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ORIGINAL ARTICLE

Evaluating the efficacy of a group of nontraditional plasticizers on the glass transition temperature of ethyl cellulose polymer

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Abstract

Objective: The aim of this study was to investigate the efficiency of a homologous series of esters of dicarboxylic acid on ethyl cellulose polymer in terms of their glass transition temperatures (T_g). *Methods*: Ethyl cellulose polymer was plasticized with succinates (C-2), glutarates (C-5), adipates (C-6), pimelates (C-7), suberates (C-8), and sebacates (C-10) at different concentration levels. The film formation and physical state of plasticizers within the polymer were investigated and incompatibility of plasticizers was determined by nonhomogeneous system. *Results*: A decrease in T_g of the plasticized polymer was used as an indicator of plasticizing efficiency. Experimental T_g values were correlated with the theoretical ones predicted by Gordon–Taylor equation. Most of the experimental T_g values did not fit with the predicted ones. For all plasticizers (except succinates) the measured T_g was lower than calculated indicating negative deviation from the ideal behavior. Anti-plasticization was obtained with lower plasticizers concentration. Fourier transform infrared spectroscopy was used to determine the interactions between the polymer and plasticizers on T_g values in predicting the efficiency. *Conclusions*: The correlation between experimental and calculated T_g values verifies that physiochemical properties are the primary factors influencing the plasticization efficiency. However, further studies are needed to establish the plasticization efficiency.

Key words: Adipates, dicarboxylic acid esters, glutarates, pimelates, sebacates, suberates, succinates

Introduction

Glass transition temperature (T_g) is one of the most important properties of amorphous polymers that make them unique and perhaps the most important parameter which decides the application of noncrystalline polymers. T_g is the temperature below which molecules have little relative mobility and it is different for each polymer. Above T_g, the secondary, noncovalent bonds between the polymer chains become weak in comparison to thermal motion, and the polymer becomes rubbery and capable of elastic or plastic deformation without fracture. Ethyl cellulose (EC) is a hydrophobic, thermoplastic polymer used in sustained release drug delivery systems[1,2]. Two commercially available EC aqueous dispersions are Surelease® (Colorcon Inc., Hareysville, PA, USA) and Aquacoat (FMC Corp., Summit, NJ, USA). Surelease has medium-chain triglycerides as plasticizer and Aquacoat does not contain any plasticizer but it has other chemicals on it; therefore, EC powder was used in the study to see the plasticizers effect on it.

A plasticizer is a polymer additive that serves to increase the polymer's flexibility, elongation, or ease of processing (workability). In more technical terms, the addition of a plasticizer generally causes a reduction in the cohesive intermolecular forces along the polymer chains. The chains can then move more freely to one another, and the stiffness of the polymer is reduced. Plasticizers work by embedding themselves between the chains of polymers, space them apart (increasing of the free volume), and thus significantly lowering the T_g of the polymer and making it softer. Therefore, addition of

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Table 1. Example of dicarboxylic acids.

Number of carbons (straight)	Common name	Formula
C2	Oxalic acid (ethanedioic acid)	HOOCCOOH
C3	Malonic acid (propanedioic acid)	$HOOCCH_2COOH$
C4	Succinic acid (butanedioic acid)	$HOOC(CH_2)_2COOH$
C5	Glutaric acid (pentanedioic acid)	$HOOC(CH_2)_3COOH$
C6	Adipic acid (hexanedioic acid)	$HOOC(CH_2)_4COOH$
C7	Pimelic acid (heptanedioic acid)	$HOOC(CH_2)_5COOH$
C8	Suberic acid (octanedioic acid)	$HOOC(CH_2)_6COOH$
C9	Azelaic acid (nonanedioic acid)	$HOOC(CH_2)_7COOH$
C10	Sebacic acid (decanedioic acid)	$HOOC(CH_2)_8COOH$

a plasticizer in essence allows a polymer to behave at room temperature in a way the pure resin would work at elevated temperatures. Effective plasticization leads to a decrease in the T_g of the polymer, which normally results in a more flexible film structure. A homologous series of dicarboxylic acid esters with the general formula, $HOOC(CH_2)_nCOOH$ is shown in Table 1[3]. Where $n = 0$ for oxalic acid, $n = 1$ for malonic acid, and $n = 2$ for succinic acid, and so on. Based on the availability and according to the material safety data, dicarboxylic acid esters succinates (C–4), glutarates (C–5), adipates (C–6), pimelates (C–7), suberates (C–8), and sebacates (C–10) were used in the study for EC polymer. The aim of the work was to find the plasticization efficiency of these nontraditional plasticizers for EC polymer and provide an understanding of the interactions between different groups of plasticizers and the polymer. T_g of the polymer is considered as the relevant property to provide efficiency for different plasticizers. Experimental T_g values were fitted with the theoretical ones predicted by the Gordon–Taylor (GT) equation to describe the nature of association between the plasticizers and the polymer.

