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Preparation, characterization and evaluation of new additives for PVC formulations

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Abstract

A new family of sulfur-containing plasticizers derived from oleic acid and thiopropionic acid has been developed. The synthesis is based on thiol–ene addition of thiopropionic acid to the double bond of oleic acid, followed by oxidation of the sulfide group to sulfone groups. The prepared compounds methyl 10(3-methoxy-3-oxobutanesulfonyl) octadecanoate (M3) and ethyl 10(3-ethoxy-3-oxobutanesulfonyl) octadecanoate (M4) were characterized by FT-IR and ^{1}HNMR. F1 and F2 are formulations of PVC with M3 and M4, respectively, in addition to F0 as blank with dioctyl phthalate (DOP) (40% wt).The mechanical properties and thermal analysis of the prepared formulations films were investigated. Also in this study we evaluated the antibacterial activity and antitoxic effect of the prepared compounds. It was found that the synthesized plasticizers M3 and M4 have plasticization effect similar to DOP on PVC. The prepared M3 and M4 were found to enhance activity on the inhibition zone of bacterial growth compared to DOP. M4 was found to be safe material since it's very active against VERO line cell with IC50 value 206.18 while DOP with IC50 value 197.06.

Keywords: Plasticizers, Oleic acid, Poly(vinyl chloride) (PVC), Antibacterial activity, Cytotoxicity.

1. Introduction

Polyvinyl chloride (PVC) is one of the most generally used and multipurpose synthetic polymers in the world [1,2]. PVC mixes with various additives, which determines by the aim application. These additives are mainly plasticizers, antioxidants, stabilizers, antifogging agents, antistatic agents, lubricants, flame retardants and impact modifiers [3-6].

Plasticizers are important additives used extremely in mollifying PVC properties [7], thus, soft PVC formulations are used in making a lot of unlike materials such as packing materials, electronic materials, medical devices, artificial leather and toys [8-12]. Plasticizers are compounds that can change a substance from rigid to relatively more flexible and softer compounds when we add plasticizers to it [13]. Moreover it can faster filler incorporation and dispersion, lowering the processing temperatures and enhancing flow properties [14-15]. Early studies on the phthalate plasticizers family such as di(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DOP),the most common plasticizers, confirm their negative effects on reproductive health and infant nutrition. When the phthalate plasticizers are used in a number of applications for example medical devices, food packaging and children's toys, there are changes in long-term properties of products when plasticizers was lost and also has a potential biological effect on the human body [16-18]. To resolve this problem, researches focused on different plasticizers based on azelate, benzoate, citrate, sebacate, adipate and other polymeric plasticizers, etc.[19-21]lately, there is an attention for natural-based plasticizers, particularly for derivatives of modified fatty acid (acetylated fatty esters, sulfonyl fatty esters, epoxidized oils, fatty acid polyesters)[22-27].

In this work, we synthesized methyl 10(3-methoxy-3-oxobutanesulfonyl) octadecanoate (M3) and ethyl

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10(3-ethoxy-3-oxobutanesulfonyl) octadecanoate (M4) as new plasticizers from 10-[(carboxyethyl)sulfanyl]octadecanoic acid (M1). All the prepared plasticizers were evaluated, added to PVC in different formulations and compared to that the commercial plasticizer dioctyl phthalate (DOP). On the other hand, (M3) and (M4) perform multifunctional properties such as antibacterial activity.

2. Experimental

2.1. Materials

Oleic acid (OA), Thiopropionic acid (TBA), dimethylformamide (DMF), ethanol 96%, p-toluenesulfonic acid monohydrate (TsOH), methanol, hydrogen peroxide 30% (H_2O_2),anhydrous magnesium sulfate ($MgSO_4$),ethyl acetate, sodium hydrogen carbonate ($NaHCO_3$), tetrahydrofuran (THF), dioctyl phthalate (DOP), PVC with a K value 72, All the materials and solvents without further purification were used as received.

