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Effect of microwave heating on the stability of Some Plasticizers, used in Plastic Packing Industry, in aqueous food simulants

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Abstract: Stability of di(ethyl hexyl) adipate (DEHA), diisobutyl adipate(DIBA), dibutyl adipate (DBA), di(ethyl hexyl) sebacate (DEHS) and dibutyl sebacate (DBS) in the three aqueous food simulants: distilled water, 3%w/v acetic acid and 10%v/v ethanol., during microwave heating has been studied. the percent of recovery of each plasticizers was determined using direct HPLC method. Stability was depended on heating (exposure) time, microwave power setting, and the nature of the food simulant. In general, studied plasticizers appeared to be more stable in 10%v/v ethanol, than in distilled water, The 3%w/v acetic acid showed good stability with the lower molecular weight compounds even at full power, while the higher molecular weight compounds decomposed rapidly.
Keywords: plasticizers, microwave, stability, migration, food simulants, HPLC.

1- Introduction:

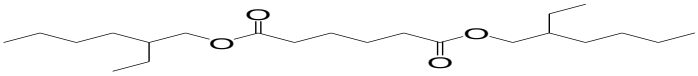
Microwaving is becoming an increasingly used process for heating of foodstuffs in both the industrial and home sectors. The microwave oven is used for a variety of purposes such as cooking, backing, frying, defrosting, reheating, pasteurization, sterilization..etc [1]. Microwave processing offers several advantages over conventional heating methods. These advantages include speed of operation, energy savings and precise process control [2, 3]. A variety of foods have been developed and modified over the past few years for the microwave market. Numerous of these food products are cooked along with the packaging material (container, wrapping film) in the microwave oven [4,5]. Such microwavable packaging material include plastics, paperboard and composites. However, during microwave cooking, the constituents of numerous of the above-mentioned packaging materials, i.e. plasticizers, antioxidants, stabilizers, monomers..etc., may result in the deterioration of food quality and even promote toxicity [6]. Microwave migration studies represent a unique challenge because of their shorter cooking times, and microwave distributions can influence cooking times. Quite high package temperatures may be achieved when the package absorbs microwave energy and converts it to heat. Microwave cooking not only produces temperature rises in packaging and food, but there is also a microwave effect which could increase the magnitude of the migration process [7].

Four types of food simulants are stabilized to perform the migration test by Directives [8-11], three of them are aqueous simulants., A (distilled water), B (3% w/v acetic acid), and C (10%v/v ethanol)., and the other is a fatty food simulant., simulant D (rectified olive oil., that could be replaced by sunflower oil or corn oil., If these fatty food simulants can not be used for technical reasons connected with the method of analysis, simulant D could be substituted by isooctane or 95% ethanol). An incomplete list of additives., that can be used

in the manufacture of plastic materials and articles that are intended to come into contact with foodstuffs., is established by Directives [12,13], which also lays out specific migration levels (SML) according to their individual toxicity that must not be exceeded in the migration tests.

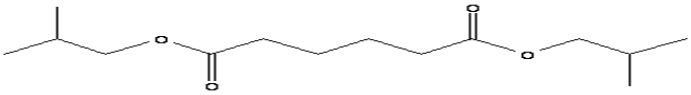
To carry out the specific migration test, plastic material is put in contact with food simulant, under determined temperature and time conditions. However, it must be considered that this value will not be representative of the real migration level from the packaging if the analyte is not stable during the test. While considerable researches have been focused on the stability of plastic additives during processing, there is a lack of studies on the stability of additives in food simulants [14-20]., therefore, the study of stability in food simulants is necessary to know the types of additive that may undergo degradation in food simulants and their degradation products, as well as on the type of media or heat exposure to which they are more sensitive.

Because the plasticizers are the most common additives used in polymers processing and applications [21,22]., the stability of some plasticizers di (ethylhexel) adipate (DEHA), diisobutyl adipate (DIBA), dibutyl adipate (DBA), di (ethyl hexyl) sebacate (DEHS), and dibutyl Sebacate (DBS) has been tested here in three aqueous food simulants after they have been exposed to microwave at medium (≈ 725 w) and full power (≈ 1450 w)., The chemical structures of these plasticizers are shown in figure 1.