Materials and Methods

Materials

Ethyl cellulose, NF (Ethocel Std. 10 FP Premium) was obtained from Dow Chemicals, New Milford, CT, USA, Lot # TH10013T01. Ethanol 200 proof, Lot # P217638 was obtained from Sigma-Aldrich chemical company Saint Louis, MO, USA. Dimethyl acetyl succinate (DMAS) from Aldrich, Lot # S33781-465. Methyl-4-acetyl-5-oxohexanoate (MAO) from Aldrich, Lot # 11526JH. Dimethyl adipate (DMA) from Aldrich, Batch # 06527KS; diethyl adipate (DEA) from Aldrich, Lot # S32699-296; dibutyl adipate (DBA) from Aldrich, Batch # 02930JS; bis-2-ethylhexyl adipate (Bis-2-EHA) from Aldrich, Lot # 21615P1; and bis-1-butylpentyl adipate (Bis-1-BPA) from Fluka Buchs, Switzerland, Lot # 02150. Dimethyl pimelate (DMP) from Aldrich, Lot # 04708MB and diethyl pimelate (DEP) from Aldrich, Lot # D99706. Dimethyl suberate (DMSu) from Aldrich, Lot # 149012 and diethyl suberate (DESu) from Aldrich, Batch # 21615P1. Dibutyl sebacate (DBSe) from Aldrich, Batch # 14622BE; bis-2-butoxy sebacate (Bis-2-BESe), Batch # 21615P1 from Aldrich; and dioctyl sebacate (DOS) from Haltermann, UK, Batch # QA 20088. The chemical formula and molecular weights (MW) of the plasticizers used in the study are tabulated in Table 2[4].

Table 2. Chemical formula and molecular weights (MW) of the plasticizers.

Plasticizers	Chemical formula	MW (gm)
Dimethyl acetyl succinates (DMAS)	$CH_3OOCCHCOCH_3CH_2COOCH_3$	188
Methyl-4-acetyl-5-oxohexate (MAO)	$(CH_3CO)_2CHCH_2CH_2COOCH_3$	186
Dimethyl adipates (DMA)	$CH_3OCO(CH_2)_4COOCH_3$	174
Diethyl adipate (DEA)	$C_2H_5OCO(CH_2)_4COOC_2H_5$	202
Dibutyl adipate (DBA)	$[CH_2CH_2CO_2(CH_2)_3CH_3]_2$	258
Bis-2-ethylhexyl adipate (Bis-2-EHA)	$[-CH_2CH_2CO_2CH_2CH(C_2H_5)(CH_2)_3CH_3]_2$	371
Bis-1-butylpentyl adipate (Bis-1-BPA)	$C_{24}H_{46}O_4$	399
Dimethyl pimelate (DMP)	$CH_3O_2C(CH_2)_5CO_2CH_3$	188
Diethyl pimelate (DEP)	$C_2H_5OCO(CH_2)_5COOC_2H_5$	216
Dimethyl suberate (DMSu)	$CH_3O_2C(CH_2)_6CO_2CH_3$	202
Diethyl suberate (DESu)	$C_2H_5O_2C(CH_2)_6CO_2\ C_2H_5$	230
Dibutyl sebacate (DBSe)	$[(CH_2)_4CO_2(CH_2)_3CH_3]_2$	314
Bis-2-butoxy sebacate (Bis-2-BESe)	$[-(CH_2)_4CO_2CH_2CH_2O(CH_2)_3CH_3]_2$	403
Dioctyl sebacate (DOSe)	$(CH_2)_8(COOC_8H_{17})_2$	427

Methods

Preparation of films

The solvent-based films were prepared by dissolving EC powder in ethanol (7%, w/w) by stirring overnight. Dicarboxylic acid esters in different concentrations ranging from 1.4% to 20% (w/w) of polymeric solution were slowly added by stirring and kept overnight for plasticization. About 10 g of the above solution was then casted onto a glass petri dish (casting area was 100 × 20 mm^2) and allowed to stand for 4–5 days at room temperature (25–28°C), to dry, and the solvent to evaporate completely. The films were then peeled off and the thickness was measured at different locations using slide caliper (Mitutoyo, Tokyo, Japan). All films were stored into glass container with cap.

