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Synthesis and evaluation of *N,N*-dibutylundecenamide as new eco-friendly plasticizer for polyvinyl chloride

Sergiy Rogalsky^{1,*} , Oksana Tarasyuk¹, Alina Vashchuk², Valeriy Davydenko³, Oleg Dzhuzha¹, Sviatoslav Motrunich², Tetiana Cherniavska⁴, Oleksii Papeikin¹, Larysa Bodachivska¹, and Jean-François Bardeau⁵

¹ V. P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, 50, Kharkivske schose, Kyiv 02160, Ukraine

² E.O. Paton Electric Welding Institute, National Academy of Sciences of Ukraine, 11, Kazymyr Malevych St., Kyiv 03150, Ukraine ³

Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, 48, Kharkivske schose, Kyiv 02160, Ukraine ⁴

Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, 17, General Naumov Str., Kyiv 03680, Ukraine ⁵

Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France

Address correspondence to E-mail: sergey.rogalsky@gmail.com

ABSTRACT

Tertiary fatty amide, namely *N,N*-dibutylundecenamide (DBUA), has been synthesized and evaluated as potential plasticizer for polyvinyl chloride (PVC). Homogeneous PVC/DBUA composite films containing 20, 30 and 40 wt% of DBUA were prepared by solvent casting. Infrared analysis of PVC/DBUA blends indicated molecular interactions between polar –CH–Cl group of PVC and carbonyl group of tertiary amide. According to results of mechanical test-ing, PVC/DBUA films containing 30 and 40% of DBUA have significantly increased elasticity with reduced Young's modulus of over 90%, as well as increased elongation at break of approximately 130% compared with neat polymer. Good plasticizing efficacy of DBUA toward PVC has also been revealed by differential scanning calorimetry analysis. Thus, the introduction of DBUA (20% and 30%) into PVC significantly reduced its glass transition temperature by 64.8 and 91.4 °C, respectively. The results of thermal gravimetric analysis revealed reduced thermal stability of PVC/DBUA blends compared to neat PVC, as well as polymer compositions containing common plasticizer bis(2-ethylhexyl)phthalate (BEHP). However, the thermal degradation point of plasticized material (217 °C) still remained higher than the actual temperature of its processing by common methods. DBUA plasticizer was also found to have higher volatility, but better resistance to migration from PVC films, compared to PVC/BEHP blends. The biodegradability of DBUA determined by primary biodegradation test CEC L-33-A93 was found to be 92.6% after 21 days. Overall,

the obtained results indicate that tertiary fatty amide DBUA is promising eco-friendly plasticizer for PVC which combines good low-temperature performance, high biodegradability, as well as resistance to migration from polymer matrix.

Introduction

Polyvinyl chloride (PVC) is an economical and versatile thermoplastic polymer widely used in building and construction industry, automotive industry, as well as in healthcare sector. PVC global demand is expected to grow and reach 50 million tons in 2022 having growth rate per year of about 5%. Plasticizers are usually added to PVC to an extent of 30 to 50 weight percent (wt%) in order to facilitate melt processing and make it flexible enough for a broad range of applications such as tubing systems, automotive parts, wire and cable insulations, food packaging, drink bottles, and children toys [1, 2]. Until recently, phthalic acid esters were the most common plasticizers for PVC. However, these compounds are known to leach out from PVC articles over time and diffuse into air, water and soil. In nature, phthalates are not easily removed by hydrolysis or photolysis. Numerous studies have shown that phthalates are reproductive and development toxicants, as well as potential carcinogens [1]. Moreover, the most commonly used industrial plasticizer, bis(2-ethylhexyl) phthalate (BEHP) and its dominant metabolites, mono (2-ethylhexyl) phthalate and phthalic acid, were found to produce adverse developmental, neurological, respiratory, and immune effects in humans [3]. Therefore, many countries such as the USA and European Union have restricted BEHP utilization in flexible PVC products.

Extensive research has been carried out to develop new non-toxic plasticizers. A number of petroleum and natural resource-based substances have been identified as alternative plasticizers for PVC, including octyl esters of terephthalic, trimellitic, adipic and sebacic acids, acetyl tributyl citrate, dipropylene glycol dibenzoate, as well as epoxidated soybean oil, epoxidated fatty acid esters, acetylated monoglycerides of fully hydrogenated or epoxidated castor oil [1, 2, 4–7]. These compounds were found to be eco-friendly in nature due to their biodegradability, as well as low volatility and high migration resistance. However, the plasticized PVC compositions have

serious drawback such as high susceptibility to microbial attack, and by fungi in particular [8]. Many fungi use ester compounds as a source of nutrient carbon. Loss of plasticizer from PVC due to microbial degradation results in brittleness, shrinkage, and ultimately failure of the polymer article in its intended application. Thus, the design of novel plasticizers for PVC which combine low environmental toxicity, high plasticization efficiency and resistance to fungal attack seems a very promising approach to develop flexible polymers with significantly improved long-term performance.

