

# Effect of type of conductive fillers and poly (ethylene glycol) diglycidyl ether on the electrical conductivity and morphology properties of poly (vinyl chloride)/poly (ethylene oxide) conductive films

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**Abstract** The addition of poly (ethylene glycol) diglycidyl ether (PEDGE) as surface modifier and type of conductive fillers into poly (vinyl chloride) (PVC)/poly (ethylene oxide) (PEO) blends was studied. PVC/PEO blends conductive films with 15 wt% of carbon black (CB), poly (aniline) (PAni), and poly (pyrrole) (PPy) were prepared using solution casting technique. The addition of PEGDE showed lower tensile strength, but higher modulus of elasticity and electrical conductivity for all compositions of PVC/PEO conductive films. Scanning electron microscopy (SEM) results show that the addition of PEGDE in conductive films gives good dispersion between matrix and fillers. The PVC/PEO conductive films demonstrated less thermal stability with the addition of PEGDE compared to without PEDGE.

**Keywords** Poly (vinyl chloride) · Poly (ethylene oxide) · Poly (ethylene glycol) diglycidyl ether

## Introduction

Polymer blending is one of the most important contemporary ways for the development of new polymeric materials and it is a useful technique for designing materials with a wide variety of properties. Poly (ethylene oxide), PEO, is the most common crystalline polymer which widely used in polymer electrolytes due to its solvating characteristics. The main drawback of using PEO as single matrix in

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conductive polymer composites is the high degree of crystallization. The way to overcome this drawback is by blending with other type of polymer.

Poly (vinyl chloride), PVC, consists of lone pair electrons at chlorine atom where the inorganic salts can be solvated electrolyte systems [1]. The PVC also enables to form homogenous hybrid film, inexpensive and commercially available. By owing unique characteristics easy process ability and well compatible with wide range of plasticizers, PVC forms miscible blend with PEO in this study. The blends of PVC/PEO have been widely used in polymer electrolytes as a matrix.

The most broadly used material to improve conductivity is carbon black. Carbon black (CB) is composed of about 97–99 % elemental carbon. The other major constituents are hydrogen and oxygen. The hydrogen is distributed as hydrocarbon throughout the CB. These atoms are set into several organic functional groups such as –OH (hydroxyl), –COOH (carboxyl) on its surface. Besides the oxygen and hydrogen groups, CB may contain very small amounts of nitrogen and sulfur depending upon the nature of hydrocarbons used in the manufacture [2].

Polyaniline is one of the most remarkable inherently conductive polymers. It is an organic conducting polymer that early reported about 100 years ago. Lately, there has been a flow in research on polyaniline since it was shown that its conductivity could be increased by more than ten order magnitudes by doping them with proton acids [3]. Supri et al. [4] investigated the effect of polyaniline content on the electrical conductivity and morphology of low density polyethylene/natural rubber/water hyacinth fiber composites. The addition of polyaniline of composites has higher conductivity than the composites without the polyaniline. This finding might be due to the conductive filler being heterogeneously distributed in one phase of the blended matrix and/or at the interface between the conductive films.

Polypyrrole is also one of the most broadly studied conducting polymers and has been well characterized. Polypyrrole is gained in the form of black powder by monomer oxidation. It is the most broadly studied conducting polymer since a pyrrole monomer is water soluble, good redox properties and high electrical properties [5]. Polypyrrole-based materials can be used as antistatic coating and coating to protect against corrosion and oxidation. However, there is some limitation in application of polypyrrole which is low mechanical strength thus low processability.

However, the homogeneity between the matrix and filler material influenced the degradation of the mechanical properties of conductive polymer composites. The dispersion of fillers concern in the polymer matrix for conductive film which can be achieved by addition of surface modifier and modification of filler particles with chemical treatments in order to improve their film surface to impart conductivity in non-conductive polymer blends.