2.2. Preparation of 10-[(carboxyethyl)sulfanyl] octadecanoic acid (M1)

OA (50 g, 0.176 mol), TBA (56 ml, 0.528 mol) and THF (42 ml) were mixed and stirred to get a homogeneous mixture. Then, the mixture was irradiated by Vilber Lourmat UV lamp at 6W-254 nm for 24h at room temperature. THF was evaporated by using rotary evaporator. Ethyl acetate was added to dissolve the reaction mixture and washed with distillated water (3 × 250 mL) and brine (2 × 250 mL) in separation funnel to remove the excess of TBA. The organic layer was dried by using $MgSO_4$ and filtered. Then the evaporation of the ethyl acetate was occurring by using rotary evaporator under reduced pressure. Finally neat thiolated oleic acid was obtained.

2.3. Preparation of 10-(carboxyethanesulfonyl) octadecanoic acid (M2)

The prepared M1(30g) was dissolved in ethyl acetate (90ml) and then H_2O_2 (0.39 mol) was added to the mixture in a round flask equipped with condenser and stirring for 30 min. Addition of (0.78mol) H_2O_2 was added again to the mixture and heated to 80 °With stirring for 24 h. The mixture was cooled down at room temperature and the product was washed several times in a separation funnel with an aqueous solution of sodium sulfite and then dried by using $MgSO_4$ and filtered. Finally the product (M2) was obtained by evaporating ethyl acetate using rotary evaporator.

2.4. Preparation of methyl 10(3-methoxy-3-oxobutanesulfonyl) octadecanoate (methanolysis of M2(M3))

A mixture of M2 (12g), methanol (36 ml) and p-Toluenesulfonic acid (0.2 g) were reacted together in a round-bottomed flask equipped with condenser at 70 °C for 12 h. Then, the excess of methanol was extracted by using rotary evaporator at reduced pressure. Ethyl acetate used to dissolve the obtained material and neutralized by washing with a $NaHCO_3$ solution (10 wt%). The solution transmits to a separation funnel and washed with brine and water (2 ×250 mL). Finally dried over $MgSO_4$ and filtered. Ethyl acetate was removed by using rotary evaporator to obtain the final product (M3).

2.5. Preparation of ethyl 10(3-ethoxy-3-oxobutanesulfonyl) octadecanoate (ethanolysis of M2 (M4))

A mixture of M2 (12g), ethanol (36 ml) and p-Toluenesulfonic acid (0.2 g) were reacted together in a round-bottomed flask equipped with condenser at 70 °C for 12 h. Then, the excess of ethanol was extracted using rotary evaporator at reduced pressure. Ethyl acetate used to dissolve the obtained material and neutralized by washing with a $NaHCO_3$ solution (10 wt%). The solution transmits to a separation funnel and washed with brine and water (2 ×250 mL). Finally dried over $MgSO_4$ and filtered. Ethyl acetate was removed by using rotary evaporator to obtain the final product (M4).

2.6.Characterization techniques of the prepared materials

Nuclear magnetic resonance (^{1}H NMR) spectra of the prepared additives was listed on Jeol ECA-500 run at 500 MHZ. $CDCl_3$ was used to dissolve in the prepared additives and the reference standard was tetramethylsilane **Infrared spectroscopy (FTIR)** spectra of the prepared additives were listed by JASCO FTIR 6100 using KBr pellets from 4000 to 400 cm^{-1}. **Antibacterial activity measurements** Antibacterial activities to gram-positive bacteria* (G^+) such as *Staphylococcus aureus* and gram-negative bacteria* (G^-) such as *Escherichia coli* were determined by Hioki 3522-50 LCR Hitester (Japan) by modified Kirby–Bauer disk diffusion technique **(Bauer, *et al.*, 1966)** [28]**.** Determination of

susceptibility of microorganisms to antimicrobial agents by using Mueller–Hinton agar. Measurements were doing at "Micro Analytical Center," Faculty of Science, Cairo University.

**Gram staining: is a staining method utilized to assort bacterial species into two large groups; gram-negative bacteria stained pink while gram-positive bacteria is stained violet*

Cytotoxicity assay the Potential cytotoxicity was tested using the method of MTT test (**Berridge M**, **et al, 1993**) [29] for their activity against (VERO) cell line. The test was achieved at the National Cancer Institute, Cancer Biology Department, Pharmacology Department and Cairo University.

2.7. Preparation of PVC films

To prepare the films, the prepared additives M3 and M4 (0.4g) were mixed with PVC (1 g), followed by the addition of THF (20 mL) as shown in table 1. The mixture was agitated until a homogenous solution was obtained. Films were obtained by casting this solution on pettrydish and leave untill the solvent was removed.