Thermal analysis

Modulated differential scanning calorimeter

Thermal analysis was performed to determine the glass transition temperature (T_g) of EC polymer, EC film without any plasticizer, and with the series of plasticizers using a modulated differential scanning calorimeter (MDSC) from TA Instruments Inc., model Q1000 (New castle, DE, USA). About 10–15 mg of sample was placed in an aluminum pan and was sealed hermetically along with a reference pan. Nitrogen was used as a purge gas with a flow rate of 50 mL/min. The DSC was calibrated using indium (melting point 156.7 ± 0.6°C) as standard. The scans were performed at 3.0°C/min (modulated with ±1.0°C amplitude in every 60-second period), with an equilibration temperature of 25°C for 5 minutes, followed by heating to 200°C. The results were analyzed by using the TA instruments universal analysis software. All samples were analyzed in quadruplets.

Fourier transform infrared spectroscopy

The infrared spectra of EC polymer, different plasticizers, and EC polymer with different amounts of plasticizers were analyzed by using a Nexus 670 FTIR (Nicolet Thermo fisher Corporation, Madison, WI, USA) spectrometer. Attenuated total reflectance technique with ZnSe crystal was used for all samples. The scan number and resolution was set 90 and 8, respectively, for entire method. Background spectrum was collected before running each sample. The samples were analyzed between wave numbers 4000 and 600 cm^{-1}. The scanning spectrums were analyzed using Omni Software^{TM} (West Cavina, CA, USA).

Results and discussion

Film appearance

The film formation, homogeneity of content, and the appearance of each film surface were examined visually and the plasticizers of the homologous series were found to be compatible with EC polymer. The films had thickness in the range of 100–150 µm. EC film formation with various plasticizers was classified into four different categories, as shown in Table 3. About 3% of all plasticizers resulted in hard and brittle films, 5–7% produced flexible films, and 15–20% plasticizers formed gel with EC. Suberates at 7% of its concentration resulted gel so higher concentrations for suberates were not considered here. The plasticizers used in this study were compatible with EC polymer and there was no sign of phase separation.

MDSC analysis

From multiple MDSC experiments, the T_g of EC polymer was found to be 132–135°C and a melting was found at about 180°C. The melting indicated the presence of crystalline phase in the polymer. Another experiment of subsequent heating and cooling cycles of EC polymer in DSC demonstrated the reproducibility of glass transition and melting events as shown in Figure 1. A similar reproducible transition was observed by Nyamweya and Hoag[5]. They hypothesized that the second transition was because of the melting of a crystalline phase present in EC. T_g of EC polymer was determined experimentally and was also estimated from its melting point (T_m) based on the empirical relationship[6]:

$$T_g \approx 0.7T_m. \tag{1}$$

The estimated T_g calculated for EC polymer from Equation (1) was 126°C but experimentally it was found to be 132–135°C, which is higher than the calculated one. It also supported the crystalline phase into the polymer. The presence of an external plasticizer within a polymeric system decreases the attractive forces between the

Table 3. Film formation of EC polymer with the plasticizers was classified into four different groups.

Plasticizers (%)	Succinates	Glutarates	Adipates	Pimelates	Suberates	Sebacates
3	Group 1	Group 1	Group 2	n/a	Group 1	Group 2
5	n/a	Group 2	n/a	Group 2	n/a	n/a
7	Group 3	Group 2	Group 2	n/a	Group 4	Group 2
15	Group 3	n/a	Group 2	Group 3	n/a	Group 4
20	n/a	n/a	Group 4	Group 4	n/a	Group 4

Group 1: Clear film and was hard to take off from the petri dish. Group 2: Clear film and was easy to take off from the petri dish. Group 3: Dense and cloudy film and was easy to take off from the petri dish. Group 4: Clear gel (no more film), n/a, not applicable.