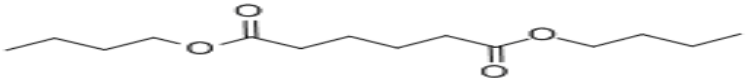
Di (ethylhexel) Adipate (DEHA)

Mw= 370.57 g/mol



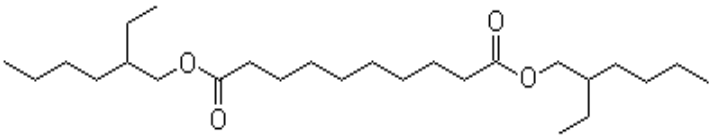
Diisobutyl adipate (DIBA)

Mw= 258.350 g/mol



Dibutyl adipate (DBA)

Mw= 258.350 g/mol



Di (ethyl hexyl) sebacate(DEHS)

Mw= 426.68 g/mol

Dibutyl Sebacate (DBS)

Mw= 314 g/mol

Figure 1: The structure formula of the studied plasticizers.

2-Experimental procedure:

2.1-Materials: Di (ethylhexel) adipate (DEHA), diisobutyl adipate (DIBA), dibutyl adipate (DBA), di (ethyl hexyl) sebacate(DEHS), and dibutyl Sebacate (DBS) (99%) were obtained from Sigma-Aldrich (Aldrich, Milan ,Italy), methanol (HPLC- gradient grade) was supplied by (Panreac -EU), acetonitrile and ethanol (HPLC-gradient grade) were obtained from Sigma-Aldrich (Germany), 2-propanol (HPLC-gradient grade) was supplied by sham lab (Syria), acetic acid (HPLC-gradient grade) was supplied by Scharlaus ChemiesA (Barcelona, Spain). Distilled water (water was purified in our lab).

2.2-Apparatus: **2.2.1-**The Microwave Oven: Wattar (WST-61) a domestic microwave oven (Wattar microwave was opened from its top and a refax condenser apparatus was then fixed on it)

2.2.2- Micro lab ultrapure water system (Hamilton Laboratory Glass, LTD**)**

2.2.3-The High Performance Liquid Chromatographic (Shimadzu, Japan, Kyoto). The device was supplied with; pump model(LC-20AT), the oven model (CTO- 20A); DEHA, DIBP, DEHS and DBS were completely separated using a stainless steel column of dimension (4.6 × 250 mm^2) packed with symmetry C_{18} and 4 µm particle size (Merck , Germany). The detection system model (SPD - M20A, UV-PDA), the signal acquired from detector was recorded by a personal computer operated by using LC solution program. Micro liter syringe for HPLC (Hamilton- Bonduz, Schweiz, Switzerland, 100µl).

2.2.4-The Gas Chromatographic: (GC-2010Shimadzu (it was Supplied with auto injector)Shimadzu - Auto injector (AOC-20).*Separation Column: non polar Column (CBP1-M50-O25- 221-28635-5)., (0.25 µm.، 50× 0.22m m^2).,(Shimadzu – Kyoto- Japan).

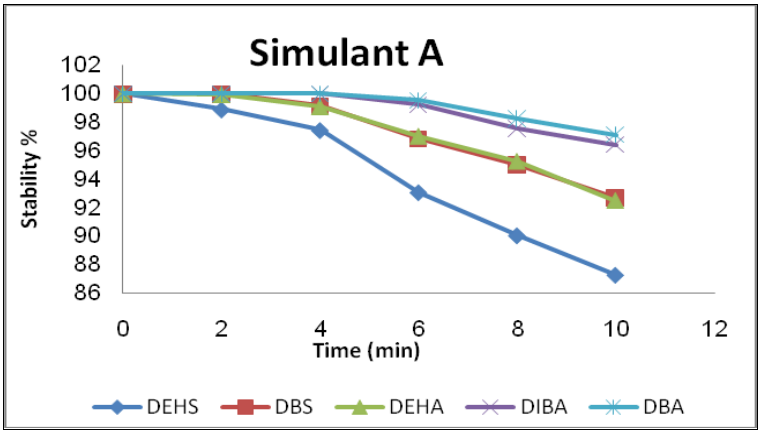
2.3-Chromatographic Experiments: the chromatographic experiments for analysis of the aqueous simulant samples were carried out by using HPLC as follows.

