

Mechanical and Flame-Retardant Properties of Exoxy Epikote 240/Epoxidized Linseed Oil Composites Using Fiber-Glass

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ABSTRACT

Flammability of polymer composite appears to be one of the greatest threats and hence limits its advanced applications. Polymer composite materials can be designed to obtain wide ranges of properties in comparison with traditional materials. However, almost common polymers include the intrinsic flammability, restricting their applications in spite of their flexibility and performance efficiency. In this study, a material based on epoxy Epikote 240 resin 90 phr and epoxidized linseed oil 10 phr was prepared. In order to improve the material's flame retardancy ability but maintain its mechanical strength, the mixture of flame retardants including 9 phr antimony trioxide and 11 phr chlorinated paraffins along with amin compounds as a curing agent were added into the material. In addition, E-glass woven fabric (E 600g/m²) was used to improve mechanical strength of the material. As a result, the material was considered as the flame-retardant material with LOI index to be 30.3%.

Key Words: Flame Retardant, Epoxy Resin, Antimony Trioxide, Epoxidized Linseed Oil, Chlorinated Paraffins, E-glass.

1. BACKGROUND

ELO (Epoxidized Linseed Oil) has been one of plasticizers and stabilizers for plastic production including PVC (Polyvinyl Chloride) and polymers with a purpose of keeping them flexible as well as ductile. ELO provides stability, heat and light. It was used instead of DOP (Diocetyl Phthalate) because its biodegradable is better than common phthalate plasticizer. In recent years, under pressure of environmental pollution, bio-composite materials have increasingly attracted attention of researchers. In 2010, ESO (Epoxidized Soybean Oil) was used to replace a part of epoxy diene background based on bisphenol A in composite materials reinforced with glass beads. Mechanical properties of this type of plastic background with 60% wt of ESO were equivalent to epoxy

diene background [1-2]. Takashi Tsujimoto et al studied to create green nanocomposite based on ESO reinforced nanosilica 30 nm in size (95,5% wt). Hardness and Young's modulus were significantly increased by using silane adhesive than no silane (9-22 N/nm² and from 210-620 MPa). ESO was also used to increase the impact resistance of unsaturated polyester (PEKN): when no ESO, the impact resistance of PEKN was 26 J/m, it increased 38% with 10% wt of ESO. When amount of ESO increased 20%, the impact resistance was 77%. However, the tensile strength of PEKN/ESO with ratio of 80/20 decreased 5% compared to pure PEKN resin [3-4]. Epoxy resins are known to have high mechanical strength but have brittle disadvantages, low fire resistance, and non biodegradability. Therefore,

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modifying epoxy resin to have good mechanical properties and high fire resistance has been researched by many [5-7]. In addition, to enhance the mechanical properties epoxy materials are reinforced by nano additives and glass fiber combined Kevlar fiber [8-10]. In this study, we studied the flammability and mechanical properties of composites with epoxy/ELO background and presence of flame retardants Sb_2O_3 and chlorinated paraffins.

2. EXPERIMENTAL SETUP

2.1 Raw Materials and Chemicals

Epoxy Epikote 240 (Epoxy E 240) resin of Dow Chemicals (USA) with epoxy group content of 24,6%, Mw: 5100-5400mmol/kg; density:1,12, viscosity at 250C: 007-1.1Pa.s. DETA (Diethylenetriamine) of Dow Chemincals (USA), density 0.95, boiling point 207°C, Mw: 103. Chlorinated paraffin (S52) (China), Maximum amount of chlorine included in chlorinated paraffin is 52%. Antimony trioxide (China), Content of antimony trioxide > 99.0%, some important properties of antimony trioxide are as follows: it is a white powder, melting point of 656°C, specific gravity of 5,7, the amount of included metallic antimony of approximately 83%. Commercial powder of epoxidized linseed oil was collected from Akcros Chemicals Limited with the size of 1.5 μ . Appearance: Liquid Solidifies at low temperatures Colour: Light (or pale) Yellow - Water-white Solubility: Insoluble in water viscosity at 25°C: 800 cSt, with epoxy group content of 22,89%

2.2 Research Methods Used

The fire retardancy of epoxy/epoxidized linseed oil/ Sb_2O_3 /chlorinated paraffins mixture was determined by limiting oxygen index (LOI) method with ASTM 2863 standard using LOI analyzer (Dynisco) in oxygen-nitrogen atmosphere. The LOI values show the minimum level of oxygen which is needed for combustion process carried out by a Bunsen burner. In these experiments, the samples were combusted vertically. The level of oxygen in the atmosphere was increased steadily until the flame was extinguished but the burning time is 3 minutes or burned part of the sample reaches 5 cm (Fig. 1(a)).

The UL-94HB rating was tested according to the UL-94HB (ASTMD635-12) with sheet dimensions of 125 \pm 5 mm long by 13.0 \pm 0.5 mm wide, and provided in the minimum thickness and 3.0 (-0.0 +0.2) mm thick (Fig. 1(b)).

FE-SEM method using a S-4800 scanning electron microscope was used to observe dispersion of structure of the samples cut into small pieces and coated with gold before measuring.

Measurement method (Tensile strength, Flexural strength, Compressive strength) and fabrication pattern are shown in Fig. 2(b) and Fig. 3.