Analysis of the literature data indicated that some tertiary amides of fatty acids could satisfy to such requirements. In particular, morpholide and *N,N*-dibutylamide of oleic acid were found to have low-temperature plasticizing properties on PVC comparable to those of commonly used adipate and sebacate esters [9–11]. Savvashe et al. [12] reported synthesis of new primary plasticizer for PVC based on ester-amide of ricinoleic acid by a two-step reaction with dibutylamine and benzoic acid. PVC composition containing 40 phr of plasticizer demonstrated significant decrease in tensile modulus (by 88%), flexural modulus (by 78%), and glass transition temperature (by 99 °C), as well as increase in elongation at break by about 35 times, compared to neat PVC. However, high antifungal activity has been detected for tertiary amides of the C₉ to C₁₂ straight-chain fatty acids [11]. One of the best-known antifungal fatty acids is undecenoic acid, which is a pyrolysis product of ricinoleic acid from castor oil [13]. Moreover, some undecenoic acid derivatives such as *N*-undecenoyl morpholine and 1-monoundecenoyl glycerol were also found to inhibit fungal growth [11, 14]. However, plasticizing efficacy of tertiary amides of undecylenic acid on PVC has not yet been studied.

In this article, *N,N*-dibutylundecenamide (DBUA) has been synthesized and studied as potential eco-friendly plasticizer for PVC. This new plasticizer was characterized in terms of biodegradability, volatility and resistance to migration from polymer matrix, as

well as its impact on mechanical and thermal properties of PVC.

Materials and methods

Materials

Following chemicals were used for the synthesis: undecenoic acid (98%), dibutylamine (99.5%), thionyl chloride (97%), chloroform (99%), dichloromethane (99.8%), 1,2-dichloroethane (99.8%), hydrochloric acid (37%) (Sigma-Aldrich). Suspension polyvinyl chloride KSF-70 was purchased from Karpat-naftochim (Ukraine).

Synthesis of *N,N*-dibutylundecenamide (DBUA)

To the stirred solution of undecenoic acid (25 g, 0.13 mol) in 200 ml of chloroform were added thionyl chloride (12 ml, 0.16 mol) and few drops of triethylamine. The mixture was brought to a boil for 6 h. Chloroform was distilled off, and residual volatile products were removed under vacuum of 10 mbar at 50 °C.

The solution of dibutylamine (12.9 g, 0.1 mol) and triethylamine (10 g, 0.1 mol) in 150 ml of dichloromethane was cooled in an ice bath. To this stirred mixture was added dropwise crude undecenoyl chloride. The reaction was carried out for 1 h at 0–5 °C and 3 h at room temperature. The mixture was then washed with water (200 ml), diluted hydrochloric acid (5%, 2 × 100 ml) and water solution of 10% potassium hydroxide (200 ml). The solution of product in dichloromethane was dried over sodium sulfate. Dichloromethane was removed by distillation. The prepared low viscous oily product of light yellow color was dried in vacuum 10 mbar at 70 °C.

The structure of synthesized compound was confirmed by nuclear magnetic resonance (NMR) technique. ¹H NMR spectrum was recorded in CDCl₃ on a Varian Gemini-2000 (400 MHz) spectrometer.

¹H NMR (400 MHz, CDCl₃) δ: 0.93 (t, 6H, CH₃), 1.3 (m, 14H, (CH₂)₅, -NCH₂CH₂CH₂), 1.49 (m, 4H, NCH₂CH₂), 1.63 (m, 2H, -CH₂CH₂CO-), 2.03 (m, 2H, CH₂ = CH-CH₂-), 2.28 (t, 2H, -CH₂CO-), 3.2 (t, 2H, NCH₂), 3.3 (t, 2H, NCH₂), 4.94 (m, 2H, CH₂ = CH-), 5.82 (m, 1H, CH₂ = CH-).

Preparation of plasticized PVC films

PVC solutions in dichloroethane were prepared in concentration of 5 g/100 ml. To this solution was added plasticizer DBUA at plasticizer-to-PVC ratios of 20 to 80, 30 to 70, and 40 to 60 wt%. The solutions were poured onto glass support and the solvent evaporated at room temperature for 24 h, revealing transparent PVC/DBUA composite films. Residual solvent was removed under vacuum of 10 mbar at 60 °C for 12 h. The thickness of polymer films was approximately 300 μm.

Pure PVC films, as well as plasticized PVC films containing 30 wt% of common plasticizer BEHP, were also prepared for control experiments.

Characterization of PVC/DBUA composite films

The vibrational properties of plasticized PVC compositions were studied using a Vertex-70 Bruker (Germany) Fourier transform infrared (FT-IR) spectrometer equipped with a DTGS detector. Polymer films were placed into contact with the single reflection diamond ATR (Attenuated Total Reflection) crystal, and the spectra were collected over the range of 400–4000 cm⁻¹ at a resolution of 1 cm⁻¹.

Tensile tests were conducted at ambient condition according to the ISO 527-1 and ISO 527-3 standards using the universal testing machine 2054 R-5 equipped with a load cell of 500 N. Five specimens with the dimension of 100 × 10 mm were cut into dog-bone shapes from the fabricated samples. The tensile load was applied at a constant displacement rate of 2 mm/min. The Young's modulus *E* for each sample was calculated as the slope of the linear part of the stress-strain curve.

Thermal gravimetric analysis (TGA) was made in air using a Q-1500D thermal analyzer. About 100 mg of each sample was heated from 30 to 700 °C with a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) analyses were performed from -90 to 150 °C on a TA Q2000 calorimeter with a heating rate of 20 °C/min.

To evaluate the resistance of plasticizer to migration, PVC/DBUA films of 80 × 80 mm size were placed between two lists of filter paper. The sandwiched materials were kept in contact by placing them between glass plates. The migration of plasticizer was studied at 25 °C over a 21-days test period.