The addition of plasticizers in conductive polymer is one of the most effective approaches to improve the mobility of ionic or/and the interfacial interaction among conductive filler and polar groups in polymer chains. The choice of plasticizer and its concentration can affect film permeability and mechanical properties [6]. The other advantage of plasticization is to modify the polymeric matrix and provide the enhanced conductivity. In general, low molecular weight and high dielectric constant additive, such as polyethylene glycol (PEG), ethylene carbonate (EC),

dioctyl phthalate (DOP) or propylene carbonate (PC) is used to modify the permeability of the polymer film [7]. The addition of plasticizer in polymer matrix tends to decrease the glass transition temperature and increase deformability, viscosity, elasticity and abrasion resistance. Qiao et al. [8] have studied the effect of PEGDE content as plasticizers on the ionic conductivity of (PEO-PMA)-based polymeric gel. The result shows that the ionic conductivity increases with an increase in the content of PEGDE.

In this paper, the effect of poly (ethylene glycol) diglycidyl ether as surface modifier and type of conductive fillers on the tensile properties, morphology, electrical conductivity, and thermal degradation analysis of PVC/PEO conductive films were investigated.

## Experimental

### Materials

The PVC powder (molecular weight = 220,000 g mol<sup>-1</sup>, melting temperature = 100–260 °C, and glass transition temperature = 84 °C) and PEO powder (molecular weight = 100,000 g mol<sup>-1</sup>, melting temperature = 65 °C, and glass transition temperature = -53 to -45 °C) as the host polymer for thin conductive film were supplied by AR Alatan Sdn. Bhd.. Three type of conductive fillers used in this research, carbon black type Conductex (K Ultra) (particle size = 177 μm and density at 25 °C = 1.75 g cm<sup>-3</sup>), Polyaniline (emeraldine base with 20 wt% polyaniline on carbon black) (approximate Mw ~ 5000 and melting point = 300 °C) and Polypyrrole (PPy) (doped composites with 20 % carbon black), were obtained from Mega Makmur Sdn. Bhd, Penang, Malaysia. Tetrahydrofuran (molecular weight = 72.11 g mol<sup>-1</sup>, boiling point = 66 °C and density = 0.888 g mL<sup>-1</sup> at 20 °C) is used as a solvent to dissolve PVC and PEO was purchased from AR Alatan Sdn. Bhd.. Dioctyl terephthalate (molecular weight = 390 g mol<sup>-1</sup>, melting point = -48 °C and density = 0.986 g mL<sup>-1</sup> at 25 °C) was used in this research as a plasticizer was supplied by AR Alatan Sdn. Bhd. Poly (ethylene glycol) diglycidyl ether (density = 1.14 g mL<sup>-1</sup> at 25 °C, boiling point = 112 °C, and molecular weight = 526 g mL<sup>-1</sup>) used in this research as a surface modifier for PVC/PEO conductive film was purchased from Sigma-Aldrich.

### Preparation of PVC/PEO blends with conductive fillers

PVC and PEO are dissolved separately in tetrahydrofuran (THF). After that the PVC and PEO were mixed together and stirred until a homogenous solution was formed. Then, the conductive filler, DOTP and PEGDE as a surface modifier were added simultaneously into the solution. The solution was mixed together and stirred with magnetic stirrer for 4 h to achieve a homogeneous solution. When they were completely homogeneous, the solution was poured in the glass plate and left in fume cupboard. Thin conductive film was formed when solution dried and THF is

completely evaporated. The formulation of PVC/PEO blends with addition of poly (ethylene glycol) diglycidyl ether in several types of conductive fillers is shown in Table 1.

### Tensile test

Tensile test was carried out according to ASTM D-638 using Instron 5569 with crosshead speed of  $10 \text{ mm min}^{-1}$ . The dimension of dumbbell shaped sample was  $150 \times 130 \times 15 \text{ mm}$ . The test was performed at  $25 \pm 3 \text{ }^\circ\text{C}$ . Five dumbbell shapes samples were used for each films composition. The tensile strength and modulus of elasticity of each of the films were obtained from the test.

### Scanning electron microscopy (SEM)

The surface morphology of the PVC/PEO conductive films with type of conductive fillers and PEGDE were extracted with toluene at room temperature for 24 h was analyzed by using a scanning electron microscopy (SEM) apparatus (Model JEOL JSM-6460 LA made in Japan). The specimen surfaces were sputter-coated with a thin layer of palladium using an auto fine coater (Model JEOL JFC 1600).