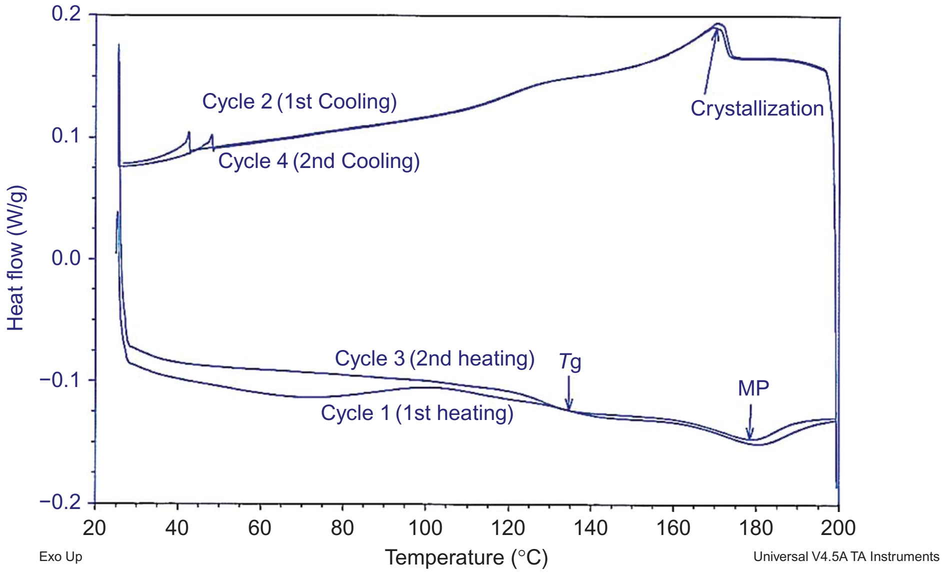


Figure 1. Heating and cooling cycles of heat flow for EC polymer in DSC.

macromolecules, resulting in increased mobilities. Consequently, the temperature at which an amorphous polymer undergoes the transition from the glassy to the rubbery state and vice versa (T_g) decreases. The extent to which the T_g is lowered is an important measure for the efficiency of the plasticizer[7–10]. The effect of the homologous groups of plasticizers on the T_g of EC polymer is shown in Figures 2–4. Plasticization generally produces a decrease in the T_g of the plasticized polymeric film. For DMAS, in Figure 2, the T_g of EC did not decrease for 3–7% of DMAS concentration and it showed higher T_g than EC polymer. This observation might be explained by the antiplasticization phenomena[11]. On the contrary, MAO from 3% to 10% of its concentration was able to lower the T_g of EC. It could be because of the differences in the plasticizer, carbon content, and their interactions with the polymer. According to Sears and Darby, when a small quantity of plasticizer was added, polymers tend to increase the number and sizes of their crystallites because with the small increase of the free volume, a new redistribution of the configuration takes place and results in a more rigid structure with higher T_g, which is known as antiplasticization. As the small quantity of

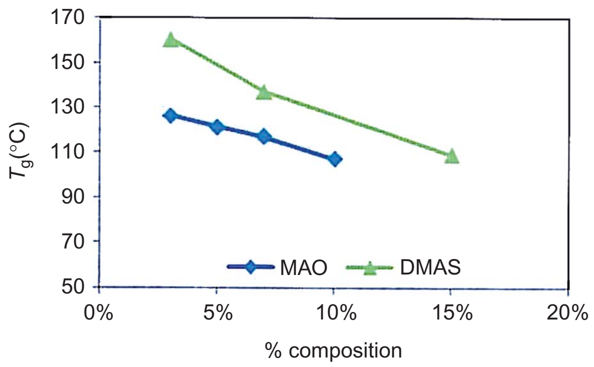


Figure 2. Effect of DMAS and MAO on the glass transition temperature of EC polymer.

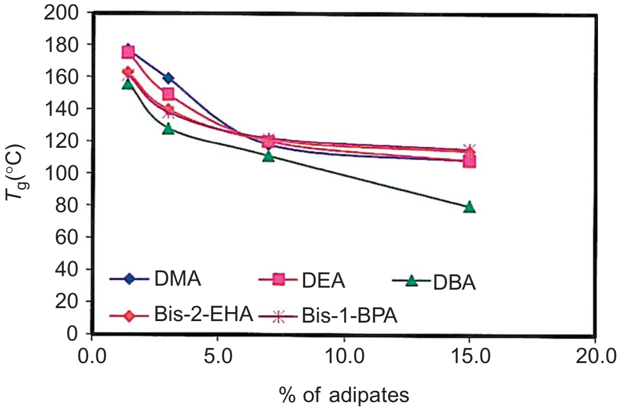


Figure 3. Glass transition temperature of EC polymer with different types and amounts of adipates.

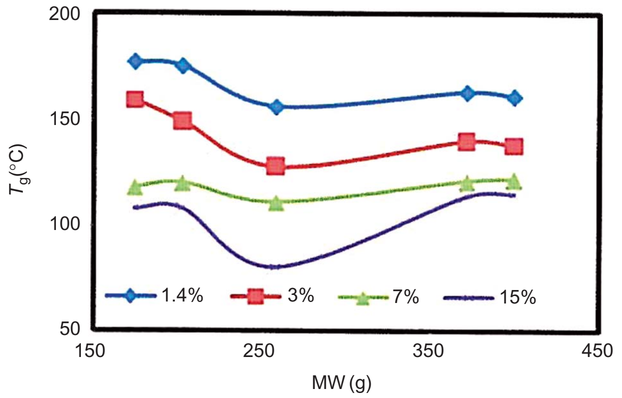


Figure 4. Effect of glass transition temperature on the molecular weights of adipates.

plasticizer molecules would strongly attach to the polymer, it will restrict the polymer–polymer contacts necessary to absorb the mechanical energy. Plasticizer molecules situate themselves around the polymer chains, preferentially in the amorphous areas. When more plasticizers were added to EC, the crystallinity might increase but the amorphous areas were swollen and resulted in a softer film. When even more plasticizers were added, the crystallites were dissolved and gel was obtained and the polymer was saturated with plasticizer molecule[11].

