



PREPARATION AND CHARACTERIZATION OF UNSATURATED POLYESTER MATERIAL BLENDED WITH CELLULOSE AND WITH ETHYL CELLULOSE.

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Modified unsaturated polyester (MUPE) was blended with Cellulose (CIs) and with ethyl cellulose (ECIs) at ambient conditions in the presence of ethyl methyl ketone peroxide (EMKP) as hardener. The blends containing different weight percentages (5-25 %) of CIs or ECIs. Mechanical properties (impact strength, hardness, and bending) and dielectric constant were determined. The results observed that CIs increases the impact strength, hardness, and dielectric constant and decreases the bending of the MUPS, while ECIs causes an increase in the three mechanical behaviours and a decrease in the dielectric constant of the MU-PS.

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INTRODUCTION

Unsaturated polyester resins are the group of polyester in which the acid component is part of the ester and partially composed of fumaric acid, maleic anhydride is the predominant source of this fumarate when this anhydride is incorporated in the polyester backbone and then isomerised to provide polyester¹.

Cellulose is a biopolymer consisting of D-anhydro glucose repeating units joined by α -1,4-glycosidic linkages at C-1 and C-4 positions, and each repeating unit contains three primary OH groups have the ability of hydrogen bonding and that govern the physical properties of CIs.² Ethyl cellulose is a cellulose ether distinguished by its versatility, and its molecular structure is similar to the CIs molecular structure but with 55% ethoxyl substitution and the variation in this percentage depends on its application demands.^{3,4}

Polymer blends are made by physical mixing of two or more different polymers or copolymers to produce a mixture of desirable mechanical and physical properties.⁵ Compatible polymer blends are immiscible mixtures but they exhibiting macroscopically uniform physical properties and that due to the modification of the interfacial character of the blend by the compatibiliser (polymer or copolymer) of the blend which stabilizes the morphology.⁶ Polymer blends are heterogeneous which don't form single phase system and their properties are largely dependent on the mechanical dispersion, ductility, and the degree of adhesion between the phases.⁷⁻⁹ The presence of cellulose OH groups and ethoxyl groups of ECIs in the blend can change the surface energy, polarity, wet ability, mechanical properties, and dielectric constant of the unsaturated polyester.¹⁰⁻¹¹

The aim of this work is to study the effect of CIs and ECIs on the mechanical properties (impact strength, hardness, and bending) and dielectric constant of MUPS.

Experimental

Materials

Cellulose and toluene were purchased from MERCK, ethyl cellulose from Riedel de Haen, MUPE from Enc International Corporation- South Korea, MEKP from Metric Engineering- India, and ZnO from BDH. All material were used without further purification.

Preparation of MUPE mold

The mold used for preparing the samples was a metallic plate of dimensions (20 x 15 x 1 cm). The plate was cleaned by hot caustic alkali solution and later by distilled water, then treated with a thin layer of liquid paraffin that helps to peel the samples easily.

To 100 gm of MUPE, 2 ml of MEKP as hardener was added and mixed well. The mixture was then immediately poured into the mold and left in a dark not humid place at room temperature ($\sim 25^\circ\text{C}$) for complete solidification after 24 h. The solid mold was peeled off and stored for further use.

Preparation of blended MUPE molds

The required weight present (5- 25 %) of CIs or ECIs was mixed with 100 g of MUPE at room temperature for several hours to obtain a homogeneous mixture, followed by mixing 2 ml of MEKP with the mixture and then poured immediately into the mold and left in a dark not humid place at room temperature for complete solidification after 48 h. The solid blend mold was peeled off and stored for further use.

Impact strength test

Charpy impact instrument of model IMI was used for this test which involves a pendulum swiping downing from a special height to hit the piece under test. Each sample was prepared according to ISO- 179 with fixed dimensions (55 x 10 x 10 mm). The test was carried out at room temperature

and the impact strength (I_s , in kJ m^{-2}) was obtained from equation 1:^{12,13}

$$IS = \frac{E}{A} \quad (1)$$

where

E energy of fraction
 A cross sectional area

Brinell hardness test

Hydraulic piston type LEYBOLD instrument was used for this test. The sample was prepared according to ISO-179 with fixed dimensions (5mm thickness and 20mm in diameter). The test consists of inducing the sample under test with a 5 mm diameter hardened steel ball subjected to a load of 100 and 500 N and full load was applied for 10 s.