Tensile strength was determined according to ISO 178-1993 standard in INSTRON (USA) equipment with crosshead speed 2 mm/min, temperature 25°C and humidity 75%.

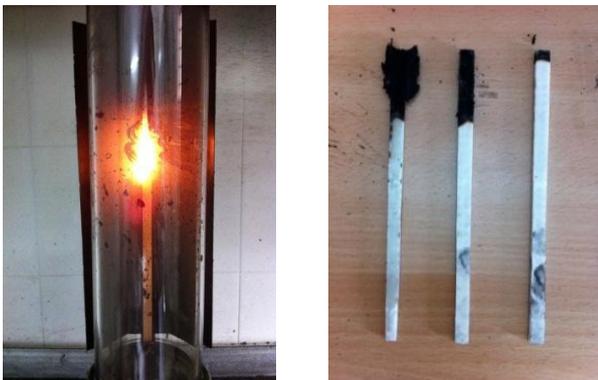


FIG. 1(A). IMAGE OF FIRE RETARDANT TEST ACCORDING TO LOI

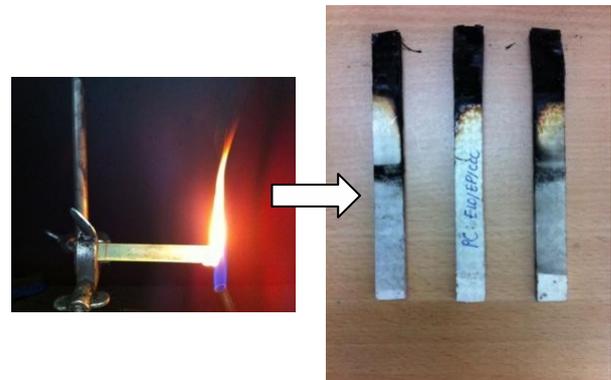


FIG. 1(B).UL 94HB (B)

Flexural strength was determined according to ISO 178-1993 standard in INSTRON (USA) equipment with

crosshead speed 2 mm/min, temperature 25°C and humidity 75%.

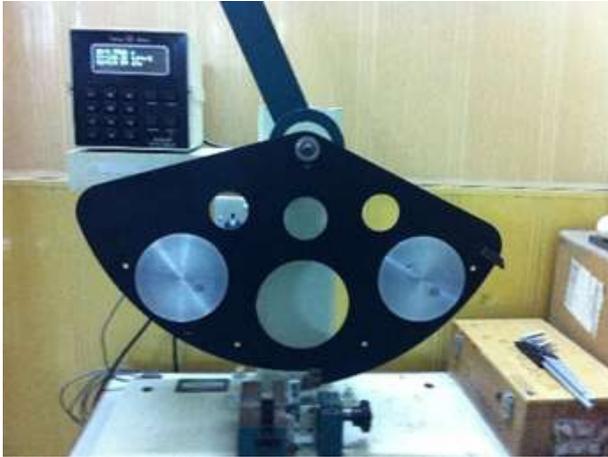


FIG. 2(A). IZOD IMPACT TESTERS



FIG. 2(B). UL-94HB RATING (B)



Tensile Strength



Flexural Strength



Compressive Strength



FIG. 3. MECHANICAL STRENGTH MEASUREMENT

Compressive strength was determined according to ISO 178-1993 standard in INSTRON (USA).

Izod Impact Strength was determined according to ASTM D265 standard in Tinius Olsen (USA). Specimen size: The standard specimen for ASTM is 64x12.7x3.2 mm (2½x½x1/8 inch). Izod Sample Geometry: 2 mm. Model manufacturing as shown in Fig. 4 and image measuring equipment Fig. 2(A).

2.3 Preparation of Epoxy/Epoxy Linseed Oil/Sb₂O₃/Chlorinated Paraffins Mixture

Specimen Preparations Blend Epoxy Epikote 240/ELO: Epoxy Epikote 240 resin was mixed with Epoxy Linseed Oil (90/10 phr) in 250 ml round bottomed three neck flask, mixture was stirred 1500 rpm in 1 hour and it had a thermal stability at 80°C. The bubble free mixture was put into a mold and cured at room temperature within 24 h, then dried within 3 h at 80°C. After 7 days, mixture was analyzed and mechanical properties (EO-Epoxy/ELO) were measured. Aluminum mould with a release agent (Wax 8.0, USA) was used to harden the blend and make it easier for removing product to outside.

Specimen Preparations Blend Epoxy Epikote 240/ELO/Sb₂O₃/Chlorinated paraffins: 55g Epoxy Epikote 240 resin was mixed with 2,894 Epoxy Linseed Oil (EP/ELO = 90/10 phr), 4.95 g Sb₂O₃ and 6.05g Chlorinated paraffins (Sb₂O₃/Chlorinated paraffins = 9/11 wt%) follow other ratios in 250 ml round bottomed three neck flask, mixture was stirred 1500 round/minute in 3 hour and it had a thermal stability

at 80°C. Homogeneous mixture was cured by DETA at room temperature in 24 hours, then it was dried at 80°C in 3 hours. After 7 days, mixture was analyzed and measured mechanical properties (EAP-Epoxy/ Sb₂O₃ 9phr/ Chlorinated paraffins 9phr) (See Fig. 5).