The loss of plasticizer was determined gravimetrically as a percentage of its total content in PVC composite film. The volatility of plasticizer was determined by the activated carbon method A [15]. In this test method, the plasticized PVC films (in the form of disks 50 mm in diameter and 1 mm in thickness) were kept in contact with the activated carbon (with a grain-size of about 4–6 mm) at 70 °C for 24 h. The loss of sample mass Δ_m was calculated from the equation:

$$\Delta_m = (m_0 - m_1) / m_0 \times 100$$

where m_0 is the mass of the test specimen in grams, and m_1 is the mass of the test specimen after thermal treatment.

The biodegradability of plasticizer DBUA was estimated by using a primary biodegradation test CEC L-33-A93 "Biodegradability of Two-Stroke Cycle Outboard Engine Oils in Water" [16]. The CEC method consists of measuring the loss of extractable hydrocarbon in tested materials (depletion of $\text{CH}_2\text{-CH}_3$ bonds) using infrared absorbance of specific IR bands, and relating it to a biodegradation level in % of loss.

Following water solutions of inorganic salts were prepared. Solution A: KH_2PO_4 (8.5 g), K_2HPO_4 (21.75 g), $\text{Na}_2\text{HPO}_4 \times 2 \text{H}_2\text{O}$ (33.4 g), NH_4Cl (15 g) / 1 L H_2O . Solution B: $\text{MgSO}_4 \times 7\text{H}_2\text{O}$ (22.5 g) / 1 L H_2O . Solution C: $\text{CaCl}_2 \times 2\text{H}_2\text{O}$ (36.4 g) / 1 L H_2O . Solution D: H_3BO_3 (0.75 g), $\text{FeSO}_4 \times 7 \text{H}_2\text{O}$ (3 g), $\text{ZnSO}_4 \times \text{H}_2\text{O}$ (0.1 g), $\text{MnSO}_4 \times 4 \text{H}_2\text{O}$ (0.5 g), $\text{CuSO}_4 \times 5 \text{H}_2\text{O}$ (0.05 g), CoSO_4 (0.1 g), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \times 4 \text{H}_2\text{O}$ (0.05 g) / 1 L H_2O . Inorganic substrate was prepared by mixing solutions A, B, C, D (per 1 mL of each) followed by dilution with water to the volume of 1 L. The control material RL 130 (H. Krüger Prüfmaschinenbau) was used as received from the manufacturer, without further purification.

Mother liquors of tested material (DBUA), as well as control material (RL 130), were prepared by dissolution of each substance (15 g) in 100 ml of CCl_4 . The water solutions of mercury (II) chloride (0.03 M) and hydrochloric acid (1 M) were also prepared. Carbon tetrachloride (99.5%, Sigma-Aldrich) was used as extractant.

Sewage sludge from local wastewater treatment plant was used as inoculant. The concentration of bacterial colonies was 10^5 CFU/mL. Inoculated samples (21 days flasks, 3 solutions of each) were prepared by mixing of inorganic substrate (150 ml)

with inoculant (1 mL) followed by addition of 0.05 mL of mother liquor of DBUA or control material. Sterilized samples (poisoned flasks, 2 solutions of each) were prepared by mixing of inorganic substrate (150 mL) with 0.03 M water solution of HgCl_2 (1 mL) followed by addition of 0.05 mL of mother liquor of tested material or control material.

The vessels closed with pure cotton swabs were incubated in dark place at 25 ± 1 °C at constant stirring with rotational speed 2 to 3.7 s^{-1} for 21 days. Inoculated non-incubated samples (0-day flask, 3 solutions of each) were prepared by mixing the inorganic substrate (150 mL) with the inoculant (1 mL) followed by the addition of 0.05 mL of mother liquor of DBUA or control material. Neutral samples were prepared by mixing an inorganic substrate (150 mL) with an inoculant (1 mL). Non-incubated samples were tested as prepared. Contents of flasks containing both incubated and non-incubated samples were subjected to ultrasonic irradiation at 20 to 40 kHz for 2 min at 25 °C. In each flask, 1 mL of 1 M HCl and 30 g of NaCl were added. The mixtures were stirred until the salt was completely dissolved. Then, 25 mL of extractant was added, and the flask was vigorously shaken for 2 min. The content of each flask was transferred into closed separating funnel and was left to settle to ensure complete phase separation. The organic phase (extract) was then analyzed by infrared spectroscopy measuring the absorption value of C-H stretching vibrations at $2930 \pm 10 \text{ cm}^{-1}$.

Residual content of the tested substance (R_T) was calculated using the formula:

$$R_T = \frac{(D_{T21} - D_N) \cdot 100}{D_{T0}} \quad (1)$$

where D_{T21} — absorption value of the tested sample after incubation, D_N — absorption value of the neutral solution, D_{T0} — adsorption value of non-incubated tested sample which is considered as 100% substance.

Residual content of sterilized sample (R_S) was calculated by similar manner:

$$R_S = \frac{(D_{S21} - D_N) \cdot 100}{D_{T0}} \quad (2)$$

where D_{S21} — absorption value of sterilized sample after standing for 21 days, D_N — absorption value of the neutral solution, D_{T0} — adsorption value of non-incubated tested sample.

Biodegradation of the tested material was calculated as follows:

$$B_T = \frac{(R_S - R_T) \cdot 100}{R_S} \quad (3)$$

Results and discussion

Infrared characterization of PVC/DBUA compositions

IR spectrum of neat PVC (Fig. 1) contains the following main characteristic peaks: C-H stretching vibrations from CHCl at 2966 cm^{-1} , asymmetric CH_2 stretching vibrations at 2911 cm^{-1} , methylene deformation at 1425 cm^{-1} , C-H deformations from CHCl at 1330 and 1253 cm^{-1} , C-C stretching vibration at 1094 cm^{-1} , methylene rocking vibration at 957 cm^{-1} and C-Cl stretching vibrations in the region $600\text{--}700 \text{ cm}^{-1}$. The bands located at 607 and 634 cm^{-1} are attributed to long planar syndiotactic sequences [17–20]. The broad band between $670\text{--}710 \text{ cm}^{-1}$ region is attributed to carbon–chlorine stretching of noncrystalline structures (meaning two possible isotactic and syndiotactic conformations of C-Cl pairs) in PVC [17, 18].