*Mobile phase: Acetonitrile and methanol (90 : 10)., *column oven temperature: 30°C., *injection volume: 20 µl., *flow rate: 1ml/min for(DEHA, DEHS) and 0.8ml/min for (DIBA, DBS)., *wave length: 273nm., The three aqueous food simulants were analyzed directly. DEHA, DIBA, DEHS and DBS were identified by comparison of theirs retention time with corresponding peak in the stander solution and its UV spectrum. Quantification was carried out using a calibration plot of external standard. * The chromatographic experiments when Gas Chromatographic was used were carried out as follows:

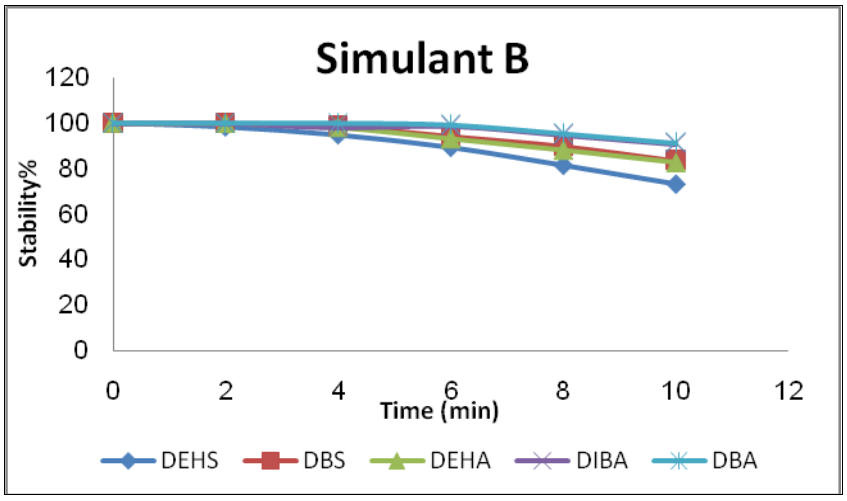
gas career: nitrogen., pressure: 50Kpa., flow rate: 1.50ml/min. thermal program

{1000C hold 1 min→ 2200C at300C/min→2400C at100C/min→2800C hold 10min}.

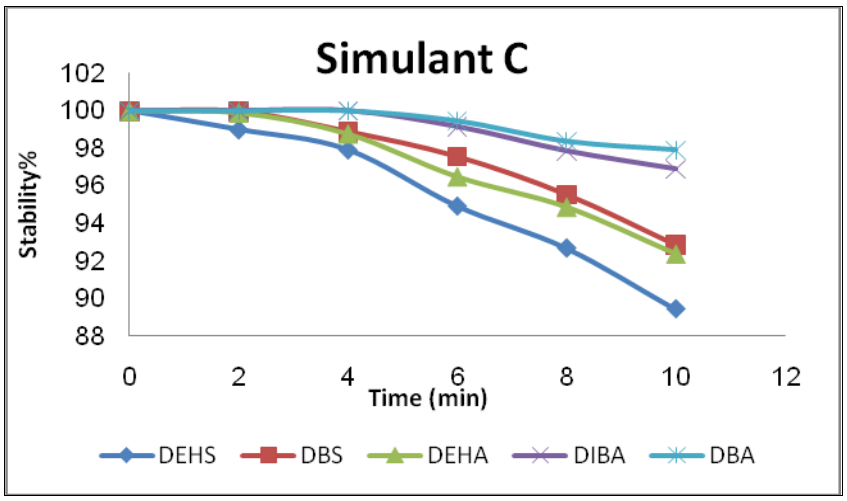
2.4 Stability test procedure and preparation of samples: for stability test., individual stock standard solution of each plasticizer (1000 mg/L) was prepared in 2-propanol, then, this stock solution was diluted with 2-propanol to obtain individual working solution (100mg/l)., this working solution was used to spike individual samples solutions around specific migration limit for each plasticizers (18ppm) in simulant A, simulant B, and simulant C [12]. The samples solutions of the aqueous simulants were kept in glass ware and exposed to a microwave oven at a medium (≈ 725 w) and full power (≈ 1450 w)., for 2, 4, 6, 8, 10 min.



Stability of some plasticizers in simulant A at medium power level of microwave oven.



Stability of some plasticizers in simulant B at medium power level of microwave oven.



Stability of some plasticizers in simulant C at medium power level of microwave oven.

Figure 2: Stability of Some plasticizers in aqueous food simulants at medium power level of microwave oven.