The sheets of Epoxy/ELO/Sb₂O₃/Chlorinated paraffins/glass fibers PC were prepared by the manual methods after dispersing Sb₂O₃ and chlorinated paraffins into epoxy resin: E-glass/epoxy composites were made by hand lay-up method. Firstly, epoxy resin modified with ELO/Sb₂O₃/Chlorinated paraffins was spread uniformly by a paint brush on each E-glass woven fabric layer. Secondly, a panel including 9 layers stacked together was formed. Thirdly, the panel was dried at room temperature within 24 h. Finally, the panel was dried at 80°C within 3 h. The final thickness of the panel was measured to be 4 mm (Fig. 6.).

3. RESULTS AND DISCUSSION

3.1 Effects of Process Variables on Morphological Structure of Materials

Morphological structure of materials was studied by scanning electron microscope. Fig.7 and Fig. 8 show SEM images of several typical material samples. Realized that: in EO, ESO particles are uniformly distributed in epoxy resin background with about 1-5µm in size. The compatibility between ELO and epoxy resin is high due to increased level of dispersion, created homogeneous mixture before curing. In formation process of cross-link had phase separating created ELO particles acted as filler.



FIG. 4. MECHANICAL STRENGTH MEASUREMENT

They increased mechanical properties of epoxy background materials.

On the other hand, the FE-SEM image of Fig.8 shows that Sb_2O_3 and chlorinated paraffin are fairly uniformly distributed. Chlorinated paraffin is distributed in a smaller size in epoxy resin that is clearly visible. The chlorinated paraffin drops are low molecular organic compounds in liquid form that are mixed with Epoxy E240 distributed in

granular form in epoxy E240 background phase to create a plasticizing effect.

Therefore, the fire retardation is improved, while the mechanical properties remain high. This result is consistent with the results of determining the mechanical properties and fire retardation mentioned above. Antimony oxide particles were dispersed fairly well and wetted well, no holes appeared and Sb_2O_3 particles

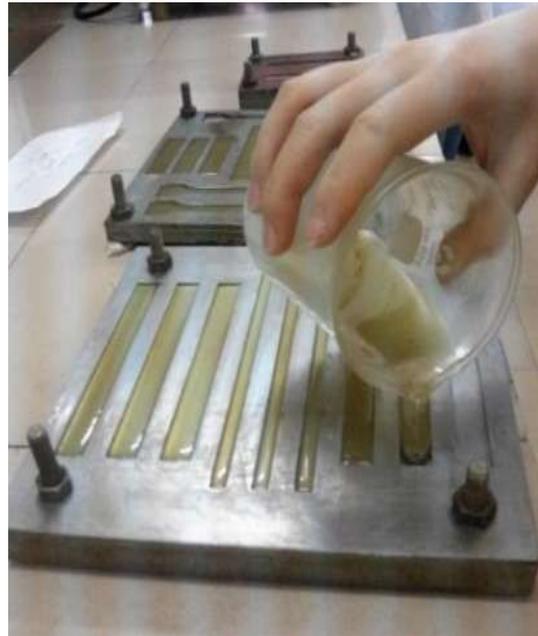


FIG. 5. MANUFACTURING SET UP OF EPOXY COMPOSITE: EPOXY EPIKOTE 240/ELO/ Sb_2O_3 /CHLORINATED PARAFFINS



FIG. 6. FIBER GLASS/EPOXY/ELO Sb_2O_3 /CHLORINATED PARAFFINS/ COMPOSITES

adhered well to E240 epoxy, the broken surface of the material is smooth.

The size and extent of distribution of the ELO particles dispersed in epoxy is one of the important factors, if appropriate size would improve the material properties. If the size is appropriate, it will improve the properties of the material. In this case, the ELO is formed in epoxy resin in the form of spherical particles elastic as rubber, with the appropriate size and level of distribution, hence the bending strength and impact strength Izod increased compared to E 240 epoxy resin (Fig. 8).

3.2 Mechanical of Polymer Epoxy Materials

Blend material between epoxy Epikote (EP) and ELO with ratio EP/ELO = 90/10phr was created. Fig.9. shows that EP/ELO blend material had the slight increasing in the flexural strength were achieved value 88.7 MPa. When mixture of two flame retardants Sb_2O_3 and chlorinated paraffins with ratio 9/11 wt% was mixed in epoxy, the flexural of epoxy material increased 3% compared to neat epoxy value 89.26 MPa. This is due to the presence of chlorinated paraffins acted as plasticizer thus increased the flexural strength of material. But when mixture epoxy/ELO/ Sb_2O_3 /chlorinated was mixed with each other, the

