper makes an attempt to study the changes in responses of EIS in different cans and pouches, which will help in predicting the quality of cans during processing and storage of food products.

Materials and methods

The details of cans and pouches used for the study are given in Table 1. The pouches and cans were emptied and washed with labolene carefully without disturbing the coating surface of the film and immediately subjected to EIS using Autolab PGSTAT 30 corrosion measurement system fitted with FRA2 module. The impedance measurement of new unused can was also recorded. The experiment was conducted in a flat cell using Ag/AgCl as reference electrode, Pt as counter electrode and 3% NaCl as electrolyte. The impedance was recorded 1MHz to 50Hz (single sine wave). Pore resistance (Rp), constant phase element (CPE), number of electron involved in charge transfer reaction (n) and capacitance were calculated from the impedance data using the software FRA for Windows version 4.8.

Results and Discussion

Canned seafood products are subjected to thermal sterilization. A comparison was made between the unused tin free steel (TFS) can, retort pouches and see through pouches and cans and pouches processed with food. The impedance data revealed that the pore

Table 1. Details of the cans and pouches used for the study

	Material	Filled with	Age of sample	Processing conditions
1	Tin free steel can	New unused		
2	Tin free steel can	Prawn	1 month	115°C for 30 min
3	Tin free steel can	Prawn	4 months	115°C for 30 min
4	Tin free steel can	Mackerel curry	6 months	121°C for 40 min
5	Retort pouches	New		
6	Retort pouches	Mackerel curry	6 months	121°C for 40 min
7	Retort pouches	Tuna in oil	11 months	121°C for 50 min
8	Retort pouches	Mackerel curry	16 months	121°C for 40 min
9	Retort pouches	*Payasam*	24 months	115°C for 20 min
10	See through retort pouches	New unused		
11	See through retort pouches	Fish sausage	13 months	115°C for 30 min

resistance of the body and lid of processed TFS cans decreased significantly than the unused (Table 2).

Table 2. Pore resistance (Ω) of tin free steel cans.

TFS can	Can body	Lid
New unused	1.43×10^6	9.19×10^7
1 month	2.95×10^5	1.52×10^3
4 month	2.42×10^4	7.28×10^3
6 month	5.15×10^5	6.16×10^3
scratched	61.95	30.17

The 4 month old prawn- can gave low pore resistance compared to six month old mackerel curry and one month old prawn can. On visual examination it was found that the upper part of the can was corroded. White (1999) noted that the lacquer capacitance was decreased after some time of processing and it slowly increased and according to him the reason is not known. One probable reason for the decrease in Rp during storage of sterilized prawns is the corrosive effect of salt used in filling medium. The canned mackerel curry showed slightly higher Rp compared to prawn, which might be due to the effect of fat in the curry medium. The impedance of the can was also determined after making a small pin scratch over fresh TFS can. It was found that the Bode plot was flat as well as the pore resistance was reduced to 62Ω. The Bode plot of the new can body and lid followed the equivalent circuit RC and processed cans recorded varied equivalent circuits. This may be due to the lower capacitance, charge transfer resistance and sample variability. The coating capacitance, which is the ratio of the capacitance of processed can after and before processing, varied from 0.032 to 0.041. The lids of the TFS can were subjected to the impedance separately since it contains different internal coating. The Bode plot revealed that fresh lid followed equivalent circuit RC with pore resistance of 9.19×10^7 Ω. The pore resistance reduced significantly in all the lids

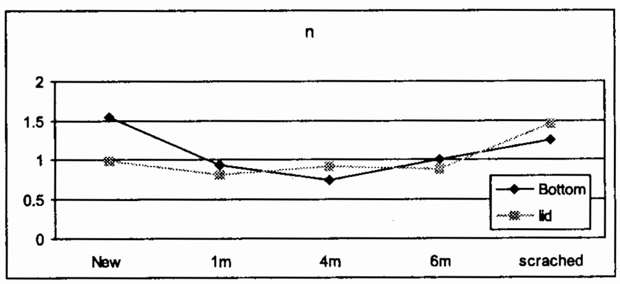

Fig. 1. Constant phase element of TFS can

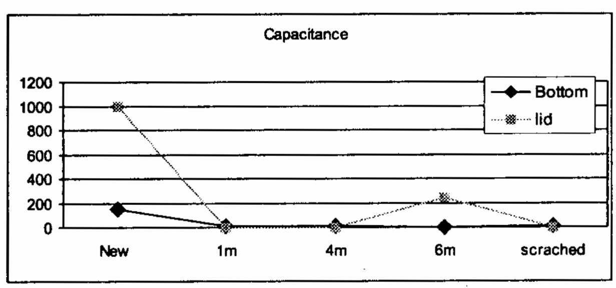

Fig 2. No of electrons involved in charge transfer reactions in TFS can.