Adipates were not recommended for EC polymeric film[12]. Five different types of adipates were used here and found to be effective for EC polymer. In Figure 3, it shows that DMA, DEA, Bis-2-EHA, and Bis-1-BPA were efficient for reducing the T_g of EC from 7% of their concentrations, and in low concentrations of 1.4–3%, the T_g was high. DMA and DEA displayed almost similar transitions. Bis-2-EHA and Bis-1-BPA also showed identical T_g's. Except DBA, it was able to reduce the EC T_g from 3% to 15% of its concentrations and displayed the greatest plasticizing properties by depressing the T_g to the minimum[13], and demonstrated itself as the most effective plasticizer among all adipates. Effects of adipates' MW on the T_g of EC are shown in Figure 4. The T_g has decreased with increasing the MW of adipates until DBA and then started to increase for higher MW adipates. It was also noticed that the effect of T_g on MW was not significant for 7% adipates compared to other concentrations.

Pimelates, DMP, and DEP worked well with EC polymer and lowered the T_g of EC significantly from 5% to 20% of their concentrations. In sebacates, like others 3% was not able to reduce the T_g of EC. But 7–20% sebacates were efficient in reducing the T_g. DBSe was found to be the most efficient plasticizer among other sebacates in reducing the T_g, as shown in Figure 5. According to the free volume theory[12], in respect to the MW of the plasticizer, on a weight basis, the total free volume increment could be greater for small MW plasticizers. Figure 6 showed the T_g of EC polymer was high for higher MW sebacates. In general, the most effective plasticizer closely resembles the polymer it plasticizes[14]. Therefore, it could be assumed that plasticization efficiency is mostly related to the structure of plasticizers' molecule, and their compatibility with the polymer. T_g has been demonstrated to be a good indicator of polymer's structure and chain mobility because the purpose of a plasticizer is to increase the chain mobility. The measurement of T_g, as a function of plasticizers' concentration also reflect its miscibility or lack of it with the polymer. A miscible polymer–plasticizer blend would show a single transition between T_g of the two components. With increasing immiscibility, there will be a broadening of the transition, where as an incompatible system would be marked by the separate transitions of the polymer and plasticizer components[15]. In MDSC study, the series of plasticizers with EC had shown single T_g's over the whole range of compositions. No separate melting or crystallization peaks were observed, indicating no phase separation between EC polymer and the plasticizers. The existence of crystalline phase in EC polymer (Figure 1) disappeared by the addition of low amount of plasticizer. In fact, 1.4% adipates was not able to reduce the T_g of EC, but it was enough to remove the crystalline phase from the polymer as shown in Figure 7. A decrease in T_g of the plasticized EC polymer was used as an indicator for the plasticization efficiency. To provide a better understanding of the interactions between these nontraditional plasticizers and EC polymer, experimental T_g values were compared with the predicted ones calculated from the GT Equation (2)[16].

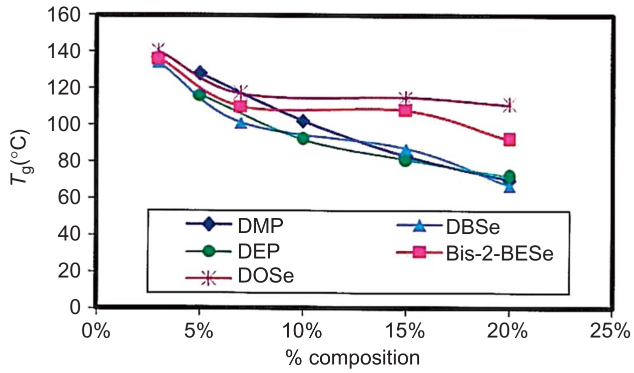


Figure 5. Effect of different pimelates and sebacates on the glass transition temperature of EC.