Table 1. Formulations of PVC films.

Formula / Name	B	F0	F1	F2
PVC (g)	1	1	1	1
DOP(g)		0.4		
M3(g)			0.4	
M4(g)				0.4

2.7.1. Characterization of the prepared additives as plasticizers in PVC formulations

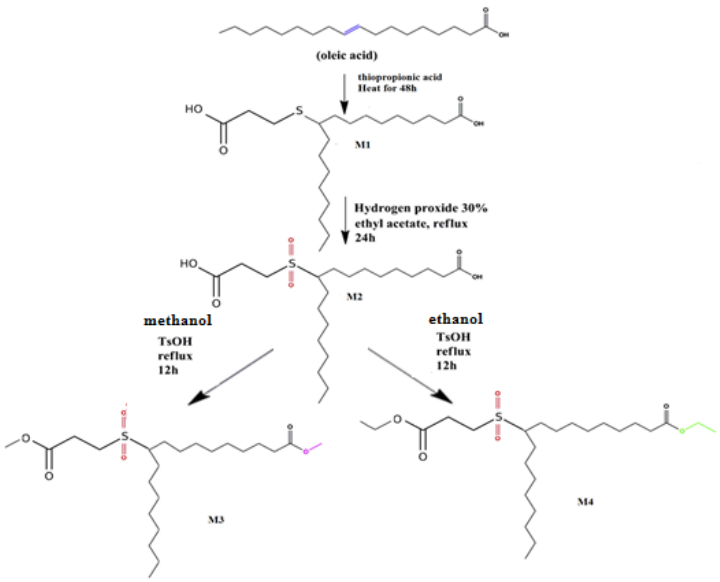
TGA analysis was determined via Shimadzu TGA-50 thermogravimetric analyzer, Colombia, EUA, at a heating rate of 10 °C/min in nitrogen atmosphere. **Differential scanning calorimetry analysis (DSC)** was carried on Shimadzu DSC-60 differential scanning calorimeter Columbia, EUA. All the prepared additives were heated/cooled by a scan rate of 10ºC/min over a temperature from -100 to 100 ºC in nitrogen atmosphere. **Mechanical properties** were carried on Zwick tensile testing machine (model Z010, Germany).**Volatility test** were carried out by placing F0, F1 and F3 (20 mm × 20 mm × 0.7 mm) in a convection oven for 24 h and 72 h at 70 °C, respectively. Then they were cooled to room temperature in a desiccator for another 2 h. The weight variations were noted before and after the treatment and volatility were determined from eq (1).Where W1 = initial weight of test specimen and W2 = final weight of test PVC specimen.

Weight loss (%) = [(W1 - W2)/ W1]×100 (1)

3. Results and discussion

3.1. M3 and M4 synthesis:

M3 and M4 were synthesized from OA and TBA. The structure of the synthesized additives was confirmed and characterized by IR and ^{1}HNMR spectroscopy. Scheme 1represented the synthetic technique of M3 and M4.



Scheme.1 Synthesis of M3 and M4 from OA.

3.2. Characterization of OA, M1, M2, M3 and M4

3.2.1. FTIR of OA, M1, M2, M3 and M4

The FTIR of OA, M1, M2, M3 and M4 are shown in Fig.1. By comparing the characteristic bands of M1 with OA could be assigned as follow; Beak at 3000 cm^{-1} related to vinyl group of OA (Fig.1a) could not be found in M1 (Fig. 1b) and appearance of new peak related to C-S band at 1250 cm^{-1} of M1 confirm that the reaction between TBA and OA was happened. In the spectra of M2 (Fig. 1c) a new beak around 1300 cm^{-1} related to sulfone group while in the spectra of M3 and M4 (Fig 1d and 1e) a broad beak from 2800-3800 cm^{-1} disappeared indicated to the esterification reaction occurred.

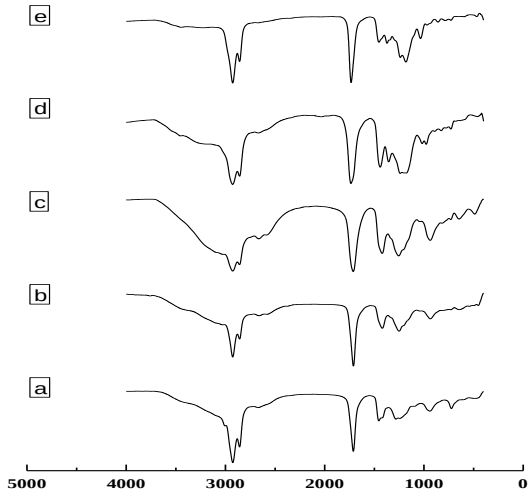


Fig.1. The FTIR spectra of OA (a) and prepared additives M1(b), M2(c), M3(d), M4(e).

