

Aqueous emulsions from oxidized polyethylene waxes stabilized with non-ionic agents

(Sponsored Article)

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Abstract: The stable emulsions from oxidized polyethylene waxes with the use of various non-ionic emulsifiers from the group of fatty alcohol ethoxylates with HLB in the range 11–16 were obtained. The effectiveness of the emulsification was assessed by measuring the dispersed phase particle size and the emulsion stability. The highest emulsifying efficiency was achieved using a non-ionic emulsifier with HLB of 16.3.

Keywords: aqueous emulsions, polyethylene waxes, emulsifier, non-ionic agents.

Emulsje wodne z utlenionych wosków polietylenowych stabilizowane środkami niejonowymi

(Artykuł Sponsorowany)

Streszczenie: Otrzymano stabilne emulsje z utlenionych wosków polietylenowych z zastosowaniem różnych emulgatorów niejonowych z grupy oksyetylenowanych alkoholi tłuszczowych o wartości HLB w zakresie 11–16. Skuteczność emulgowania oceniano na podstawie pomiaru wielkości cząstek fazy zdyspergowanej oraz stabilności emulsji. Największą efektywność emulgowania uzyskano stosując emulgator niejonowy o HLB równym 16,3.

Słowa kluczowe: emulsje wodne, woski polietylenowe, emulgator, środki niejonowe.

Waxes are important in many industries due to their diversity and physico-chemical properties. Among the group of synthetic waxes, non-polar and polar polyethylene waxes are in focus. [1–3]. Wax emulsions are oil-in-water dispersions. The dispersing phase is water, while the dispersed phase consists of various types of solid waxes particles (e.g. paraffin and/or other – natural or synthetic). The type of waxes used to prepare the emulsion determines its properties and application. The emulsions may contain 5–40 wt% of waxes. The emulsion stability, understood as the ability of not to break down into separate phases during use and storage, is the basic feature that determines the functional and commercial properties of these substances. A high degree of fragmentation and a narrow particle size distribution of the dispersed phase are the most important factors influen-

cing the emulsion stability. Obtaining this type of emulsion requires the use of various types of emulsifiers [4, 5].

Emulsifiers are surface-active substances (SPC) which adsorb at the interface and lower the surface tension, stabilizing the system [6]. Due to their structure, they are partially submerged in the hydrophobic phase and partially in the hydrophilic phase. They form a monomolecular layer at the interface. The measure of the surfactant's ability to stabilize the emulsion system is the HLB parameter (hydrophilic - lipophilic balance). It determines the hydrophilic-hydrophobic balance of the emulsifier and thus its affinity for the water and oil phases. The value of this parameter depends on the structure of the SPC molecule, mainly on the ratio of the hydrophilic to the hydrophobic part. The HLB parameter allows, among others to determine whether a given emulsifier will stabilize better a water-in-oil (w/o) emulsion or an oil-in-water (o/w) emulsion. The conventionally adopted scale of the HLB parameter, defined by William C. Griffin, is in the range 1–20. This range applies to non-ionic surfactants, but the use of this parameter has also been extended to ionic surfactants for which HLB values can be up to 50 units. Surfactants with higher HLB values (above 10) are more hydrophilic, while those with lower HLB values

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(less than 10) are more hydrophobic. If the HLB value is from 3 to 6 the emulsifier is preferred for stabilizing the w/o emulsion, while if the HLB value is from 8 to 18 for the o/w emulsion. The HLB parameter is additive, *i.e.* for a mixture of surfactants it is the sum of the values of individual compounds [5, 6].

The ability to dissociate can be taken as the basis for the chemical classification of emulsifiers. There are ionic, non-ionic, natural and powdered emulsifiers. Among the ionic there are anionic and cationic. Anionic, *i.e.* those in which the molecule has an active part in the form of an anion, *e.g.* soaps, sulfuric acid esters, polyol esters and fatty acids. On the other hand, cationic ones are those in which the active part of the molecule is a cation, *e.g.* quaternary ammonium salts or quaternary heterocyclic ammonium compounds. Non-ionic emulsifiers are esters or ethers containing two non-dissociating groups. Natural emulsifiers are substances found in nature with different chemical structures, *e.g.* milk casein, seaweed alginate, powdered solids [7, 8].

For the production of wax emulsions, non-ionic, anionic and cationic emulsifiers are used. The most frequently used non-ionic emulsifiers are ethoxylated, saturated and unsaturated fatty alcohols, fatty acid esters of polyhydric alcohols, polyoxyethylene ethers of saturated and unsaturated fatty alcohols. The degree of ethoxylation, *i.e.* the number of ethylene oxide molecules in the non-ionic emulsifier molecule, significantly affects its activity. Among the most commonly used anionic emulsifiers are high molecular weight alkylsulfonic acids, alkylbenzenesulfonic acids, alkoxylated fatty acids and their salts. Among the cationic emulsifiers are alkylamines, polyoxyalkylamines and amides formed in the reaction of these amines with high-molecular fatty acids.