### Electrical conductivity testing

The electrical conductivity tests of films were measured using two probe I–V measurement systems. The electrical measurements were obtained using Keithley Model 4200 Semiconductor Characterization System made in England. The samples were measured with voltage varying from 0 to 10 V. The conductivity was calculated using its relationship with resistivity [9]. The resistivity can be calculated using the Eq. 1 below:

$$\rho = R \cdot \left( \frac{w \times t}{l} \right) \quad (1)$$

where  $R$  is resistance of the films,  $w$  is width,  $t$  is thickness, and  $l$  is length between the metal probe contacts. The conductivity,  $\sigma$ , was calculated using the Eq. 2 below:

**Table 1** Formulations of PVC/PEO conductive films with types of conductive fillers and PEGDE

Conductive films	PVC/PE (wt%)	DOTP (wt%)	CB (wt%)	PAni (wt%)	PPy (wt%)	PEGDE (wt%)
PVC/PEO/CB-15	50/50	15	15	–	–	–
PVC/PEO/CB-15/PEGDE	50/50	15	15	–	–	6
PVC/PEO/PAni-15	50/50	15	–	15	–	–
PVC/PEO/PAni-15/PEGDE	50/50	15	–	15	–	6
PVC/PEO/PPy-15	50/50	15	–	–	15	–
PVC/PEO/PPy-15/PEGDE	50/50	15	–	–	15	6

*DOTP* dioctyl terephthalate, *CB* carbon black, *PAni* poly (aniline), *PPy* poly (pyrrole), *PEGDE* poly (ethylene glycol) diglycidyl ether

$$\sigma = \frac{1}{\rho} \quad (2)$$

where  $\rho$  is resistance.

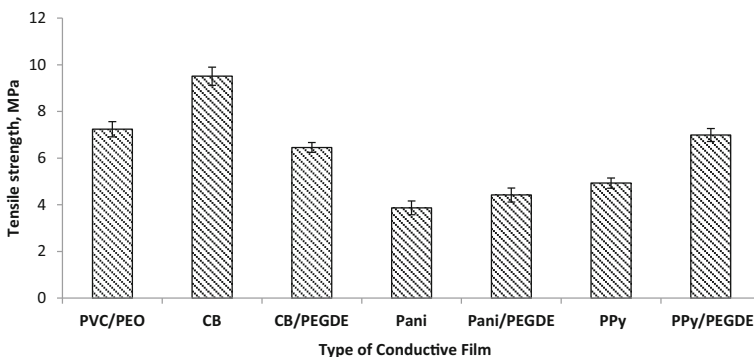
### Thermogravimetric analysis (TGA)

The thermogravimetry analysis of the conductive films was measured using Perkin Elmer Pyris Diamond TG/DTA 6000 made in USA. Specimens weight range from 7 to 10 mg were scanned from 30 to 650 °C with the heating rate of 10 °C min<sup>-1</sup> using constant nitrogen gas flow of 50 % weight loss ( $T_{-50\%WT}$ ) to prevent thermal oxidation process of polymer sample, and the residual mass of TG curve was calculated.