The diameter of the indentation left in the tested material (D_1) was measured, then the Brinell hardness number (BHN , N mm^{-2}) was calculated from equation 2¹⁴:

$$BHN = \frac{F}{\frac{1}{2} \pi D \left[D - \sqrt{D^2 - D_1^2} \right]} \quad (2)$$

where

F is the load applied
 D is the indenter diameter.

Bending test

Three point-bending testers were used according to (ASTM-D790) test to determine the modulus of elasticity. The instrument type PHYWE was used to measure the deflection values. Loads ranging from 100 to 1100 gm were used for both MUPE/CIs and MUPE/ECIs blend samples. The dimensions of each rectangular sample were (135 x 10 x 10 mm). The sample was fixed between two points and a certain load (weight) was applied to the centre of the sample at room temperature. Equation 3 was used to calculate Young's modulus (E , in MPa).^{15,16}

$$E = \frac{m g L^2}{D 481} \quad (3)$$

where

g is the gravity acceleration (9.8 m/sec^2),
 m is the mass
 D is the deflection
 L is the distance between two loaded points (m), and

I is the momentum of geometric bending which could be calculated from the equation ($I = bd^3/12$).

The mass/deflection ratio was calculated from the slope of the curve.

Dielectric constant

According to ASTM- D150 the instrument used was Type Leybold – Heraeus (Germany) which represents an electrical circuit (in series connection) consists of capacitor, resistor, ammeter, coil, and frequency generator. The sample of dimensions (40 mm diameter and 5mm thickness) was placed between the capacitor plates followed by alternating the frequency of the power supplier till reaches the maximum current value which represents the resonance frequency value (fr). After that, the (fr) was determined with the existence of air only, i.e, without the presence of the sample.¹⁷

Dielectric constant (ϵ_r) was calculated from equation 4:

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \quad (4)$$

where

ϵ and ϵ_0 are the permittivity of the medium and the free space permittivity ($8.8 \times 10^{-12} \text{ F m}^{-1}$), respectively.

RESULTS AND DISCUSSION

Prepared blends

The use of natural polymers such as cellulose and its derivatives as reinforcements in matrix is to a chive composite or blend with improved mechanical properties and stability.¹⁸ All the prepared blends in this work were 100 % solids and homogenous with no phase separation, and they were all colourless and opaque. MUPE/ECIs blends have more smooth surfaces than those for MUPE/CIs blends, that could be due to the differences of the adhesion of CIs with the hydrophobic polymer matrix and of ECIs with the same matrix, that because CIs and ECIs have different hydrophilic degree due to their different number of primary OH groups.

Impact strength test

Impact strength test is an attempt for measuring opposition to growth of craze and that depends on the mechanism of energy absorption if the material is solid.¹⁹

Table 1. Impact strength, hardness, Young's modulus, and dielectric constant for MUPE/CIs blend at 25 °C.

MUPE, wt. %	I_s , kJ m^{-2}	BHN , N mm^{-2}	E , MPa	ϵ_r
100	4.481	118.873	8796	2.553
95	4.911	119.638	11629	2.901
90	5.859	120.849	16847	3.110
85	5.733	122.788	13840	3.400

80	5.225	124.646	13551	4.103
75	4.563	124.646	12663	3.802

Table 2. Impact strength, hardness, Young's modulus, and dielectric Constant for MUPE/ECLs blend at 25°C.

MUPE, wt. %	IS, kJ m ⁻²	BHN, N mm ⁻²	E, MPa	ε _r
100	4.481	118.873	8796	2.553
95	4.822	120.397	4842	2.543
90	4.997	123.512	4570	2.521
85	5.426	126.846	4486	2.481
80	4.683	129.846	4141	2.409
75	4.468	129.391	4056	2.281

From the impact strength results (Tables 1 and 2) it was found that the impact strength values of MUPE/Cls and MUPE/ECLs blends were higher than that of the unblended MUPE (Figures 1 and 2), because MUPE behaves as an elastic material in the presence of styrene in its structure, while the presence of Cls or ECLs provides a large area for the distribution of impact forces and for same extent restricts the elasticity²⁰.