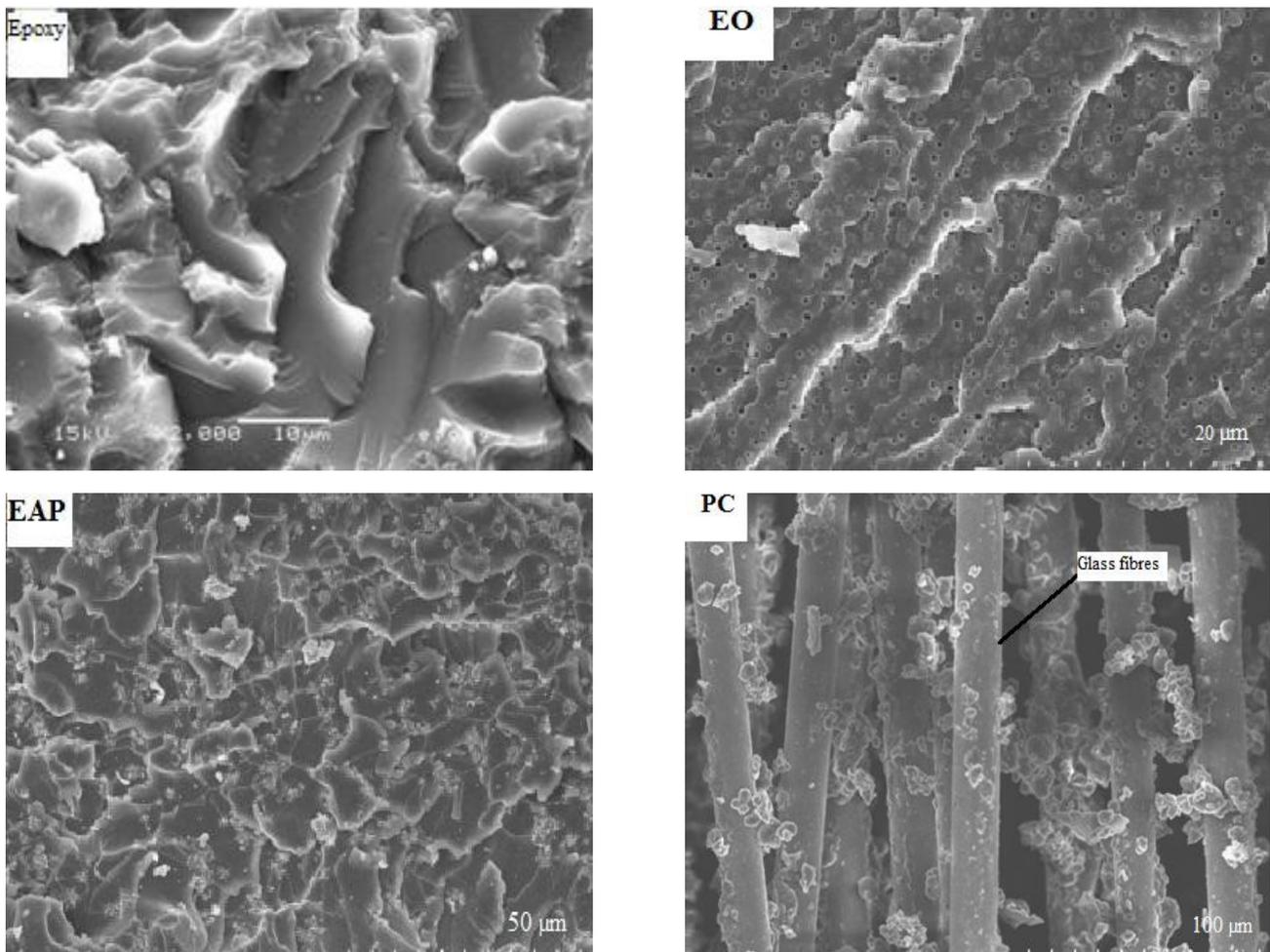


FIG. 7. FE-SEM MICROGRAPHS OF THE SAMPLES: NEAT EPOXY; EPOXY/ EPOXIDIZED LINSEED OIL (EO); EPOXY/ Sb_2O_3 9PHR /CHLORINATED PARAFFINS 9PHR (EAP); EPOXY/ELO/ Sb_2O_3 9 PHR /CHLORINATED PARAFFINS 11PHR/GLASS FIBRES (PC)

flexural strength decreased sharply and achieved value 65.60 MPa. Tensile strength also decreased, especially compressive strength.

From the results of research on the mechanical properties of the base composite material (E 240 / ELO: 90/10 PKL) with the presence of flame retardant (antimony 9 9 PKL/ paraffin 11 PKL), it is found that the compressive strength of samples decreased significantly compared with samples such as: epoxy E 240; epoxy E 240/ELO; epoxy E 240/oxide antimony 9 PKL/11 PKL chlorinated paraffin, that can be explained as follows: The presence of ELO in E 240 epoxy material acts as a plasticizer (as argued in Section 3.1) similar to chlorinated paraffin, therefore the presence of both compounds in the E 240 epoxy polymer material

enhances flexibility, reduces the brittleness compared to each compound when used alone.

This is the reason that the impact strength of Izod increases (9.93 KJ/m²), the flexural strength increases (89.40 MPa) compared with E240 epoxy resin background and the remaining materials. Thus, the presence of ELO and chlorinated paraffin increased the ductility of epoxy 240 E polymer significantly. The mechanical properties of epoxy E 240/ELO/flame retardant material combinations are shown in Fig.9.