In the IR spectrum of DBUA plasticizer, small peak at 3076 cm^{-1} is assigned to the stretching vibrations of C = C-H carbon–hydrogen bonds. The strong bands in the $2800\text{--}3000 \text{ cm}^{-1}$ region are assigned to symmetric and asymmetric stretching vibrations of C-H bonds in CH_2 and CH_3 groups (CH_2 asymmetric stretching vibrations at 2926 cm^{-1} , CH_2 symmetric stretching at 2854 cm^{-1} , CH_3 asymmetric stretching vibration at 2956 cm^{-1} and CH_3 symmetric stretching at 2872 cm^{-1}) [21]. Carbonyl band ($-\text{CO}-\text{N} <$) of tertiary amide group is observed at 1639 cm^{-1} which is overlapped with the peak of C = C stretching vibration [21, 22]. The bands at 1462 and 1421 cm^{-1} are assigned to C-H bending vibrations of methylene groups. The band at 1373 cm^{-1} belongs to symmetric bending vibrations of CH_3 groups. In the low-frequency region, out-of-plane bending vibrations of C = C-H carbon–hydrogen bonds at 991 and 908 cm^{-1} are observed, as well as methylene wagging at 731 cm^{-1} [21].

In the IR spectrum of PVC/DBUA composites (Fig. 1) containing 20 and 30% DBUA, the characteristic peak of carbonyl band of tertiary amide group

shifted by 7 cm^{-1} to lower frequencies. At 40% DBUA content, the shift of carbonyl band was lower (5 cm^{-1}). It should be noted that similar changes were observed in IR spectra of PVC compositions plasticized with common phthalate and succinate esters [19, 23, 24], as well as ester-amide of ricinoleic acid [12]. According to [24], the changes in carbonyl wavenumber shifts become smaller with increasing the plasticizer content to 40–50% which can be explained by reaching a saturation point for effective interactions due to steric effect of long alkyl radicals.

Moreover, the intensity of the PVC band at 607 cm^{-1} decreases slightly with the introduction of DBUA (20 and 30%) confirming the perturbation of the carbon–chlorine stretching vibrations of long planar syndiotactic sequences. For PVC/DBUA (40%), the band at 613 cm^{-1} , assigned to amorphous region of the PVC, is then more visible and the band previously observed at 634 cm^{-1} shifts to 636 cm^{-1} . These results indicate the presence of molecular interactions with the long planar syndiotactic sequences of the PVC, thus confirming the crystallinity of the composites decreases with the introduction of the plasticizer. Such a result is consistent with reported XRD study of PVC plasticized by ester-amide of ricinoleic acid showing a decrease in polymer crystallinity [12]. Let us finally notice that the broad band at 690 cm^{-1} which is assigned to C-Cl stretching of noncrystalline structures in PVC shifted to 692 cm^{-1} in the spectra of PVC/DBUA compositions (Fig. 1) and the C-C stretching modes of PVC chains in PVC/DBUA compositions presents a more pronounced band at 1102 cm^{-1} (previously centered at 1097 cm^{-1}) most likely resulting from an increased mobility of short macromolecular segments (Scheme 1).

Two possible mechanisms of PVC plasticization are widely discussed in the literature. The first one involves hydrogen bonding between carbonyl group of the plasticizer and acidic hydrogen Cl-C-H of the polymer [23–27]. The repeating unit of PVC contains α -hydrogen $-\text{CHCl}$ and can be considered as a weak “acid” or proton donor. The molecule of plasticizer contains “basic” or proton acceptor group, in particular carbonyl group of tertiary amide, ester or ketone allowing for weak acid–base interactions between PVC and the polar group of a plasticizer [26]. On the other hand, every repeating unit in the PVC polymer chain contains a polarized carbon–chlorine bond which may interact with polar parts of plasticizers via