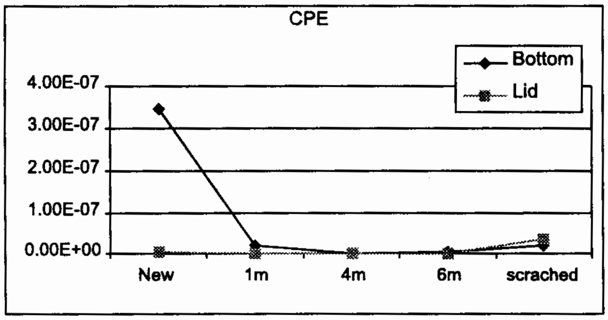

Fig. 3. Double layer capacitance in TFS can.

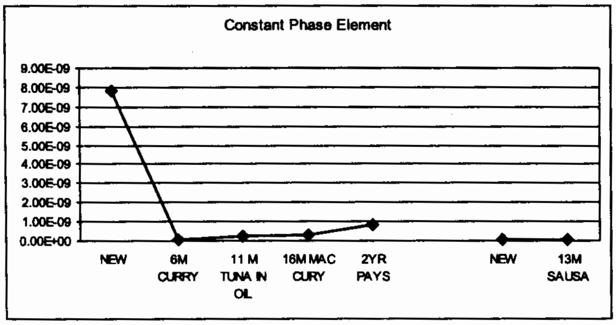

Fig. 4. Constant phase element of retort pouches

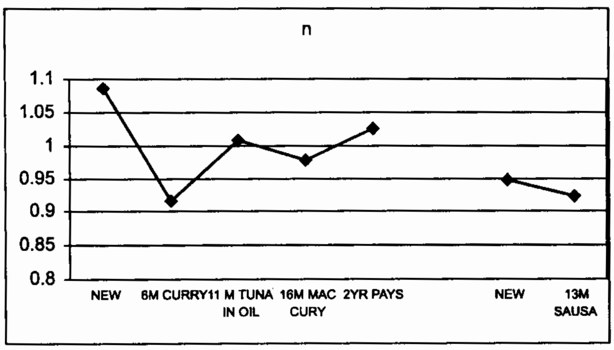

Fig. 5. No of electrons involved in charge transfer reaction in retort pouches.

and was less than 1% of the new can. Among the lids, the Rp of one month old can was only 1524Ω and that of scratched was 30.1Ω. This was further confirmed its Bode plots. The coating capacitance, which varied from 9.96×10^{-5} to 2.38×10^{-3} implies the coating was more prone to deterioration and delamination. The equivalent circuit in processed TFS lids followed different combination. In both the cases the deterioration was thought to be caused by water being absorbed into coating, reaching the metal substrate to initiate corrosion and delamination of coating (White 1999). The constant phase element (CPE) (Fig 1), n (No of electrons involved in charge transfer reaction) (Fig 2) and double layer capacitance (Fig 5) are also prominent indicators of deterioration. These marked changes on processing are to be expected and EIS is a potential technique to monitor the stability or compatibility of the container for a particular processing technique.

Retort pouches are commonly recommended for longer storage of pouch processed seafood products. On examining the Bode plots of retort pouches, it was found that all are following straight lines and had perfect equivalent circuit RC having capacitance >200pF.

Table 3. Rp of retort pouches

Retort pouches	Rp in ohms
New unused	3.68×10^9
Mackerel curry (6 months)	1.81×10^7
Tuna in oil (11 months)	4.01×10^7
Mackerel curry (16 months)	3.14×10^8
Payasam (24 months)	1.87×10^7
New see through retort pouch	6.64×10^4
Sausages in see through pouches (13 months)	6.52×10^4

The Rp (table 3) of new pouch was 3.68 $\times 10^9$ Ω and that of the 6 to 24 month old pouches varied between 1.81 $\times 10^7$ and 3.4 $\times 10^8$ Ω. Similarly the constant phase element (fig. 4), and n (fig. 5) decreased in all the processed pouches compared to the unused ones. These results reveal that the water absorption in pouches was comparatively low and their efficiency in this respect was higher compared to TFS cans. The Bode plot was recorded for processed and unused see through pouches. The Rp value recorded for fresh see through pouch was 6.64 $\times 10^4$ Ω and that of 13 month old sausage filled pouch was having Rp 6.52 $\times 10^4$Ω (table 3) and both followed RC equivalent circuits. A marked decrease in CPE and n was observed in processed see through pouch. Results indicate the potential of electrochemical impedance spectroscopy for predicting the behavior of cans and pouches at different conditions of processing and storage of food products.

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