SEM image in Fig.9, shows that the flame retardant Sb₂O₃, chlorinated paraffin and epoxidized linseed oil are uniformly

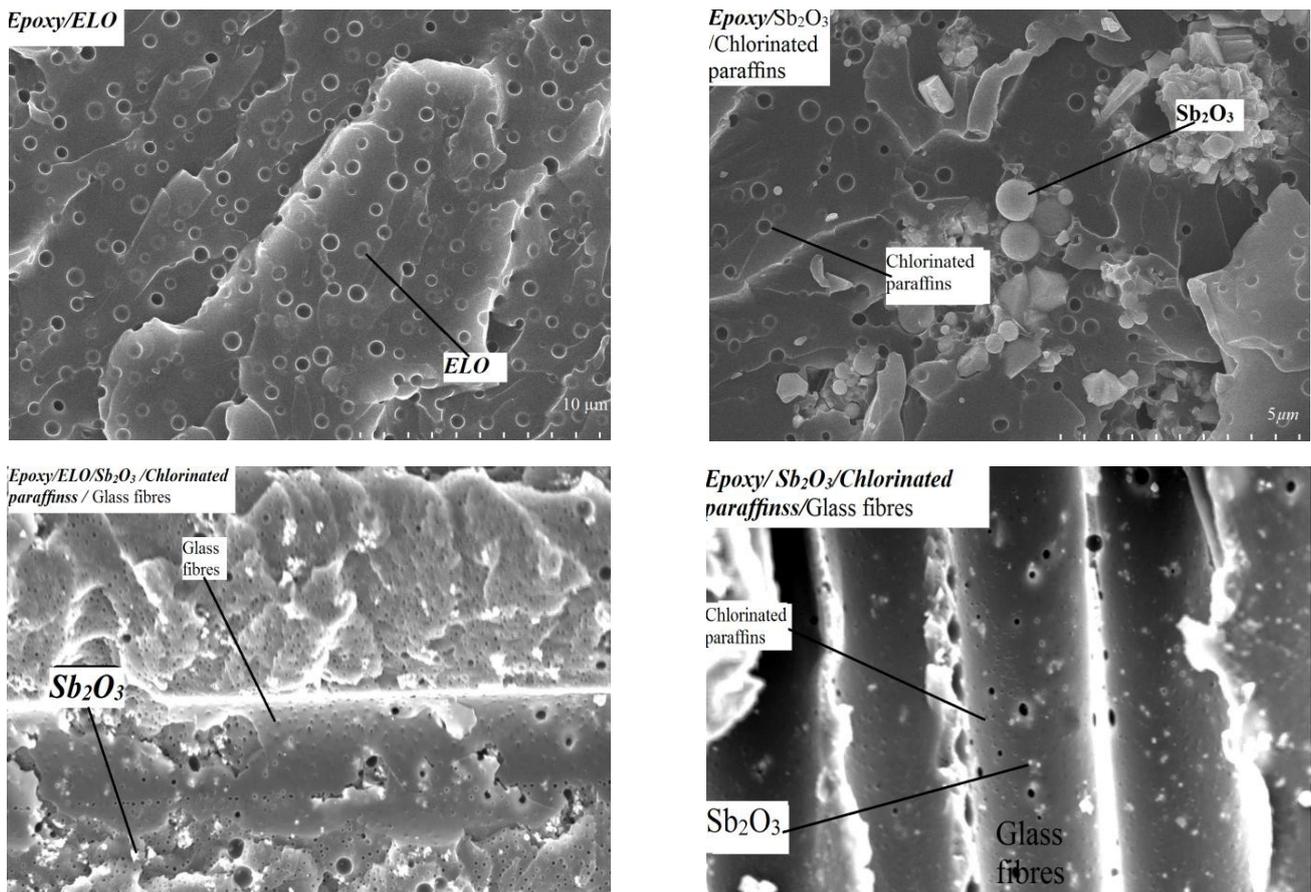


FIG. 8. FE-SEM MICROGRAPHS OF THE SAMPLES: EPOXY/ELO/ SB₂O₃/CHLORINATED PARAFFINS; EPOXY/SB₂O₃ /CHLORINATED PARAFFINS/ GLASS FIBRES; EPOXY/SB₂O₃ /CHLORINATED PARAFFINS/ EPOXY/ EPOXIDIZED LINSEED OIL-ELO

distributed in composite materials, chlorinated paraffin and epoxyfied linseed oil are distributed as spherical particles of uniform size in the composite, thus it has promoted the effect of improving flexibility, reducing brittleness resulting in flexural strength and impact resistance increased and compression and tensile strength reduced. The adhesion between E 240 epoxy resin and glass fiber plays an important role for the mechanical properties of composite materials and it can be directly related to the roughness of

cracks where the formation of cracks occur. The morphological structure fracture surfaces of polymeric composite samples after determining the tensile strength, the results are shown in Fig.10.