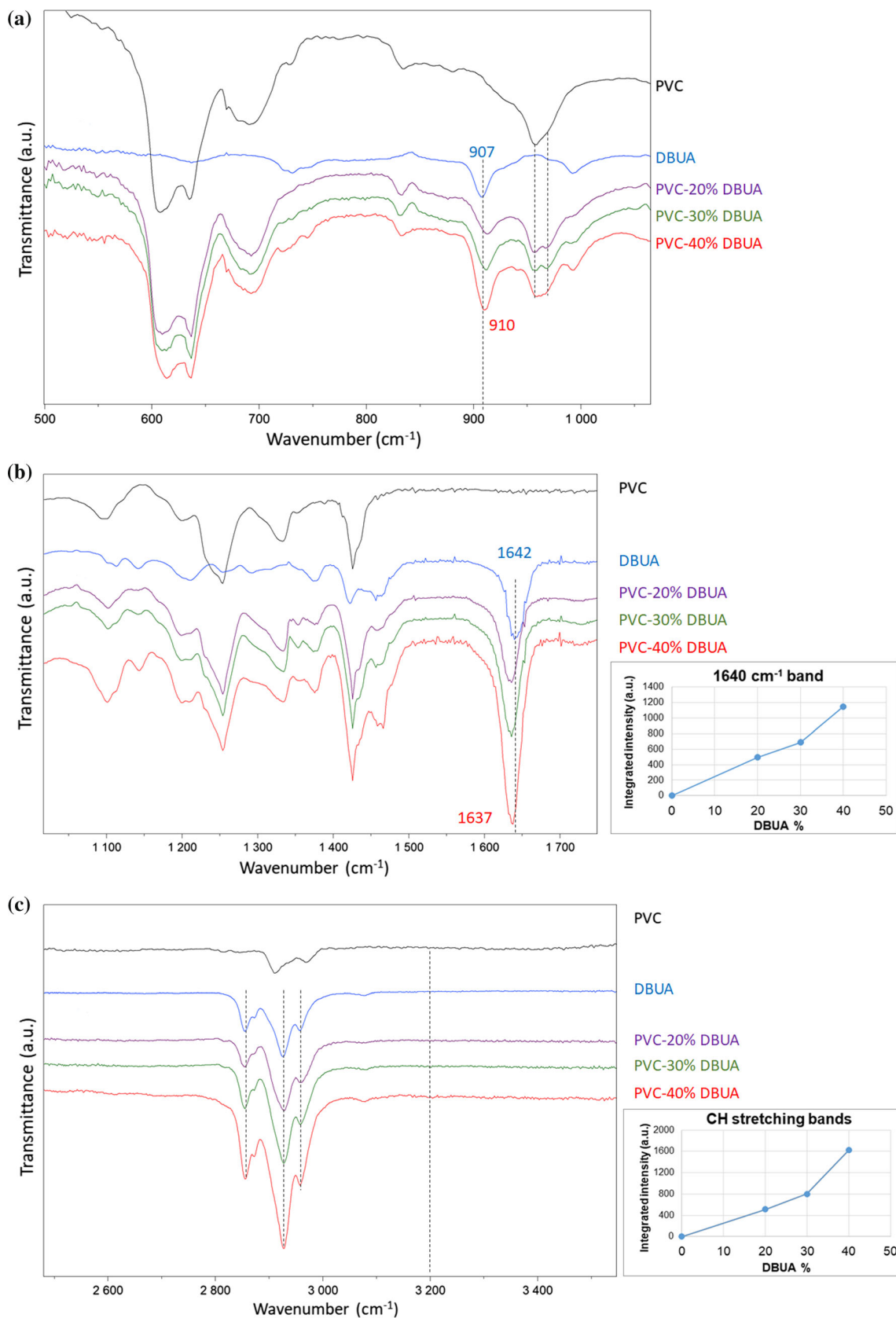
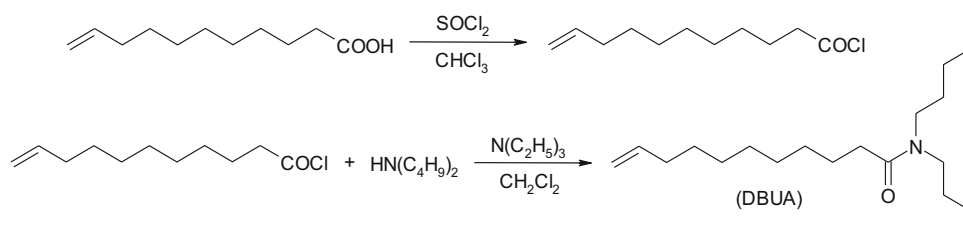
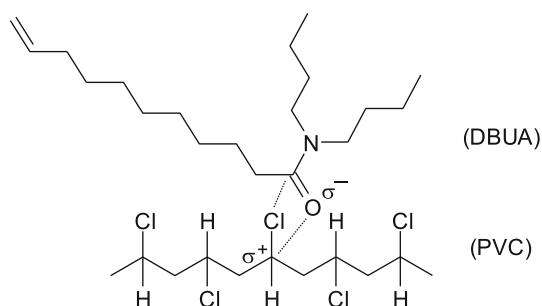


Figure 1 IR spectra of PVC/DBUA compositions in the range 500–1000 cm^{-1} (a), 1000–1700 cm^{-1} (b), 2600–3400 cm^{-1} (c).

Scheme 1 Synthesis of plasticizer DBUA.

dipole–dipole interactions [18, 28]. Thus, the second proposed mechanism of PVC plasticization is in the formation of complexes between C = O and C–Cl groups in amorphous PVC chain segments [18, 28].

Taking into account appreciable changes in the peaks position of carbonyl band of DBUA plasticizer, as well as carbon–chloride bands of PVC in the IR spectrum of PVC/DBUA compositions (Fig. 1), the formation of the complex between C = O and C–Cl groups seems the more probable physicochemical interaction between polymer and plasticizer (Scheme 2). However, the peak of C–H deformations from Cl–C–H group of PVC at 1330 cm^{-1} has also shifted to 1332 and 1334 cm^{-1} in the spectra of plasticized samples containing 20 and 30% DBUA, respectively. Moreover, the peaks at 1076 and 908 cm^{-1} which are assigned to stretching and bending vibrations of C = C–H carbon–hydrogen bonds of DBUA, noticeably shifted to 1080 and 912 cm^{-1} in the spectra of PVC/DBUA compositions (Fig. 1). Overall, these changes may indicate the formation of more disordered phase in plasticized PVC matrix leading to weaker interactions between polymer macromolecules.