The influence of the SPC structure on the emulsion stability depends on the energy barrier, which determines the minimum deformation strength of the adsorption layer, and the concentration barrier, which determines the amount of SPC in the volume unit of the adsorption layer, which determines the presence of a saturated adsorption layer on the surface of the emulsion particle. Therefore, it is important to properly select the surfactant in order to create an adsorption layer on the surface of the dispersed phase particles. It is generally believed that branched aliphatic chain emulsifiers stabilize w/o emulsions and straight chain o/w emulsions. To stabilize the dispersed phase, optimal surfactant concentration and pH are essential. In an acidic environment, cationic emulsifiers should be used, and in an alkaline environment, anionic emulsifiers. It is also important that the surfactant interacts with the remaining ingredients of the emulsion. Furthermore, the choice of the emulsifier type depends on the type of waxes used and their content in the emulsion.

The aim of the study was to obtain homogeneous emulsions of oxidized polyethylene waxes stabilized with various non-ionic emulsifiers with HLB values in

the range 11–16 from the group of fatty alcohol ethoxylates. The effectiveness of emulsifying polyethylene waxes with various surfactants was determined by the particle size of the dispersed phase and the emulsion stability.

EXPERIMENTAL PART

Materials

Oxidized polyethylene wax was produced by Wiwax Ltd according to procedure published elsewhere [9] and used in the amount of 30 wt%. The characteristics of the wax are presented in Table 1 and Fig. 1. Non-ionic emulsifiers were delivered by PCC Rokita S.A. and used in the amount of 5 to 8 wt% (Table 2). An emulsion stabilizer of the hydroxypropyl methylcellulose type in the form of a 3% solution was used in the amount of 5 wt%. As a pH regulator (in the range of 9–11) sodium or potassium hydroxide solution (10%) was used in the amount of 2 to 8 wt%.

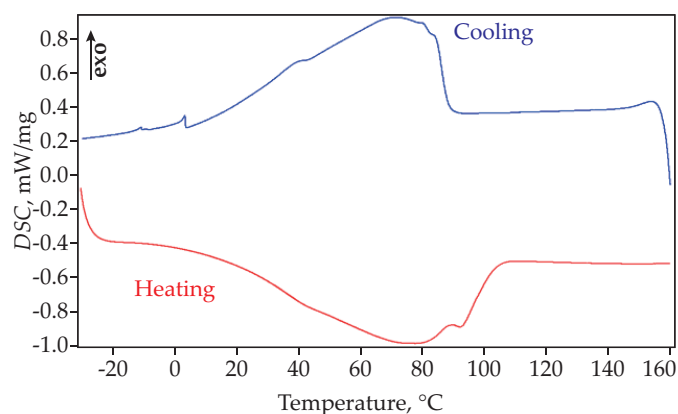


Fig. 1. DSC curves of wax

Table 1. Properties of oxidized polyethylene wax

Property	Value
Acid number, mg KOH/g	23.5
Dropping point, °C	97.7
Solidification temperature of, °C	89.0
Viscosity at 140°C, mPa·s	6.2
Density at 23°C, g/cm ³	0.94
Penetration, 0,1 mm	11.1

Table 2. Emulsifiers*

Emulsifier symbol	HLB	Degree of ethoxylation	Chemical characteristic
E1	14.5	12	Ethoxylated branched alcohols C ₁₃
E2	14.5	9	
E3	12.8	8	
E4	13.6	11	Ethoxylated alcohols C ₁₂ – C ₁₅
E5	12.0	7	
E6	16.3	18	Ethoxylated saturated and unsaturated alcohols C ₁₆ – C ₁₈
E7	14.0	14	
E8	10.8	7	
E9	12.5	6	Branched and linear ethoxylated alcohols C ₉ – C ₁₁