FE-SEM image in Fig.10 with high resolution, clearly shows that the fractured surface of the E 240 composite epoxy material reinforced with glass cloth and epoxy E 240/ELO composite material with a flame retardant

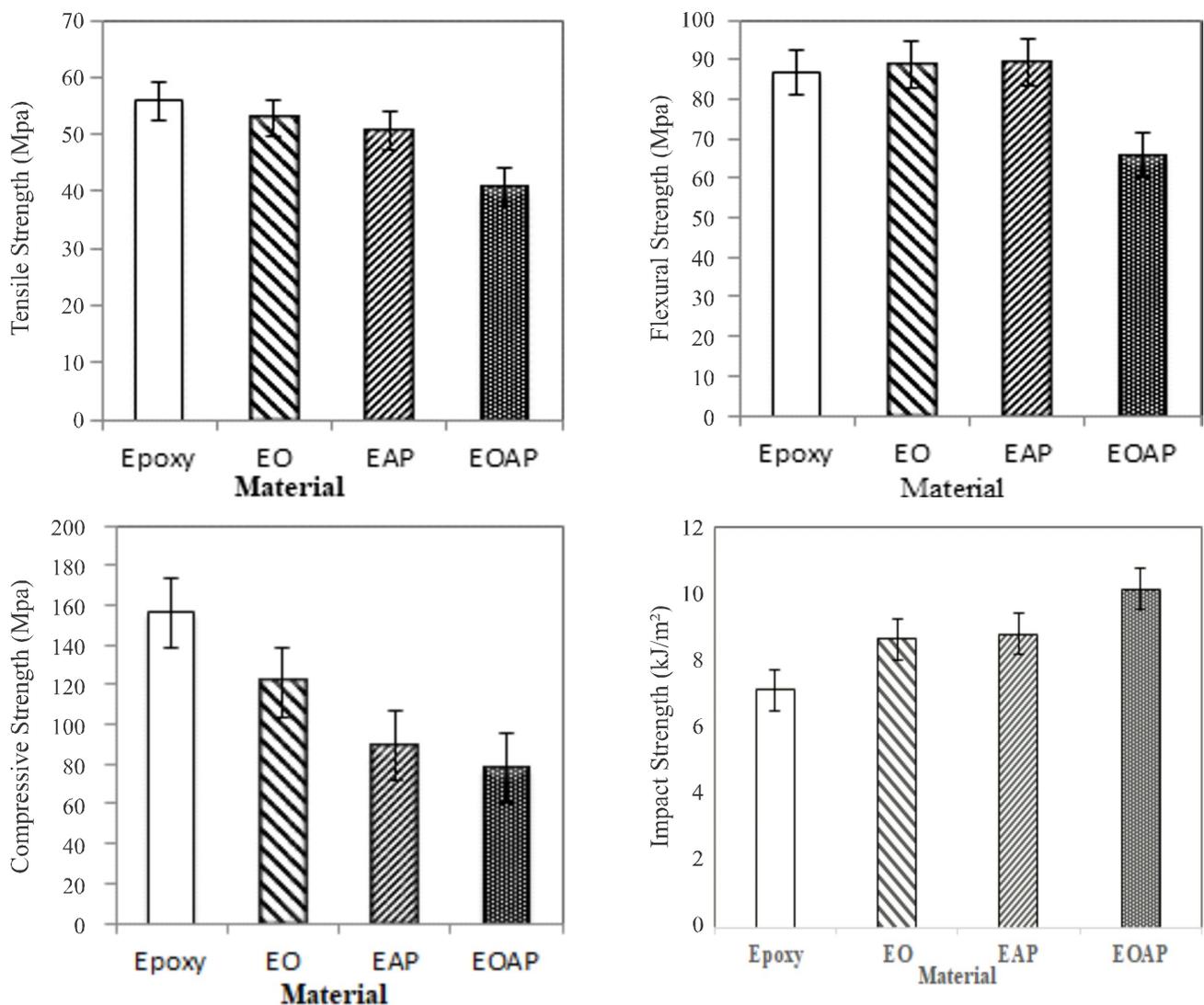
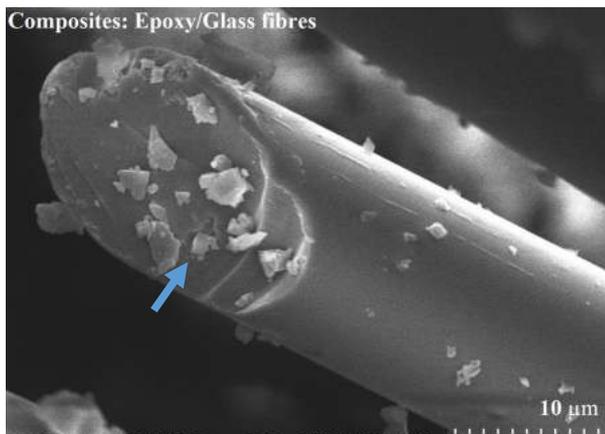


FIG. 9. MECHANICAL STRENGTH OF POLYMER EPOXY MATERIALS: NEAT EPOXY; EPOXY/EPOXIDIZED LINSEED OIL (EO); EPOXY/SB₂O₃ 9 PHR /CHLORINATED PARAFFINS 11PHR (EAP); EPOXY/ EPOXIDIZED LINSEED OIL/SB₂O₃ 9PHR / CHLORINATED PARAFFINS 9PHR (EOAP)

substrate reinforced with glass cloth which was processed by hand pressing method, is relatively smooth, epoxy E 240/ELO/Sb₂O₃/chlorinated paraffin glass cloth material shows the bond between the fiber and epoxy 240 /ELO resin is relatively good, the surface of the slot between the fiber and plastic is partially pulled out of the slot and broken, only the epoxy resin area has smooth fractured surface.