**Scheme 2** Possible physicochemical interactions between PVC and DBUA plasticizer.

Mechanical and thermal analysis of PVC/DBUA compositions

The neat PVC is a tough and hard material due to the intermolecular physicochemical interaction between chlorine and hydrogen atoms. Ester-based plasticizers are known to act through the solvation of polar PVC groups in amorphous regions thus weakening the intermolecular interactions and acting as spacers between the former links [12]. An increase in the free volume of the system causes a plasticizing effect resulting in reduction of the tensile modulus and the glass transition temperature of polymer composition, as well in its extended elongation at break.

Tensile properties were measured to assess the differences in ductile behavior between neat PVC and PVC/DBUA films. The obtained results are summarized in Table 1. The addition of 20% of DBUA caused significant decrease in tensile strength of PVC by 54% and Young's modulus by 57%, whereas elongation at break increased by about 5 times. Such changes in tensile properties indicate an improvement of material elasticity typical for plasticized PVC [6, 12]. Further increase of DBUA content in composite films led to greater plasticizing effect (Table 1). Thus, tensile strength and tensile modulus of PVC/DBUA (30%) samples decreased by 79% and 91%, respectively, and elongation increased by about 11 times. It is noteworthy that elongation at break was higher than at maximum load for all films. The last fact indicates that the breaking phenomenon of the films is a ductile failure type since the stress at break was lower than at yield point. Polymeric materials are classified by ASTM as rigid if Young's modulus exceeds 700 MPa, semi-rigid if it is between 70 and 700 MPa, and soft if it is below 70 MPa [29]. According to this classification, PVC/DBUA compositions containing 20 and 30% of plasticizer are rigid and semi-rigid, respectively, whereas PVC/DBUA (40%) may be considered as a soft material (Table 1).

Table 1 Mechanical properties for PVC/DBUA films

Sample	σ_m^a , MPa	E^b , MPa	ε_b^c , %	ε_m^d , %
PVC	54.5 ± 0.4	2185 ± 31	4.5 ± 0.4	4.3 ± 0.2
PVC/DBUA (20%)	25.2 ± 2.9	931 ± 91	22.6 ± 13.4	20.5 ± 12.5
PVC/DBUA (30%)	11.5 ± 1.6	202 ± 46	49.7 ± 12.0	47.3 ± 11.1
PVC/DBUA (40%)	6.9 ± 1.5	11 ± 2	132.5 ± 21.6	130.7 ± 21.8

^a σ_m : tensile strength^b E : Young's modulus^c ε_b : elongation at break^d ε_m : elongation at maximum load

Overall, the results of mechanical testing showed greater effect of DBUA on the tensile properties of PVC, compared to other similar compounds such as *N,N*-dibutylamides of oleic acid and palmitic acid [10], morpholide of oleic acid [9], as well as *N,N*-dibutylamide of benzoylated ricinoleic acid [12]. Probably, the higher plasticizing efficacy of DBUA is caused by its lower viscosity due to the smaller molecular size allowing higher plasticizer mobility in the polymer matrix. Thus, the measured viscosity values of DBUA and common plasticizer DEHP were 16 and 48 cP, respectively.

According to TGA data, DBUA is thermally stable to at least 219 °C (Fig. 2a, Table 2). The peak mass loss temperature is 305 °C. An introduction of DBUA into PVC significantly reduced its thermal degradation point (5% weight loss) by 40 °C (Fig. 2b, Table 2). The peak mass loss temperature in DTG curve of PVC/DBUA (40%) composition is 226 °C. PVC composition containing 40% of common plasticizer BEHP showed the thermal stability similar to neat polymer (Table 2). The reduced thermal stability of PVC/DBUA blends is probably caused by weak basic properties of tertiary amide DBUA which can accelerate dehydrochlorination of PVC at elevated temperature.

In order to evaluate thermal behavior of PVC/DBUA blends in the actual temperature range of PVC processing, short-term high-temperature stability analysis of plasticized PVC samples was carried out. Weight loss was detected from the TGA curves at 160, 180 and 200 °C, which are common PVC processing temperatures [29, 30]. PVC compositions with common plasticizer BEHP were used as reference samples. PVC/DBUA blends containing 20 and 30% plasticizer showed significantly lower weight loss than corresponding PVC/BEHP samples. At higher plasticizers content (40%), the opposite effect was observed (Table 3).

When the samples were subjected to an isothermal condition at 180 °C for 20 min, which is common processing mode for plasticized PVC compositions [12], the thermal stability of PVC/BEHP blends was found better than PVC/DBUA. The obtained results are summarized in Table 3. Despite almost three times higher weight loss of PVC/DBUA samples containing 20 and 30% DBUA, this value (around 7%) is not critical.

The loss of plasticizers from PVC blends was also evaluated using activated carbon method [15] upon

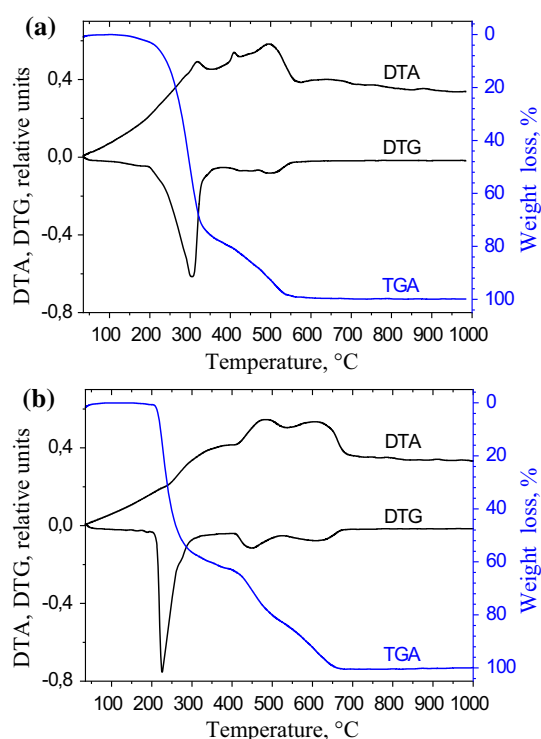
**Figure 2** TGA curves of DBUA (a) and PVC/DBUA (40%) (b) in air.