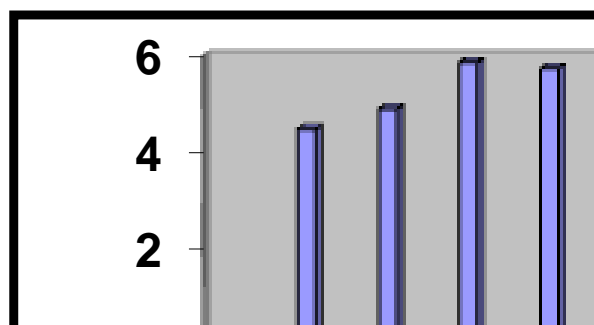


Figure 1. Impact strength for MUPE/Cls blends of Cls w% a) 0, b) 5, c) 10, d) 15, e) 20, f) 25

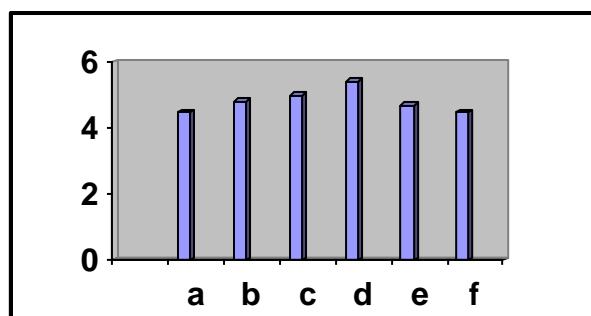


Figure 2. Impact strength for MUPE/ ECLs blends of ECLs w% a) 0, b) 5, c) 10, d) 15, e) 20, f) 25

The results also observed that MUPE/Cls blends have higher impact strength than those of MUPE/ECLs blends, that could be due to the weakness of the interfacial forces between MUPE and ECLs of less free OH groups and less inter hydrogen bonds than Cls, also the bulky size of ethoxy group affects the dispersion of ECLs particles.²¹

Brinell hardness test

Hardness means the measurement of the material resistance to a localized deformation, and the ductile material absorbs more quantity of energy, also, as the concentration of the filler is increased, the ability of the filler to form chain structure in the polymeric medium becomes increasingly important.²²⁻²⁴

Hardness results (Tables 1 and 2) showed that BHN values of MUPE/Cls and MUPE/ECLs blends were higher than that of unblended MUPE, and also, blends of Cls and ECLs have good resistance to indentation (Figures 3 and 4) and that could be due to the existence of hydrogen bonds between Cls or ECLs molecules and the MUPE matrix, that leads to transfer some of the applied stress to the filler particles to obtain isotropic blend. The hardness values of MUPE/Cls blends were lower than those of MUPE/ECLs that could be due to the presence of the bulky ethoxy groups in the later.

Three points bending test

This test gives the information about the linear behaviour or Hookean behaviour when the blends are under the load influence of horizontal vector on their surfaces, and when the load is removed the material will recover its natural shape in the range of deformation, that means the material obeys Hook's law.^{25,26} The relation between the mass and deflection (Young modulus) that occurs for the samples are listed in Tables 1 and 2, and the mass against deflection was plotted in Figures 5 – 7 for pure MUPE, 25% Cls blend, and 20% ECLs blend.

The results showed a decrease in the bending of MUPE/Cls blends, while bending were increased for MUPE/ECLs blends, that may be attributed to the higher polarity and more crystallinity of MUPE/Cls blends than MUPE/ECLs blends, because the later contains a nonpolar ethyl groups.

Dielectric constant

Dielectric constant is used to determine the ability of the insulator to store electrical energy, and this constant is the ratio of the capacitance induced by two metallic plates with sample between them to the capacitance of the same plates with air or vacuum between them.²⁷

The results listed in Tables 1 and 2 observed that dielectric constants of MUPE/Cls blends were higher than those of MUPE/ECLs blends, that could be attributed to the increase in polarity which is due to the presence of the primary OH groups in the Cls molecules leading to the orientation of the segments and a some kinetic units will be observed at definite relaxation time and that gives rise to a definite values of dielectric constant, while the presence of ECLs molecules in the blend slightly decreases the dielectric constant of unblended MUPE.²⁸⁻³⁰

CONCLUSION

Cellulose and ethyl cellulose were both compatible with the MUPE used in this study. The properties of MUPE were affected by the OH groups of Cls and ECLs compounds, as

the number of these groups was increased, the intermolecular hydrogen bonds and the polarity of the blends were increased. The best impact strength results were obtained by the (90 % MUPE + 10 % Cls) and the (85 % MUPE + 15 % ECIs) the optimum results of hardness were for (75 % blends. MUPE + 25 % Cls) and (80 % MUPE + 20 % ECIs) blends. Young's modulus of MUPE/Cls blends was higher than those of unblended MUPE and MUPE/ECIs blends. The maximum value of dielectric constant was for (80 % MUPE+20 % Cls) blend.