3.2.2. ^{1}HNMR of OA, M1, M2, M3 and M4

Figure 2 (a, b, c, d and e) shows ^{1}HNMR of OA, M1, M2, M3 and M4, respectively. The protons of the prepared additives could be assigned as follow, In the comparison of OA (Fig. 2a) and M1 (Fig. 2b) spectrum there are disappearance of vinylic protons related to OA at 5.5 ppm and appearance of a new signal at 2.7 ppm related to methylene protons attached to sulfide (-S-CH_2-) group and new peak at 2.5 ppm related to methylene group attached to carboxylic acid. Peak at 2.7 ppm was shifted to3 ppm (Fig. 2c) after oxidation of sulfide to sulfone groups. Fig. 2d and e shows new peaks appeared at 3.9 and 4.1 ppm is related to methylene and methyl groups attached to ester groups, respectively.

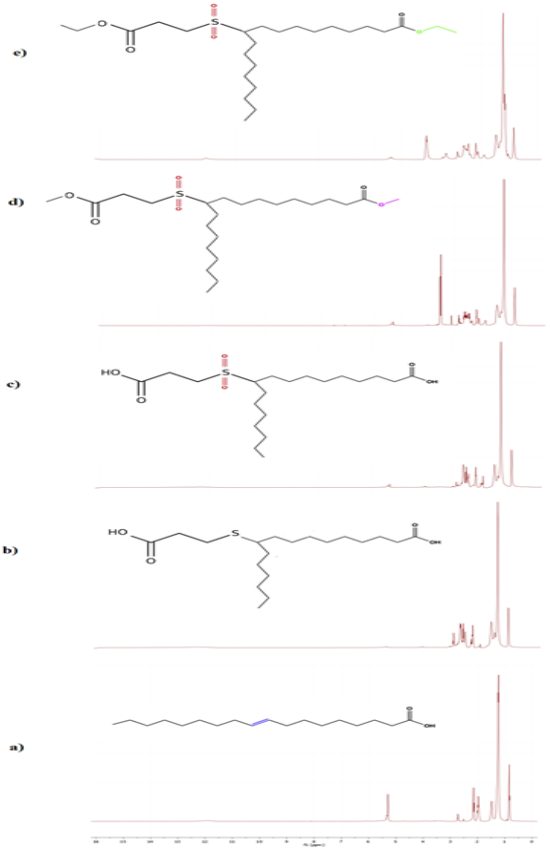


Fig.2. The ^{1}HNMR spectra of OA (a) and prepared additives M1(b), M2(c), M3(d), M4(e).

3.3. Characterization of the prepared formulations

3.3.1. DSC of the prepared formulations

Tg of un-plasticized PVC film (B) was 87^{o}C measured by DSC. DSC thermograms of the prepared formulations (F0, F1 and F2) shown in Figure 3. From the figure it can be perceived that the glass transition peak of F0 is approximately at 47^{O}C. From table 2 it can notice that the glass transition temperature (Tg) values of the PVC films (F1 and F2) decreased compared to the formula F0 that contains a commercial plasticizers DOP.

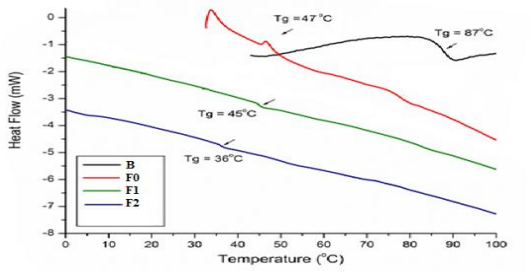


Fig.3. DSC analysis in glass transition temperature for the PVC films with different plasticizers.

Table 2. Glass transition temperatures of PVC films.