3- Results and Discussion:

The analysis of additives from food contact materials is commonly performed by gas chromatography (GC) or high performance liquid chromatography (HPLC) [23- 27]. In this study, a rapid screening method to test the stability of food contact materials was achieved using HPLC, and by using GC to determine DBA.

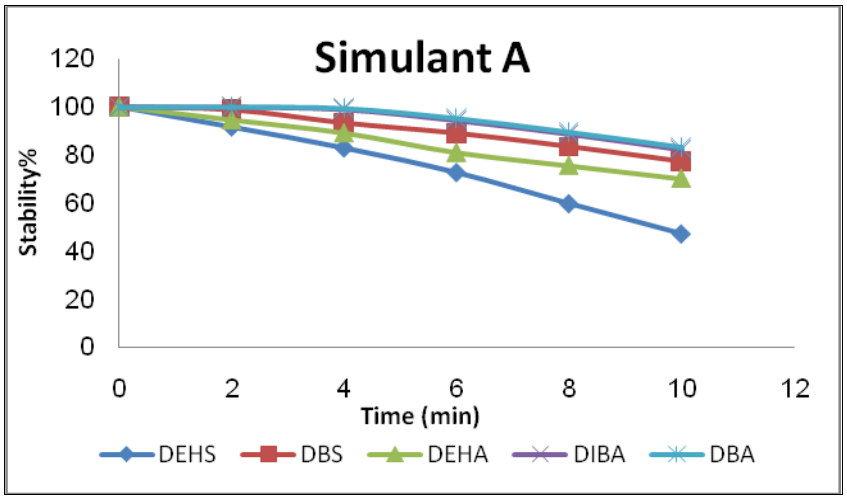
Figures 2-3 show the results obtained in the stability test of each plasticizer in simulants A, B, and C, in a time interval of 2, 4, 6, 8, 10 min, after exposure to microwave irradiation at medium (≈ 725 w) and full power (≈ 1450 w). The percent of recovery of each plasticizers has been calculated as the ratio between concentration of each plasticizers in simulant at a fixed time and the concentration of them at the end of the test. It was considered that, a recovery < 50% of the initially added amount of substance in simulant shows that the substance is not stable in that simulant at specified test conditions [14].

Figure 2 shows the results obtained at medium power (725w)., in simulants A and C, all studied plasticizers DBA, DIBD, DEHA, DBS and DEHS were stable and the percent of the stability when they were heated by exposing to a microwave irradiation at medium power for 10 min as follows: In simulant A; 97.1241% for DBA, 96.4241% for DIBD, 92.4770% for DEHA, 92.6861% for DBS and 87.2228% for DEHS., In simulant C; 97.9017% for DBA, 96.9017% for DIBD, 92.3530% for DEHA, 92.8528% for DBS and 89.4224% for DEHS. In simulant B., the most stable plasticizers were the compounds of the lower molecular weight (91.3561% for DBA and 90.7561% for DIBA., at medium power for 10 min.)., on the other hand, the compounds of the higher molecular weight DEHA and DEHS showed a recovery around 82.6924% and

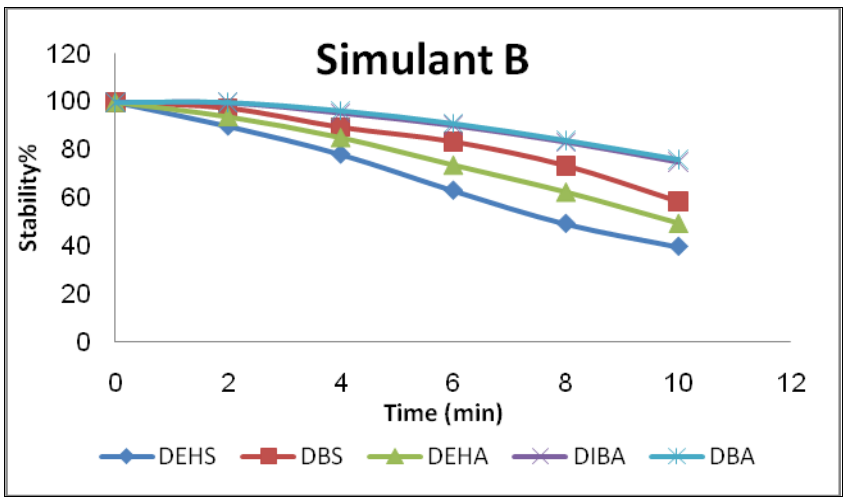
73.2896% consequently), while the percent of DBS which has a moderate molecular weight was 83.4572% at medium power for 10 min.