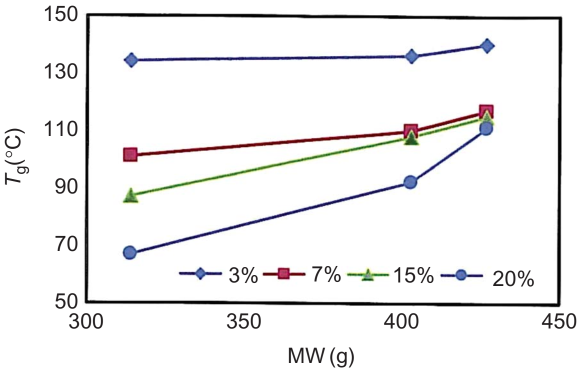


Figure 6. Effect of glass transition temperature on the molecular weights of sebacates.

$$T_{g_{\mathrm{mix}}} = \frac{w1\times T_g1+\mathrm{K}\times 2\times T_g2}{w1+\mathrm{K}\times w2}, \mathrm{K} = \frac{T_g1\times \rho 1}{T_g2\times \rho 2}, \qquad (2)$$

where $w1$ and $w2$ are the weight fractions of each component, T_g1 and T_g2 are the corresponding T_g values of each component. The constant K was estimated using free volume theory with the densities $\rho 1$ and $\rho 2$ of both

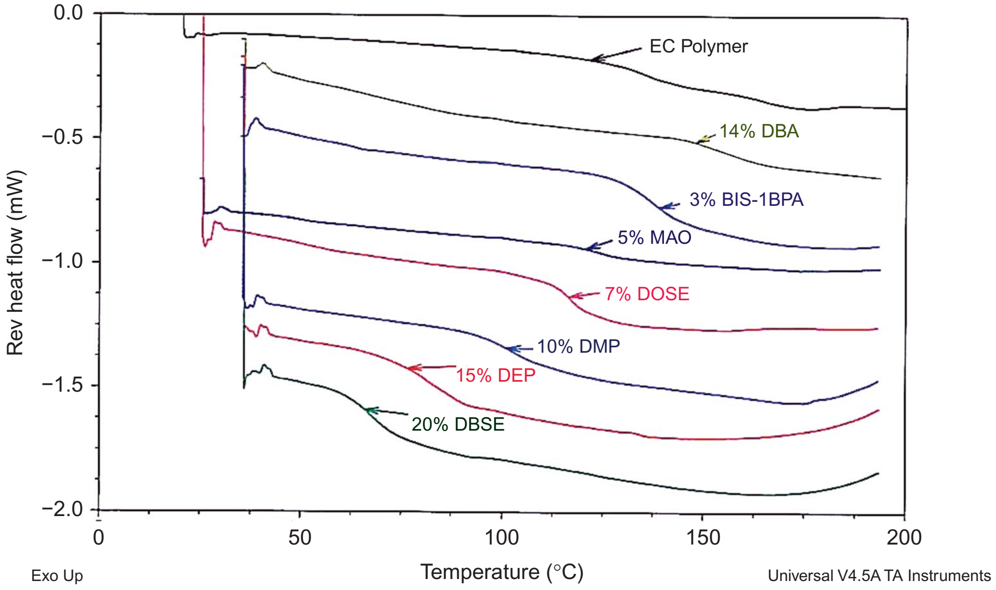


Figure 7. Single T_g has shown for all plasticizers from concentration level 1.4% to 20%.

components. If the experimental T_g is lower than predicted, by GT equation, then it suggested a negative deviation and if the measured T_g is higher, it suggested positive deviation from ideal behavior. Table 4 shows the ratio of the experimental to the predicted T_g values found for EC polymer with 7% of these plasticizers. The measured T_g values of glutarates (MAO), adipates, pimelates, suberates, and sebacates were lower than the T_g values predicted by GT equation at the considered concentration (Table 4) indicating a negative deviation from ideal behavior. Deviation from ideal behavior has often been explained in terms of the differences in strength of intermolecular interactions between the individual plasticizer components and that of the polymer[17]. The ratio of T_g from GT equation ($T_{g\,GT}$) to the measured value ($T_{g\,DSC}$) were in the range of 1.08–1.34. Only in succinates the measured T_g value was higher than the predicted, this positive deviation from ideal behavior, suggested that the plasticizers and polymer bind more strongly to each other than would be expected from the average of the pure component interactions such as hydrogen bonding. If the plasticizer and the polymer bind more strongly to each other than to themselves, the T_g will be higher than expected, because the stronger binding lowers chain mobility. In contrast, if the plasticizer and polymer bind less strongly with each other than with themselves, the T_g's of the composites are usually lower than expected. Moreover, negative deviation from the GT equation in the study may be because of the tendency of self-association through the ester groups[18] result

Table 4. Ratio of the predicted and experimental T_g values for different plasticizers with EC.

Plasticizers	Number of straight carbon chain length	$^{*}T_{g\,GT}/T_{g\,DSC}$
DMAS	4	0.52
MAO	5	1.08
DMA	6	1.14
DEA		1.09
DBA		1.14
Bis-2-EHA		1.17
Bis-1-BPA		1.02
DMP	7	1.01
DEP		1.04
DMSu	8	1.27
DESu		1.33
DBSe	10	1.24
Bis-2-BESe		1.14
DOSe		1.31

$^{*}T_{g\,GT}$ = Glass transition temperature from GT equation. $T_{g\,DSC}$ = Glass transition temperature measured from DSC.