The epoxy E 240 / ELO / Sb₂O₃/chlorinated paraffin/glass cloth material is improved, epoxy E 24/ELO (Fig.10) still adhered to the glass fiber surface after the yarn was removed from the material block and broken when there was an external force effect. Fire retardant additives (antimony oxide, chlorinated paraffin) form a homogeneous mixture with epoxy E240/ELO and they adhere to the glass fiber surface (Fig. 10). Clearly, it shows that there is a good compatibility here and no flaking, hence it has promoted the effect of slowing fire as well as not affecting too much to the decline of mechanical properties .

Thus, the combination of a flame retardant system of antimony and chlorinated paraffin as flame retardant additives for glass-reinforced PC materials based epoxy E240 has been effective and has significantly improved the fire retardation for materials.



3.3 Flame Retardancy of Polymer Epoxy Materials

The fire retardation of epoxy E 240/ELO/Sb₂O₃/chlorinated paraffin mixture is shown in Fig. 9.

Fig. 11 shows LOI of background material and composite polymer material. These show that the flammability of epoxy resin of mixed ELO increased compared to epoxy background material with no modification. Due to this, ELO acted as a plasticizer and its presence in epoxy background in liquid during curing of epoxy resin increased LOI and achieved a value of 21.5. When the flame retardants Sb₂O₃ and chlorinated paraffins were mixed in EP/ELO, LOI was increased compared to EP/Sb₂O₃/Chlorinated paraffins and LOI achieved a value of 23.2 for fire-retardant materials. For composite material, PC3 material (Epoxy/ELO/Sb₂O₃/Chlorinated paraffins/glass fibers) achieved a LOI of 30.3 for self-extinguishing materials.

Epoxy E240/ELO/oxide antimony/chlorinated paraffin materials have higher flame retardant properties than other materials, namely, oxygen index of 23.2%, combustion rate of 13.67 mm/min and the test on UL94HB equipment with a combustion rate of 20.45 mm/min. Sturdy structure with less porous holes was observed. The porous holes are the points that cause increased



FIG. 10. FE-SEM MICROGRAPHS OF THE SAMPLES: COMPOSITES EPOXY/GLASS FIBRES AND COMPOSITES EPOXY/ELO/CHLORINATED PARAFFINS/GLASS FIBRES

combustion because there are air and porous structures, which also spread the fire faster.

The surface of the material after burning with the oxygen index test using the FE-SEM method was also surveyed. Fig. 12(a) shows that the blank sample of E240 epoxy has a non-intact surface structure that is not intact and on which there are burnt porous areas and cracks (Fig. 12(b)). With composite materials based on epoxy E 240/ELO/oxyt antimony/paraffin chlorinated, there are no cracks on the surface after the fire, smooth surface without porous areas

and no visible cracks. Chlorinated paraffin and antimony oxide are produced on E 240 epoxy resin surface, a layer of ash (slag) in the form of solid films, which acts as a barrier to prevent the dispersion of heat and minimizes the loss of volume of volatile substances at epoxy resin surface E 240.

When testing the flame retardant properties of glass-reinforced PC materials, it was found that only epoxy resin E 240 was burnt with other additives, while the glass cloth remained intact.