At high power (1450 w)., Figure 3., DBA and DIBA appeared to be stable during the entire assay, in simulant A., similar to what they showed in simulant C. In simulant B., the stability was decreasing in the first minutes of assay until 75.9985% for DBA and 74.7985% for DIBA that kept constant until the end of the test. DEHA and DEHS appeared to be stable during the entire experiment in simulant C (66.0069% for DEHA and 57.9835% for DEHS., at 10 min). In simulant A., DEHA was stable during all the entire experiment., while DEHS suffered a fast decomposition by increasing exposure time to 10 min (the stability was: 47.1948%). In simulant B; DEHA and DEHS were stable, but at the end of the test, the stability of the compounds decreased making them unstable (49.4769 for DEHA and 39.7820% for DEHS., at 10 min, and also the stability of DEHS was 49.3354% at 8 min). DBS (moderate molecular weight) suffered a decomposition by increasing exposure time to 10 min., but it still stable at the end.

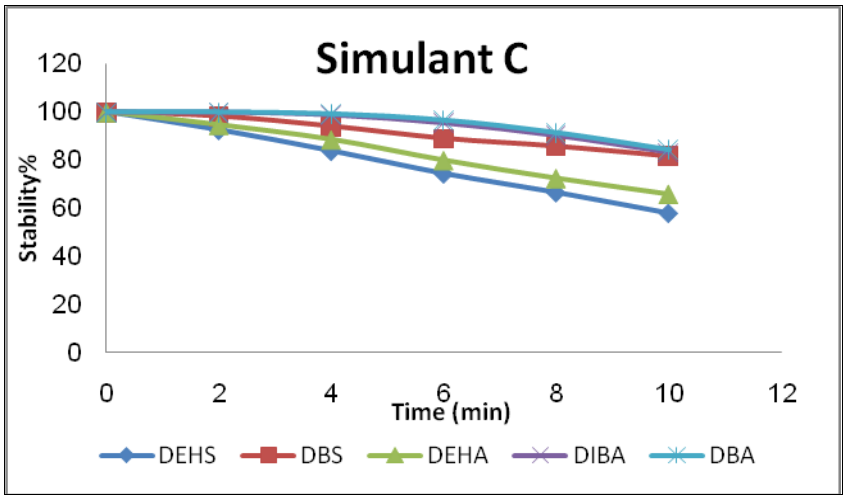
It can be seen by observing the power level of the microwave oven irradiation effects on the stability of some plasticizers., in general, that the rise in power level causes an increase of degradation, although there are difference between simulants. So, degradation increases substantially with the power level of the microwave oven in simulants B and A, whereas, the plasticizers are hardly affected in simulant C. The stability of low size plasticizers DBA and DIBA is quiet good even at high power level, and the stability decreases up to 50%, similar to the way for DBS (moderate molecular weight). The high molecular weight plasticizers DEHA and DEHS are the most degraded compounds at high power level.



Stability of some plasticizers in simulant A at full power level of microwave oven.



Stability of some plasticizers in simulant B at full power level of microwave oven.



Stability of some plasticizers in simulant C at full power level of microwave oven.

Figure 3: Stability of Some plasticizers in aqueous food simulants at full power level of microwave oven.

The obtained results have shown that the stability of the studied plasticizers is not related to the test conditions and their molecular weight only, but also related to structure of the alcohol chains. The straight-chain alcohol (like DBA) are more stable than the branched chain alcohol compound (like DIBA).

Comparing the obtained results with other published works, it can be seen some identical results of some studies [28-31].

4- Conclusions:

- Comparing the results for each simulant with increase of the power level of the microwave oven, showed that, in general, plasticizers are less stable at high power. In simulants B and A, this power level effect is higher than that in simulant C.
- Comparing the effect of each simulant on plasticizers stability at a fixed power level, it is noted that C is the simulant that offers the highest stability among the studied compounds. All considered plasticizers are stable in simulant C during 10 min at medium and high power of the microwave oven.
- The straight -chain plasticizers are more stable than their branched isomers.

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