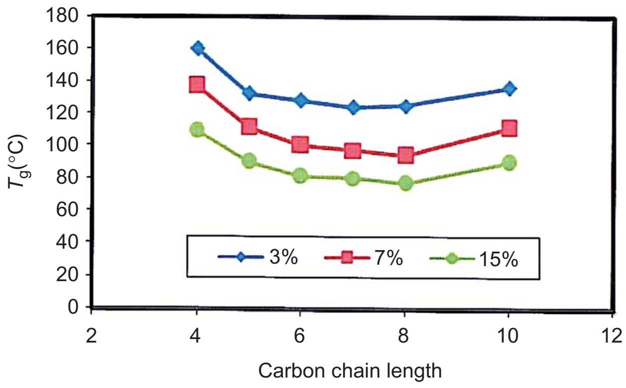
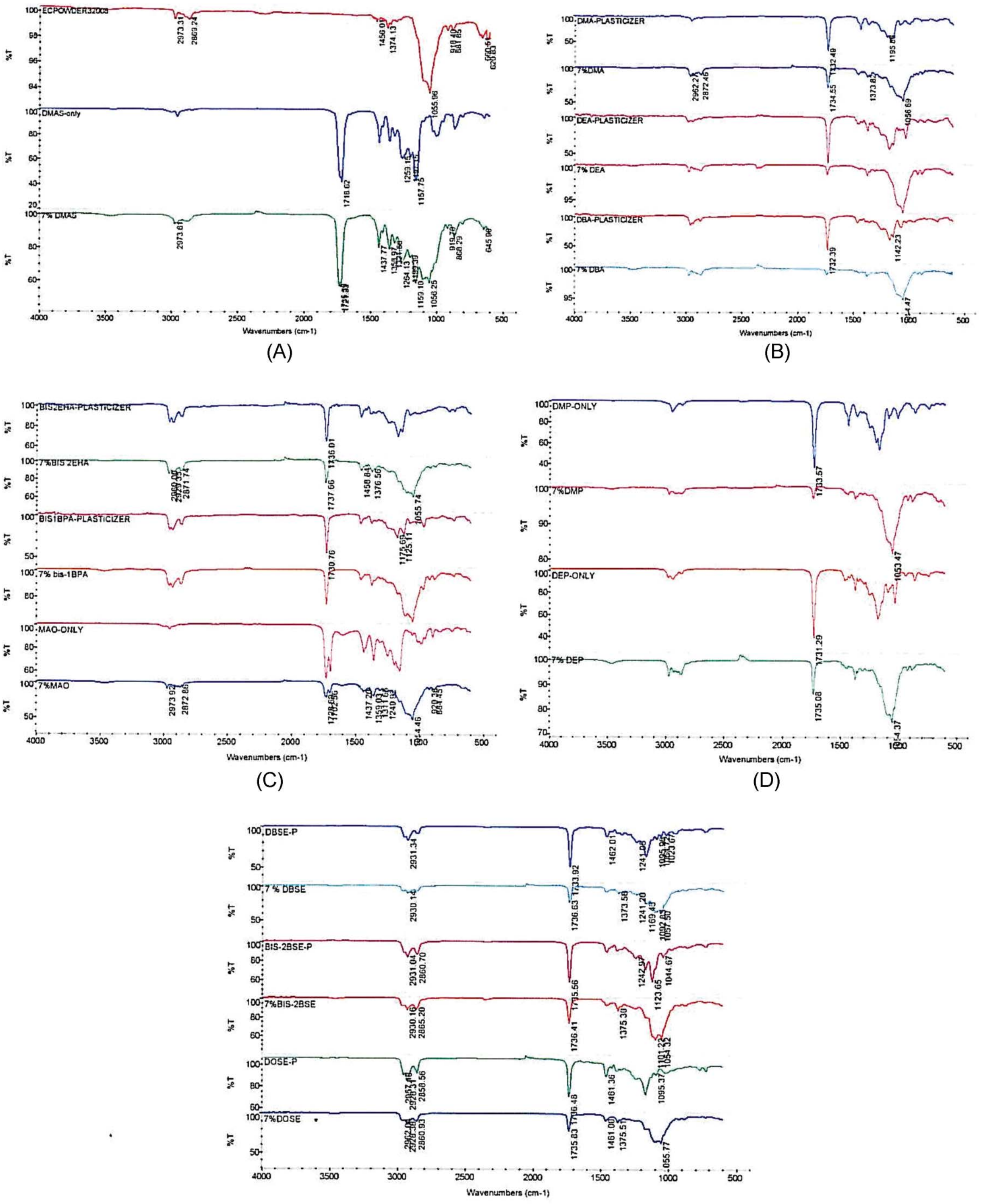


Figure 8. Effect of glass transition temperature on plasticizers carbon chain length.