* manufacturer data

Table 3. Effect of the emulsifier on emulsion properties

Property		Emulsifier E6, wt%					
		5.0	5.5	6.0	6.5	7.0	7.5
Visual assessment		liquid	liquid	liquid	liquid	liquid	liquid
pH		8.97	9.03	9.42	8.87	9.38	9.56
Viscosity, mPa · s		9.10	18.37	15.03	34.20	42.20	48.00
Density, g/cm ³		0.962	0.944	0.950	0.962	0.941	0.942
Solid content, wt%		36.96	38.77	37.02	39.51	38.50	39.13
Stability	Storage time, days	6	14	18	31	>80	>80
	Centrifuge test, min	30	60	60	60	60	60
Particle size, µm							
	Dv(10)	0.0233	0.0211	0.0208	0.0202	0.0202	0.0195
	Dv(50)	0.0914	0.0691	0.0654	0.0607	0.0608	0.0563
	Dv(90)	3.53	0.531	0.343	0.203	0.225	0.177
	Dv(99)	7.59	33.3	29.1	3.41	25.4	3.26
	Dv(100)	11.1	51.3	63.7	5.84	58.2	5.79
Dispersion coefficient		38.339	7.374	4.809	3.017	3.375	2.802

Methods

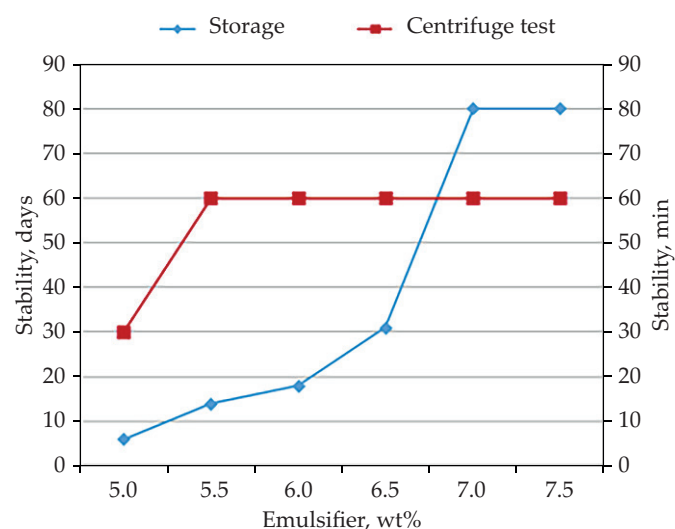
The size of the dispersed particles was measured by the dynamic light scattering method according to ISO 13320-1 using the Mastersizer 3000 analyzer manufactured by Malvern Instruments Ltd. by the “wet” method.

The emulsion viscosity was measured at 23°C with a Ford cup No. 4 according to PN-EN ISO 2431, and the pH with a Mettler Toledo FiveEasy pH meter.

The solids content was determined on a Mettler Toledo HR73 Halogen Moisture Analyzer by heating the sample to 125°C for 60 min.

The density was measured in accordance with PN-EN ISO 2811-1 using a pycnometer from BYK Additives & Instruments.

The stability of the emulsion was assessed by centrifugation at 3000 min⁻¹ for 60 min using the MPW MED Instruments Centrifuge MPW-352 and by visual observations during the emulsion storage.

**Fig. 2.** The effect of the emulsifier E6 on the emulsion stability

Preparation of wax emulsions

The homogenization process was carried out using IKA 50 ULTRA-TURRAX type homogenizer with S50N-G45M shear mixer. The emulsion components were heated to the temperature of 95–98°C and homogenized at the stirrer rotational speed above 8000 min⁻¹, and then the melted wax was introduced. After the end of the process (8–10 min), the mixture was quickly cooled to room temperature.

RESULTS AND DISCUSSION

Table 3 and Fig. 2 show the results for emulsions containing 30 wt% of oxidized wax, obtained with the use of non-ionic emulsifier E6 in the amount from 5 to 7.5 wt%. The aim of these studies was to determine the optimal amount of emulsifier to obtain a stable emulsion. The main evaluation criterion was stability as the other parameters did not differentiate the samples.

It is clear from Table 3 that increasing the amount of emulsifier did not significantly change the size of the dispersed particles and the stability of the emulsion determined by the centrifugal test (the samples did not break after 60 minutes of centrifugation). On the other hand, with the increase in the emulsifier content, there was a visible effect of improving the emulsion stability during storage. Emulsions containing 7 and 7.5 wt% emulsifier were stable, with no increase in density after 80 days (Fig. 2). Moreover, the emulsion viscosity increased. Therefore, a constant (7 wt%) addition of emulsifiers was used to evaluate the emulsification efficiency of various surfactants.

Tables 4 and 5 and Figures 3–5 show the properties of emulsions without and with a stabilizer in the amount of 5 wt% in the form of a 3% solution. The pH of the emulsion was assumed to be from 9.0 to 9.5.