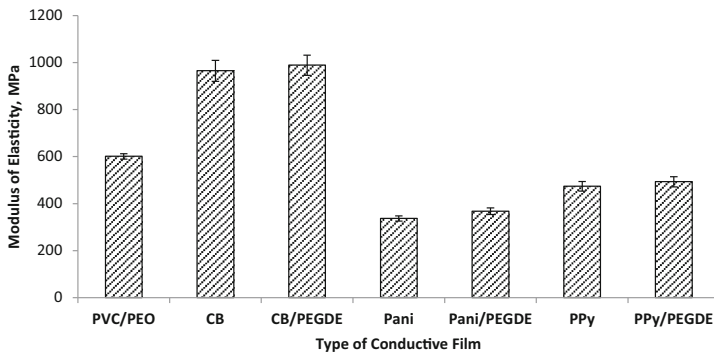
## Results and discussion

### Tensile properties

Figure 1 shows the effect of type of conductive fillers and with and without PEGDE on the tensile strength of PVC/PEO blends with 15 wt% of conductive filler. The PVC/PEO/CB-15 conductive films had the highest tensile strength followed by PVC/PEO/PPy-15, PVC/PEO/PAni-15, and PVC/PEO conductive films. The addition of intrinsic conducting polymers such as polyaniline and polypyrrole will decrease the tensile strength due to its poor tensile properties. Single component materials on the basis of PAni or PPy are characterized by extremely low mechanical properties and fragility [10]. However, the addition of 6 wt% of PEGDE as surface modifier had caused the tensile strength of all conductive films decreased. This was due to the substitution of polymer–polymer interaction with PEGDE into conductive films. Therefore, the interaction between polymer matrix and conductive filler particle was reduced.



**Fig. 1** Effect of conductive fillers and the addition of PEGDE on the tensile strength of PVC/PEO conductive films

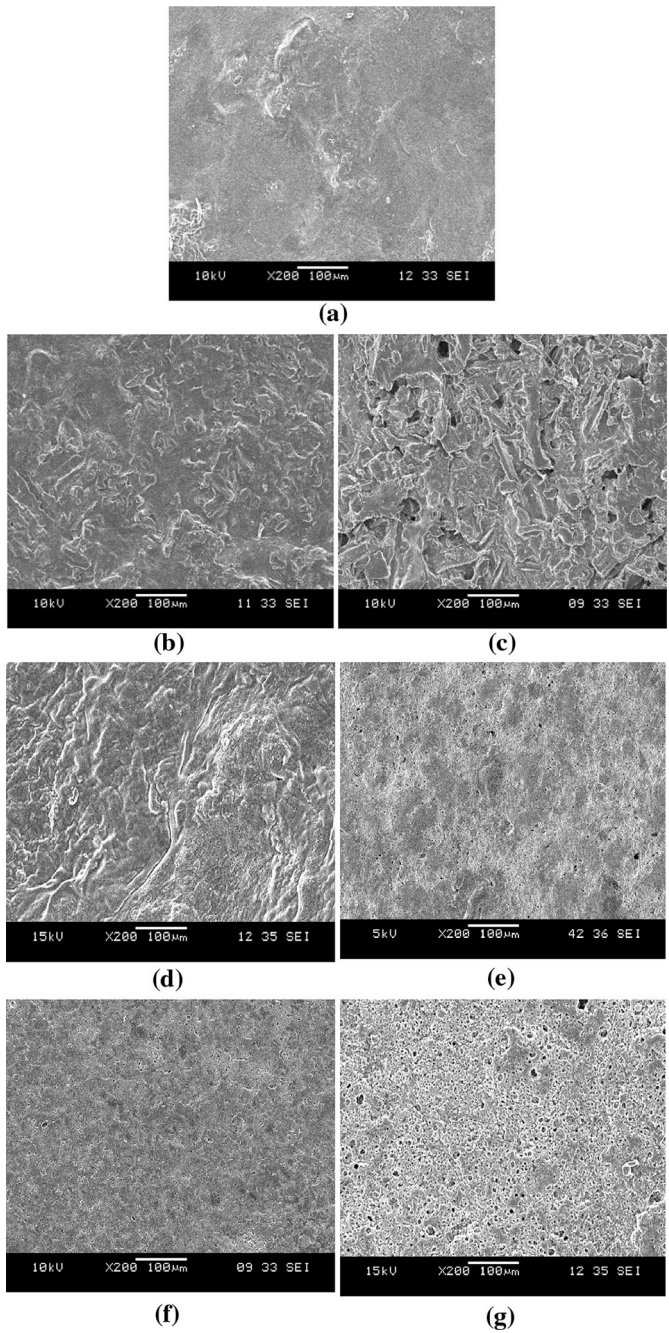


**Fig. 2** Effect of conductive fillers and the addition of PEGDE on the modulus of elasticity of PVC/PEO conductive films

The effect of type of conductive fillers and with and without PEGDE on the modulus of elasticity of PVC/PEO blends with 15 wt% of conductive filler is displayed in Fig. 2. The PVC/PEO/CB conductive film exhibited the highest modulus of elasticity followed by PVC/PEO/PPy, PVC/PEO/PAni and PVC/PEO conductive films. Generally, the modulus of elasticity of the addition of PEGDE was higher than without PEGDE. This was due to the better interfacial adhesion between PVC/PEO matrix and conductive fillers. The addition of PEGDE in PVC/PEO/CB conductive films also increased the stiffness and modulus of elasticity of polymer system.