(A) (B)

(C) (D)

(E)

Figure 9. (A) EC polymer, DMAS plasticizer, and 7% DMAS with EC. (B) Adipates and 7% adipates with EC. (C) Adipates and MAO with EC polymer. (D) Pimelates and 7% pimelates with EC. (E) Sebacates and 7% sebacates with EC polymer.

stronger plasticizer–plasticizer interaction compared to polymer–plasticizer interaction. For MAO, DEA, Bis-1-BPA, DMP, and DEP the theoretical and experimental T_g's are in closer agreement, indicating similarity between plasticizer–polymer interactions and plasticizer–plasticizer interactions. The effect of carbon chain length of these plasticizers on the T_g values of EC polymer were also studied. It was found that lowering of T_g is until certain carbon chain length (i.e., C–6), after that it remains almost constant and again started to increase with more carbon content in the chain as shown in Figure 8. It could be because of the low carbon contained in plasticizer that increased miscibility with EC and is more efficient in reducing the T_g, but for higher carbon content, miscibility might decrease and T_g started to increase.

FTIR analysis

The primary objective of this study was to determine the effect of polymer–plasticizers interactions using Fourier transform infrared (FTIR) on the T_g values of various EC polymer–plasticizers films in predicting the plasticizers efficiency. If the plasticizers and EC polymer interact, then the functional groups in the FTIR spectra would show band shifts and broadening compared to the spectra of the pure plasticizer and EC polymer. The spectrum of EC polymer in Figure 9A showed distinct absorption bands at 1055 cm^{-1} for –C–O–C stretching vibration in cyclic ether and the asymmetric peaks seen around 2869 and 2973 cm^{-1} may be due to the C–H stretching. The FTIR spectrum of pure DMAS, MAO, DMA, DEA, DBA, Bis-2-EHA, Bis-1-BPA, DMP, DEP, DBSe, Bis-2-BESe, and DOSe showed its own characteristic absorption bands between 1000 and 1500 cm^{-1} and all of them have a distinct absorption bands in the range of 1718–1737 cm^{-1} because of the ester groups C = O stretching (overlapping). The FTIR spectra in the transmission mode for the plasticizers itself and EC polymer and with different amounts of plasticizers are shown in Figure 9A–E. The spectra of 7% EC film with the above plasticizers exhibit almost all the features of both polymer and plasticizers; they have shown the summation of the characteristic peaks obtained with the pure EC and pure plasticizers. Spectra for adipates and EC film with 7% adipates and glutarates are shown in Figure 9B and C, respectively. Pimelates plasticizers and 7% with EC polymer are shown in Figure 9D. Sebacates and 7% sebacates with EC are shown in Figure 9E. There were no band shifting and broadening compared to the spectra for pure EC and plasticizers. At 7% of above plasticizers concentrations, the spectra showed sum of the characteristic peaks of individual EC and plasticizers. Band broadening and shift was observed with 7% DMAS indicating the existence of hydrogen bond formation between EC polymer and DMAS. The band at 1055 cm^{-1} in pure EC polymer becomes broader and also shifted with the addition of 7% DMAS (Figure 9A), which is the indication of hydrogen bonding between them. This type of interaction was not evident for other types of plasticizers at the same concentrations (Figure 9B–E). The hydrogen bonding also explains the high T_g value for DMAS, and a positive deviation from the GT equation (T_{gGT}/T_{gDSC} ratio value <1). The negative deviation (T_{gGT}/T_{gDSC} ratio value >1) resulted may be due to the lack of interactions between plasticizers and the polymer compared to polymer and plasticizers itself.

Conclusions

The homologous series of dicarboxylic acid esters were compatible with EC polymer and resulted in homogeneous films. In addition to the presently used traditional plasticizers, succinates, glutarates, adipates, pimelates, and sebacates would be useful and effective plasticizers for EC polymer. Results indicated that these plasticizers depending on their nature and amount reduce the T_g of EC polymer effectively. Adipates found to be useful plasticizers for EC polymer and among all adipates DBA showed the best performance in reducing the T_g of EC polymer and DBSe was the best among other sebacates. Experimental T_g values of these plasticizers were different from the predicted ones by GT equation because the degree of plasticization depends to a large extent on the interactions between the plasticizers and the polymer[19]. It was concluded that the efficiency of these nontraditional plasticizers are related to their structures.

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Declaration of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this paper.

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