Table 2 TGA data for plasticized PVC compositions

Sample	$T_{\Delta m=5\%}$, °C	$T_{\Delta m=10\%}$, °C	$T_{\Delta m=20\%}$, °C	$T_{\Delta m=50\%}$, °C
DBUA	219	241	264	300
PVC	256	263	276	301
PVC/DBUA (20%)	217	222	229	267
PVC/DBUA (30%)	216	221	229	269
PVC/DBUA (40%)	217	222	231	269
PVC/BEHP (40%)	254	267	279	299

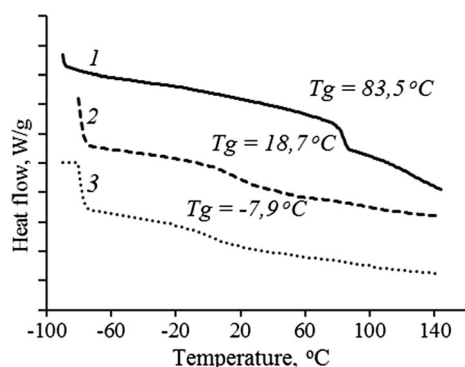
Table 3 Weight loss in plasticized PVC compositions (10 °C/min temperature ramp)

Sample	Weight loss, %			
	10 °C/min temperature ramp			Isothermal mode
	160 °C	180 °C	200 °C	
PVC/DBUA (20%)	0.47	0.77	1.31	7.1
PVC/BEHP (20%)	0.93	1.38	1.89	2.5
PVC/DBUA (30%)	0.13	0.35	0.71	7.0
PVC/BEHP (30%)	0.51	0.77	0.99	2.3
PVC/DBUA (40%)	0.39	0.65	1.2	12.1
PVC/BEHP (40%)	0.2	0.3	0.48	2.0

heating for 24 h at 70 °C. The weight loss was found to be 1.3% for PVC/BEHP (30%) and 6.8% for PVC/DBUA (30%) blends. The obtained results indicated medium volatility of the amide plasticizer DBUA in experimental conditions.

The main function of plasticizer is to reduce tensile modulus of PVC at the application temperature by lowering its glass transition temperature (T_g). The physicochemical interactions between the plasticizer and the PVC reduce the inter-chain attractions in the polymer, resulting in an increase in free volume and greater mobility of the macromolecular segments.

Glass transition curves obtained for PVC/DBUA compositions are illustrated in Fig. 3. The neat PVC

**Figure 3** Glass transition curves: 1—PVC, 2—PVC/DBUA (20%), 3—PVC/DBUA (30%).

has glass transition temperature (T_g) of 83.5 °C (Fig. 3, curve 1). The introduction of DBUA (20%) to PVC significantly reduced T_g value by 64.8 °C (Fig. 3, curve 2). Further increase in DBUA content to 30% shifted T_g to negative temperatures (Fig. 3, curve 3), which is a remarkable decrease of 91.4 °C. However, as the glass transition broadened, it was therefore difficult to determine on DSC curve for PVC/DBUA (40%) sample (not shown in figure). Such a result is in agreement with highly plasticized PVC compositions [24]. Thus, the results of DSC study agreed with mechanical testing data and confirm high plasticizing effect of the tertiary amide of undecenoic acid on PVC, similar to those of the common plasticizer bis(2-ethylhexyl) phthalate [29, 31–33], succinic acid diesters [24, 25], as well as recently reported new ester-amide plasticizer based on ricinoleic acid [12]. It is worth noting that DBUA contains only one polar carbonyl group, in contrast to commonly used bifunctional plasticizers. The high plasticizing efficacy of this compound is probably caused by higher partial negative charge on the carbonyl oxygen of tertiary amide group, compared to ester carbonyl. This may cause stronger electrostatic interaction between DBUA and C–Cl groups of PVC (Scheme 2). Moreover, DBUA plasticizer is assumed to have much higher mobility in polymer matrix than common diesters due to its significantly lower viscosity.

Migration resistance and biodegradability of DBUA plasticizer

Migration of plasticizers from flexible plastics to other solid materials is highly dependent on the diffusivity of the plasticizer in polymer matrix, and diffusivity is inversely influenced by polymer–plasticizer interactions [34]. The traditional plasticizers, especially phthalate esters, are known to have a tendency to migrate from PVC when in contact with an unplasticized surfaces [1, 4, 7, 34]. This behavior obviously has an extremely negative environmental impact. Moreover, plasticizer migration can significantly reduce the flexibility of PVC articles resulting in noticeable shrinkage [1, 2, 35].

Under experimental conditions, control PVC/BEHP (30%) samples lost 1.1% of plasticizer after 30 days exudation. The PVC/DBUA (30%) films showed better migration resistance with total plasticizer loss of 0.6%. Thus, DBUA plasticizer demonstrated lower migration from PVC film, comparable with those for bifunctional ester-amide plasticizer based on ricinoleic acid [12], although the latter has much higher viscosity, as well as molecular weight. As it was earlier noted, good retention of DBUA in PVC matrix may be caused by the formation of relatively stable complex between amide carbonyl and C–Cl groups.