REFERENCES

- ¹Grayson, M., Eckroth, D., *Encyclopedia of Chemical Technology*, **1982**, Vol. 18, John Wiley and sons. 3rd Ed., USA.
- ²Nevel, T. P., Zeronian, S. H., *Cellulose Chemistry and its Application*, **1987**, Wiley and Sons Inc., New York, USA.
- ³Park, J., Hans, S., Lee, I., *J. Ind. Eng. Chem.*, **2007**, 13(6), 1002-1008.
- ⁴Dong, H. , Xu, Q., Mo, S., Cai, S., Liu, L., *Colloids Surface B: Biointerface*, **2008**, 66(1), 26-33.
- ⁵Keenth, G., Senior, M., *Engineering Materials Properties and Selection*, **1996**, 5th Ed., New Jersey, Prentice-Hall Inc.
- ⁶Utracki, L., *Polymer Blend Handbook.*, **2003**, Netherlands: Kluwer Academic Publisher.
- ⁷Paul, D., Barlow, J., Kesklula, H., *Encyclopedia of Science and Engineering.*, **1988**, 2nd Ed., Vol. 12, USA, Wiley and Sons Inc.
- ⁸Chung, H., Wang, H., *Macromolecules*, **2006**, 39, 153-161.
- ⁹Sadiku, O., Sadiku, E., Adegboia, A., Biotiadora, O., *Mater. Sci. Appl.*, **2011**, 3, 30-41.
- ¹⁰Chan, L., Ong, K., Heng, P., *Pharm Res.* **2005**, 22, 422-476.
- ¹¹Nair, L., Laurein, C., *Polym. Sci.*, **2007**, 32, (8-9), 762-798.
- ¹²Rajput, R., *Material Science*, **2006**, Delhi, India: Kateria and Sons, NaiSarak.
- ¹³Bedezki, A., Mamun, A., Lucka, M., Gubowski, V., *Sci. J.* **2008**, 32, 413-422.
- ¹⁴Chandramohan, D., Marimuthu, K., *Int. J. Adv. Eng. Sci. Tech.*, **2011**, 6(1), 97-104.
- ¹⁵Hihher, R., *Mechanics of Material*, **2005**, Singapore, London, New York, Prentice-Hall Inc.
- ¹⁶Abdulkhalil, H., Bhat, I., Sartika, M., *BioResource.*, **2010**, 5(4), 2278-2298.
- ¹⁷Hameed, A. M., *Ph.D. Thesis*, Department of Appl. Sci. University of Technology, **2006**, Baghdad, Iraq.
- ¹⁸Marcovich, N., Reboredo, M., Aranguren, M., *Chemical Modification of Lignocellulose Materials: The Utilization of Natural Fibers as Polymer Reinforcement*, Sao Paulo: Lignocellulosic Plastic Composite USP and UNSEP, **1997**, 223-240.
- ¹⁹Dinakaran, K., Alagar, M., *Int. J. Polym. Mater.*, **2003**, 52, 957-966.
- ²⁰Al-Zubidy, G. M., *M.Sc. Thesis*, Chemistry Department College of Education Ibn-Al-Haithem Baghdad University, Baghdad, Iraq, **2007**.
- ²¹Al-Saadi, M. H., *Ph.D. Thesis*, Department of Appl. Sci. University of Technology. Baghdad, Iraq, **2006**.
- ²²Foro, C. L., Cicals, G. L., *The Energy Absorbing Properties of Composite Materials, Engineering Materials*, **2000**, UK.
- ²³Aravind, I., Ahn, K., Ranganathaiah, C., Thomas, S., *Ind. Eng. Chem. Res.*, **2009**, 48, 9942-9951.
- ²⁴Aruniit, A., Kers, J., Tall, K. *Agronomy Res. Biosystem Eng., Special Issue*, **2011**, 1, 23-29.B
- ²⁵Grayson, M., *Encyclopedia of Composite Material Components*, John Wiley and Sons, New York, **1983**.
- ²⁶Escamilla, G., Laviada, J., Mendzabel, E., Puig, J., *Composites Part A.*, **2002**, 33(4), 529-549.
- ²⁷McGrsamum, N., Read, B., Williams, G., *Elastic and Dielectric Effects in Polymer Solids.*, London: Wiley, **1967**.
- ²⁸Baird, M. F., *Electrical properties of Polymeric Materials*. London: Plastic Institute, **1973**,
- ²⁹Allcock, H., Lampe, F., Mark, J., *Contemporary Polymer Chemistry*, USA: Amazon Com., **2003**.
- ³⁰Schottky, W., *Dielectric Constant, Strength, and Loss Tangent*, Cafe Forums, **2008**.

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