Samples	Glass transition temperature (^{O}C)Tg
B	87
F0	47
F1	45
F2	36

3.3.2. TGA of the prepared formulations

TGA curves of the prepared formulations F0, F1 and F2 are shown in Fig. 4. It is obvious that there is two-step of thermal degradation process related to all the curves. In the beginning of PVC degradation, HCl was the most volatile product at approximately about 225-310^{o}C is related to dehydrochlorination of PVC, with elimination of HCl and little chlorinated hydrocarbons [30]. In the second step there are degradation at about 450-470 ^{o}C probably attributed to cross-linking having the C = C bond. Table 3 summarizes the parameters of TGA, including decomposition temperature; $T_{5\%}$, $T_{10\%}$ and 80% weight loss temperature $T_{80\%.}$ With the addition of the plasticizers, the DOP or the prepared additives M3 and M4 the interaction between the chains of PVC reduced and the thermal stability of plasticized PVC films was lower than that of the pure-PVC film B without using thermal stabilizer. HCl from the degradation of PVC could also enhance the decomposition of the plasticizer. Because there are difference in thermal stabilities of plasticizers and differences in compatibility with the PVC chain, some differences and rules could also be found in the PVC decomposition films with various plasticizers.

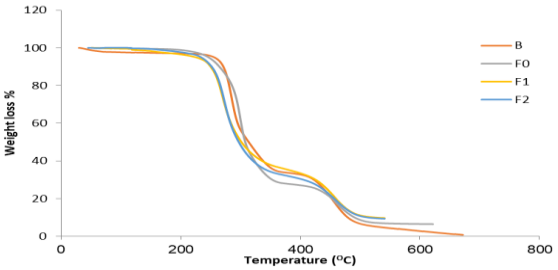


Fig.4. TGA curvesof formulations F0, F1 and F2.

Table 3.TGA data of PVC films

Samples	Temperature for specific weight loss			
	$T_{5\%}$(^{o}C)	$T_{10\%}$(^{o}C)	$T_{50\%}$(^{o}C)	$T_{80\%}$(^{o}C)
F0	246.54	264.77	307.92	453
F1	225.84	250.24	301.5	459.48
F2	234.28	251.92	297.16	456.83

3.3.3. Mechanical properties of the prepared formulations

Effect of M3 and M4 on mechanical properties of PVC composites

The elongation at break and tensile strength of different formulations B, F0, F1 and F2 were listed in table 4. It is clear that the tensile strength of PVC composites was improved with M3 and M4 addition. Also, the highest value of the tensile strength and the lowest elongation was related to B while the lowest value of the tensile strength and the highest elongation were achieved by F2 compared with F0. The elongation at break increases in F1 and F2. The obtained results reveal that the prepared compounds acts as plasticizers and their plasticizing effect may be arranged as follow: M4>M3 >DOP. This may be due to the prepared compounds have been diffused between PVC chains and reduce their interaction.

Table 4. Tensile properties, elongation at break data of PVC films.

Sample	Tensile strength (MPa)	Elongation at break (%)
B	27	20
F0	17.5	136
F1	13.2	149
F2	12	237

3.3.4. Volatility test

The volatility and exudation properties of plasticizers are an important factor on evaluating the migration of plasticizers. The amounts of exudation loss of DOP, M3 and M4 from PVC films were examined by determining the weight loss of the prepared films that were as follow: 1.11, 1 and 0.97 % after 24 h while after 72 h 2.23, 2 and 1.94 % for F0, F1 and F2 respectively (Fig. 5). These values showed that the prepared additives M3 and M4 had excellent compatibility with PVC.

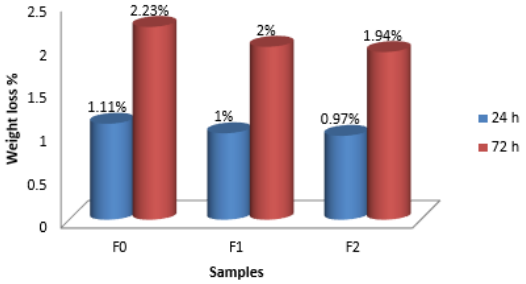


Fig.5. Weight losses of F0, F1 and F2 after volatilization for 24 h and 72 h at 70 °C

3.4. Antibacterial activity measurements

The antibacterial activities of DOP, M3 and M4 against *Staphylococcus aureus* (G^+) *and Escherichia coli* (G^-) are shown in Fig. 6 and listed in table 5. Figure 7 shows the zone inhibition around the film samples. DOP have the lowest antibacterial activity compared to M3 and M4 where it showed inhibition zone diameter of only 9 mm/mg to *Staphylococcus aureus* and *Escherichia coli*. The antimicrobial activity of M3 and M4 to *Escherichia coli* (G^-) is higher than that to *Staphylococcus aureus* (G^+).