Non-ionic emulsifiers, derivatives of ethoxylated branched and linear alcohols with various degrees of ethoxy-

Table 4. Properties of emulsions with different emulsifiers

Property		Emulsifier, wt%								
		E1	E2	E3	E4	E5	E6	E7	E8	E9
Visual assessment		liquid	liquid	liquid	liquid	liquid	liquid	liquid	liquid	liquid
pH		8.86	8.93	8.43	8.62	8.86	9.38	8.52	–	8.85
Viscosity, mPa · s		27.90	30.83	34.70	20.30	21.40	42.2	14.40	–	21.50
Density, g/cm ³		0.909	0.860	0.857	0.929	0.904	0.941	0.924	–	0.842
Solid content, wt%		38.77	37.78	37.54	37.11	37.22	38.5	38.00	–	36.88
Stability	Storage time, days	13	5	26	9	>55*	>80*	7	–	10
	Centrifuge test, min	60	60	60	60	60	60	60	–	60
Particle size, μm										
	Dv (10)	0.0218	0.0227	0.0208	0.0216	0.0202	0.0202	0.0202	6.08	0.0242
	Dv (50)	0.0772	0.0912	0.0674	0.0740	0.0607	0.0608	0.0604	15.5	0.125
	Dv (90)	9.64	31.4	9.16	11.1	0.836	0.225	0.233	70.7	22.5
	Dv (99)	31.6	848	22.7	53.4	50.1	25.4	23.9	163	43.8
	Dv (100)	51.4	2040	31.0	85.9	96.7	58.2	44.4	236	74.9
Dispersion coefficient		124.594	344.079	135.565	149.548	13.446	3.375	3.525	4.154	180.159

* follow-up

Table 5. Properties of emulsions with different emulsifiers and stabilizer

Property		Emulsifier, wt%								
		E1	E2	E3	E4	E5	E6	E7	E9	
Visual assessment		liquid	liquid	liquid	liquid	liquid	liquid	liquid	liquid	liquid
pH		8.86	8.98	9.03	9.09	9.21	9.04	9.23	9.10	
Viscosity, mPa · s		28.70	30.97	38.43	19.90	23.30	38.4	21.40	38.43	
Density, g/cm ³		0.911	0.970	0.935	0.970	0.988	0.991	0.992	0.867	
Solid content, wt%		38.77	39.17	37.37	36.55	37.54	38.04	37.23	37.71	
Stability	Storage time, days	>36*	>27*	>35*	10	>23*	>24*	>38*	14	
	Centrifuge test, min	60	60	60	60	60	60	60	45	
Particle size, μm										
	Dv (10)	0.0270	0.0270	0.0227	0.0241	0.0207	0.0208	0.0198	0.0259	
	Dv (50)	0.435	0.146	0.0909	0.0955	0.0656	0.0572	0.0572	0.259	
	Dv (90)	19.8	20.5	16.0	8.17	11.7	0.173	0.174	36.5	
	Dv (99)	35.7	65.2	43.4	35.0	58.1	3.70	0.693	69.9	
	Dv (100)	50.9	124	82.2	73.7	109	7.35	5.13	97.6	
Dispersion coefficient		45.417	139.806	175.674	85.329	178.626	2.661	2.695	141.238	

* follow-up

lation, with different hydrophilic-hydrophobic balance (above 10), and therefore with higher affinity for the water phase, stabilizing oil-in-water emulsions, were used.

The emulsion properties, similarly to the selection of the amount of emulsifier, were assessed mainly on the basis of the dispersed particles size and the stability during storage. All emulsions met the centrifuge test (60 min). The obtained emulsions were homogeneous and fluid, except for the emulsions with E8. The sizes of the dispersed particles Dv (10) and Dv (50) were comparable for most of the tested emulsions. Among the emulsifiers used, the most effective was E6 with the highest HLB value of 16.3. For the remaining emulsifiers, HLB was in the range from 10.8 to 14.5. There was no unequivocal dependence between the emulsion properties and the emulsifier HLB value. The E6 emulsion had a very small particle size of the dispersed phase and showed no signs of degradation such as cre-

aming, sedimentation, flocculation, coalescence during the storage period (> 80 days). A similarly stable emulsion was obtained using the emulsifier E5, despite the significant difference in the HLB value of these emulsifiers. The emulsion with E7 had the smallest particle size, but it did not improve the stability of the emulsion obtained, it broke after 7 days of storage. The emulsions with E2, E9, E3 and E4 emulsifiers, whose HLB was below 13 (Table 2) had larger particle sizes and these emulsions broke after 5–10 days of storage, except for the E3 emulsion, which broke after 28 days. The emulsion obtained with the addition of the E8 emulsifier (Table 4) with the lowest HLB had the largest particle size and was not fluid like the others.