Numerous studies have shown that microorganisms play a major role in the degradation of phthalates in the environment [36, 37]. It should also be noted that efficient mineralization of phthalates is always carried out only by mixed microbial cultures consortia. However, it was estimated that a significant amount of DEHP remains in sludge-amended soil for extended periods of time (almost 40% after 1 year) despite the presence of microorganisms capable of degrading the compound [3]. An aerobic biodegradation of different fatty amides has been studied by using ready biodegradability test method described in the OECD Guidelines of Testing of Chemicals [38]. The obtained results indicated that two bacteria, *Pseudomonas aeruginosa* and *Pseudomonas putida*, in mixed culture accomplished complete mineralization of both primary and secondary fatty acid amides. However, these fatty acid amides degrading isolates were not able to decompose tertiary amides [38].

Figure 4 shows IR spectra of amide plasticizer DBUA before (1) and after 21 days incubation (3) in a

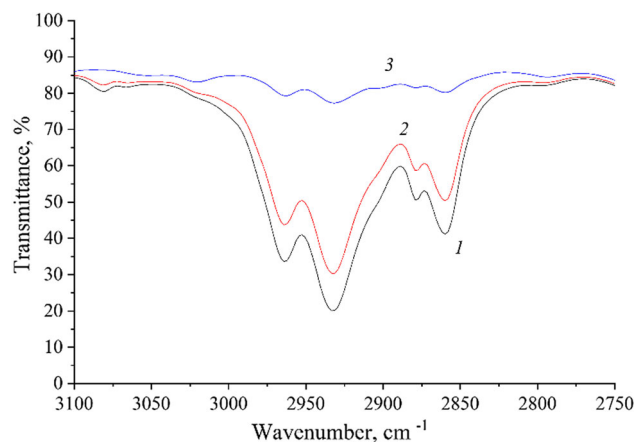


Figure 4 IR spectra of extracts after biodegradation testing of DBUA: 1—extract of non-incubated sample (D_{T0}), 2—extract of sterilized sample (D_{S21}), 3—extract of inoculated tested sample (D_{T21}).

primary biodegradation test. The main absorption bands corresponding to CH_2 asymmetric stretching vibrations at 2926 cm^{-1} , CH_2 symmetric stretching at 2854 cm^{-1} , CH_3 asymmetric stretching vibration at 2956 cm^{-1} and CH_3 symmetric stretching at 2872 cm^{-1} significantly decreased after completing the test. This result clearly indicates a deep degradation of alkyl chains of DBUA. The calculated biodegradation value B_T was 92.6%. Thus, the results of our study demonstrated high biodegradability of tertiary fatty amide-based plasticizer for PVC in the environment.

Conclusions

Tertiary amide of undecenoic acid, namely *N,N*-dibutylundecenamide (DBUA), has been synthesized by reaction of undecenoyl chloride and *N,N*-dibutylamine in methylene chloride in the presence of triethylamine. The viscosity of the synthesized compound was found to be three times lower than that of the common plasticizer BEHP. Homogeneous composite PVC/DBUA films containing 20, 30 and 40 wt% of tertiary amide were prepared by casting from dichloroethane solutions. The results of IR study indicate weak physicochemical interactions between polar $-\text{CH}-\text{Cl}$ groups of PVC and carbonyl groups of DBUA. According to results of mechanical testing, PVC/DBUA compositions containing 30% and 40% of DBUA have significantly reduced Young's modulus (over 90%), as well as increased elongation at

break (over 130%) compared to the neat polymer. This fact indicates strong plasticizing effect of tertiary fatty amide on PVC. The results of DSC study confirmed high plasticizing efficacy of DBUA. Thus, the introduction of DBUA (20 and 30%) into PVC significantly reduced T_g value by 64.8 °C and 91.4 °C, respectively.

According to TGA data, PVC/DBUA compositions have significantly reduced thermal stability (by 40 °C) compared to the neat polymer, as well as PVC blends containing common plasticizer BEHP. However, the thermal degradation point (5% weight loss) of PVC/DBUA samples (217 °C) still remained above the actual processing temperatures range (160–200 °C). In the isothermal conditions (180 °C, 20 min), PVC/DBUA blends containing 20 and 30% plasticizer showed moderate weight loss of about 7%. Similar plasticizer loss (6.7%) was determined by activated carbon method, after PVC/DBUA blends being exposed at 70 °C for 24 h. Overall, the results of thermal study indicate the availability of DBUA plasticizer for joint processing with PVC by common methods.

The high resistance of DBUA to migration from PVC films has also been demonstrated. Thus, under experimental conditions, PVC/DBUA (30%) composite films lost only 0.6% of plasticizer after 30 days exudation. This value is comparable to that of a recently reported bifunctional ester-amide plasticizer based on ricinoleic acid, although the latter has much higher viscosity, as well as molecular weight. The biodegradability of DBUA plasticizer determined by primary biodegradation test CEC L-33-A93 was found to be 92.6% after 21 days.

Thus, the results of this study clearly demonstrated that tertiary fatty amide DBUA is an efficient primary plasticizer for PVC, which has moderate volatility and high migration resistance. DBUA seems new promising eco-friendly plasticizer for PVC-based flexible plastics and protective coatings due to high biodegradability. Further studies are in progress to assess their antifungal activity, which may be an additional benefit of this plasticizer.

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