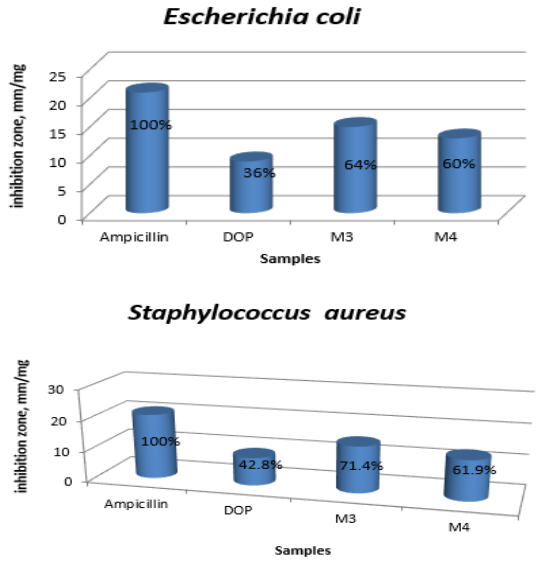


Fig.6. Antibacterial activities of DOP, M3 and M4 and their % to standards (ampicillin antibacterial agent)

Fig.7. Antibacterial activity images of M3 and M4 by agar well diffusion method

Table 5. Antibacterial activity of M3, M4 and DOP.

Sample		***Escherichia coli* (G^-)**		***Staphylococcus aureus* (G^+)**	
Control: DMSO		0.0		0.0	
Standard	**Ampicillin antibacterial agent**	25		21	
		Inhibition zone diameter (mm/mg sample)	**% to standard***	**Inhibition Zone diameter(mm/mg sample)**	**% to standard***
DOP		9	36	9	42.8
M3		16	64	15	71.4
M4		15	60	13	61.9
		***% to standard**: % of Inhibition zone diameter of the sample to that of standard. Example: Inhibition zone diameter of M3 to Escherichia coli is 16 mm/mg while that of the standard is 25 mm/mg. therefore; % to standard is equals (16/25) × 100 = 64%. Values with respect to standard: 30%., 30-60% and > 60% are considered weak, medium and high, respectively.			

3.5. Cytotoxicity assay

The prepared compound M4 and DOP were tested by MTT test for their activity against Kidney of green monkey cell line (VERO). Figure 8 shows the effect of DOP and M4 on VERO cell line**.** From table 6 M4 and DOP were found to be very active with IC50 values 206.18 and 197.06, respectively, while Doxorubicin with IC50 value 58.36.

Table 6. IC50 values of M3, DOP and Doxorubicin

Materials	IC50 (µg/ml)
Doxorubicin	58.36
M4	206.18
DOP	197.06

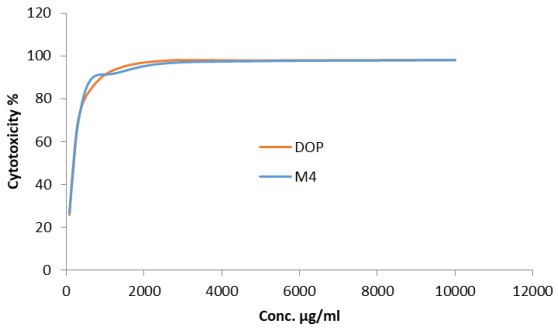


Fig.8. Effect of M4 and DOP on VERO cell line

Conclusion

In this research two materials methyl 10(3-methoxy-3-oxobutanesulfonyl) octadecanoate (M3) and ethyl 10(3-ethoxy-3-oxobutanesulfonyl) octadecanoate (M4) were successfully prepared from oleic acid. According to cytotoxicity assay they are safe and nontoxic compounds. They act as good plasticizers on PVC casting formulations. Their formulations have excellent thermal and mechanical properties compared with DOP effect. The prepared compounds showed antibacterial activity to Staphylococcus aureus and Escherichia coli which was higher than that of DOP.

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