The influence of the stabilizer on the emulsion properties, the task of which was to increase the stability, was also assessed. All emulsions, except those obtained with the E9 emulsifier, showed stability in the centrifuge

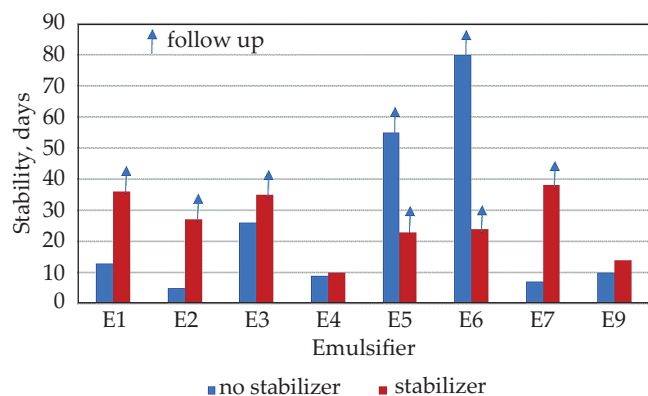


Fig. 3. Effect of stabilizer on the emulsion stability during storage

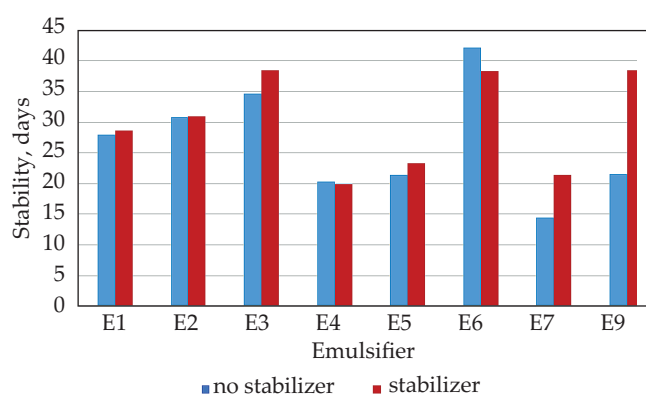


Fig. 4. Effect of stabilizer on the emulsion viscosity

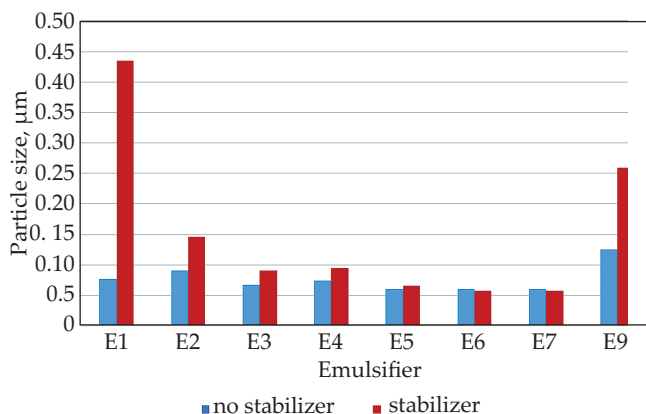


Fig. 5. Effect of stabilizer on the emulsion particle size Dv(50)

test for more than 60 min, confirming their good stability. On the other hand, the time after which the emulsions were broke during storage varied. Most emulsions with a stabilizer showed an increase in storage stability compared to emulsions without a stabilizer. In the case of emulsions with E4 and E9 emulsifiers, this increase was insignificant. The remaining emulsions were stable and did not separate, so their observation was continued (Fig. 3). The stabilizer had a beneficial effect on the emulsion stability. The use of the stabilizer increased the viscosity and density in relation to the emulsion

obtained without its participation (Fig. 4). For most emulsions, the influence of the stabilizer on the dimensions of the Dv(50) dispersed particles was small, except for the emulsions with E1 (Fig. 5).

CONCLUSIONS

Stable emulsions containing 30 wt % of oxidized polyethylene wax were prepared using various non-ionic emulsifiers from the group of ethoxylated fatty alcohols. High emulsification efficiency, assessed on the basis of the dispersed phase particle size, was obtained for most of the emulsifiers used. The particle size of the dispersed phase was in the range of 0.02–0.07 μm, which may indicate the stability of these systems. The highest emulsification efficiency (high stability and small particle size of the dispersed phase) was obtained by using the non-ionic emulsifier E6 (the most hydrophilic character) from the group of ethoxylated unsaturated alcohols with the degree of ethoxylation equal to 18. A positive effect on the stability of hydroxypropyl methylcellulose emulsions has also been demonstrated. The selection of an appropriate emulsifier is a complicated process, in which both the hydrophilic-hydrophobic balance and the type of waxes used, their content in the emulsion and the pH of the system must be taken into account.

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