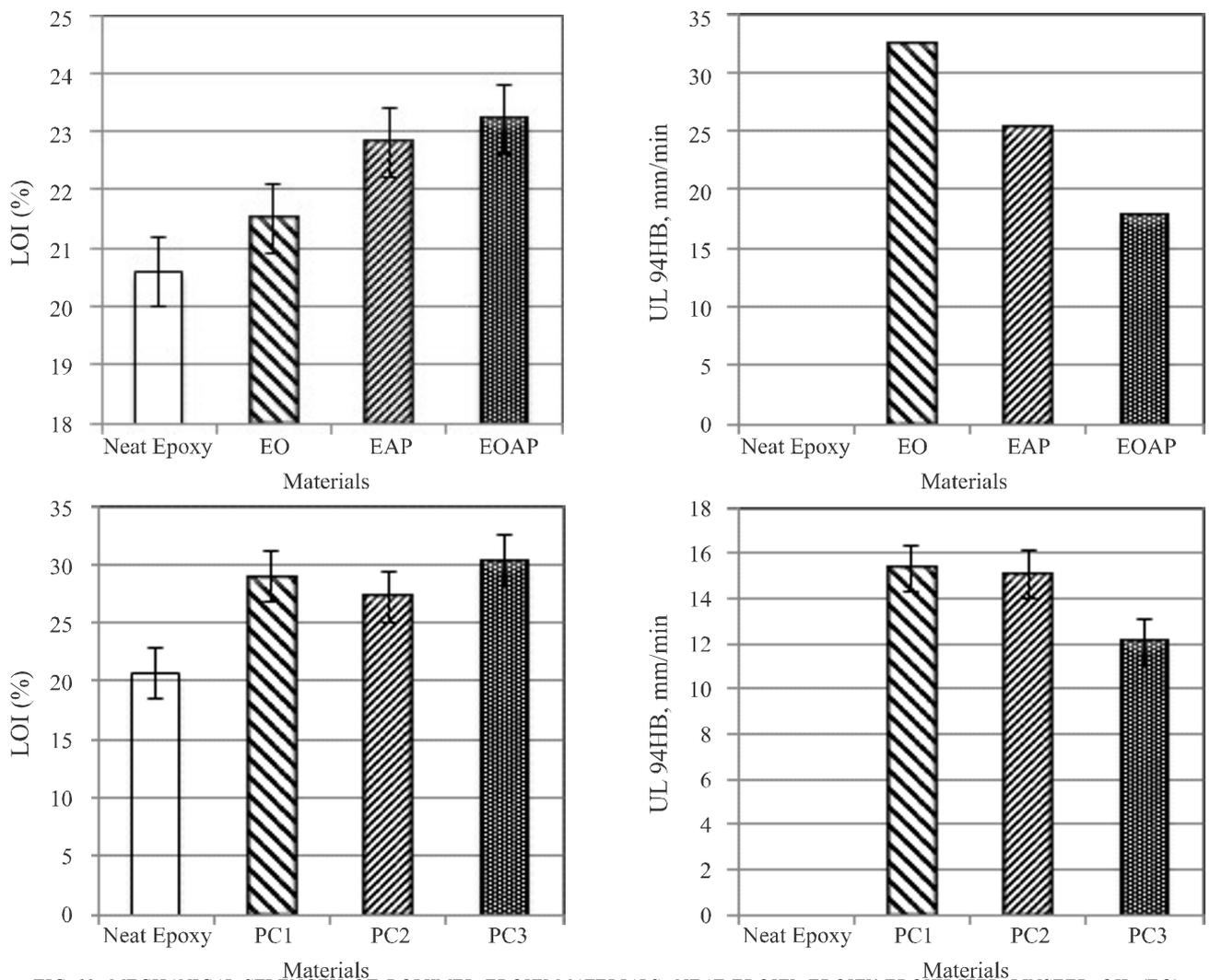


FIG. 11. MECHANICAL STRENGTH OF POLYMER EPOXY MATERIALS: NEAT EPOXY; EPOXY/ EPOXIDIZED LINSEED OIL (EO); EPOXY/SB₂O₃ 9 PHR /CHLORINATED PARAFFINS 11PHR (EAP); EPOXY/ EPOXIDIZED LINSEED OIL/SB₂O₃ 9PHR / CHLORINATED PARAFFINS 9PHR (EOAP)

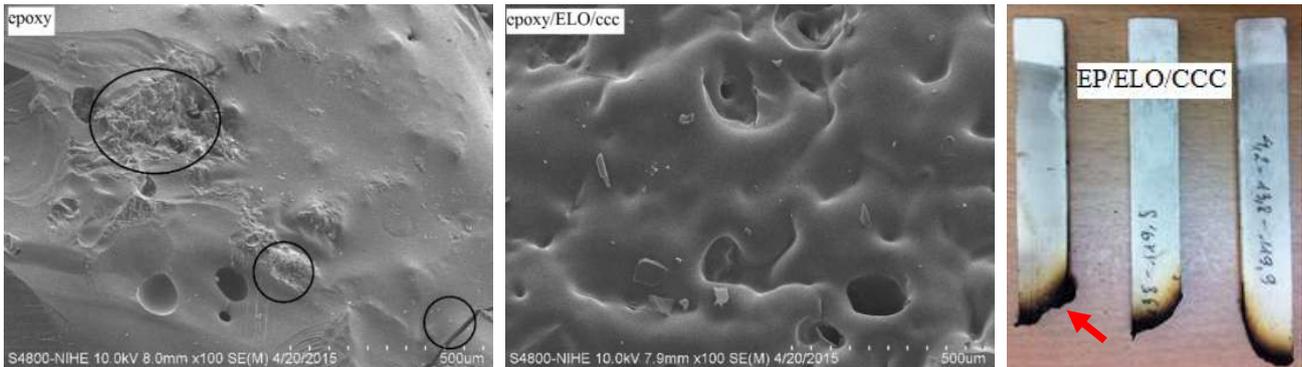


FIG. 12. FE-SEM IMAGES OF THE RESIDUA OF EPOXY/ELO/CCC COMPOSITES (CCC: Sb_2O_3 /CHLORINATED PARAFFINS)

4. CONCLUSION

In this study, we studied to create mixing of epoxy Epikote 240 with ELO and mixture of the flame retardants Sb_2O_3 with Chlorinated paraffins. The results showed that, the flammability of composites materials was improved when a part of epoxy resin was replaced by nature resin (ELO). Thus, obtained materials are not only eco-friendly but also increase the flammability with LOI achieved as 30.3. When a fire occurs, the natural plastic materials (ELO) are not only non-toxic with environment but also prevent the fire grow.

Materials E 240/ELO/oxyt antimony/chlorinated paraphin have a high fire resistance: oxygen index 23.2% and combustion rate 13.67 mm/min. According to UL 94HB method, the combustion rate reaches 20.45 mm/min and the mechanical properties are improved, the flexural strength increases to 89.40 MPa and the impact strength of Izod increases to 9.93KJ/m².

Polymer composite materials based on epoxy E240/ELO resin have a flame retardant system reinforced with "E 600g / m²" rough glass fabric with tensile strength reaching 279.45 Mpa, bending strength of 365.36 MPa and compressive strength of 229.21 MPa, Izod impact resistance reaching 158.39 KJ / m²

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