### Morphology analysis

Figure 3 shows the scanning electron microscope (SEM) morphology of extracted surface of PVC/PEO, PVC/PEO/CB-15, PVC/PEO/CB-15/PEGDE, PVC/PEO/PAni-15, PVC/PEO/PAni-15/PEGDE, PVC/PEO/PPy-15 and PVC/PEO/PPy-15/PEGDE conductive films with similar filler loading. Figure 3a shows the SEM observation of pure PVC/PEO blend films. The surface of the pure PVC/PEO films shows smooth surface. Figure 3b shows the SEM micrograph of extracted surface PVC/PEO/CB-15 conductive films and Fig. 3c shows the micrograph of extracted surface of PVC/PEO/CB-15/PEGDE conductive films. Figure 3c shows better carbon black dispersion due to the addition of PEGDE. Figure 3d shows the micrograph of extracted surface of PVC/PEO/PAni-15 and Fig. 3e shows the micrograph of extracted surface of PVC/PEO/PAni-15/PEGDE conductive films. The PVC/PEO/PAni-15 and PVC/PEO/PAni-15/PEGDE conductive films present better dispersion, smaller size of particles and smoother surface of the conductive films compared to CB filled conductive films. Figure 3f shows the micrograph of extracted surface of PVC/PEO/PPy-15 and Fig. 3g shows the micrograph extracted surface of PVC/PEO/PPy-15/PEGDE conductive films. The micrograph of PVC/PEO/PPy-15 shows PPy good distribution with PVC/PEO blends whether with or without presence of PEGDE. This was attributed to the highest electrical conductivity than other conductive films. As Fig. 3g, the addition of PEGDE in



**Fig. 3** SEM micrographs of extracted surface of PVC/PEO conductive films with type of conductive fillers and PEDGE. **a** PVC/PEO, **b** PVC/PEO/CB-15, **c** PVC/PEO/CB-15/PEDGE, **d** PVC/PEO/PAni-15, **e** PVC/PEO/PAni-15/PEDGE, **f** PVC/PEO/PPy-15, **g** PVC/PEO/PPy-15/PEDGE

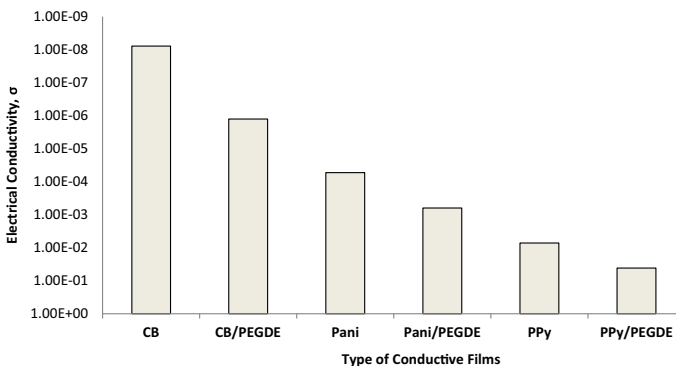
PVC/PEO/PPy-15 shows number of particles interconnected and improved conducting pathways between conductive filler and matrix. Therefore, the PVC/PEO/PPy-15/PEGDE significantly increased in electrical conductivity compared to PVC/PEO/CB-15 and PVC/PEO/PAni-15 conductive films.

### Electrical conductivity

Figure 4 shows the electrical conductivity of PVC/PEO conductive films for different type of conductive fillers, CB, PAni and PPy at 15 wt% and with addition of PEGDE. It can be seen that the highest and lowest value of electrical conductivity belongs to PVC/PEO/PPy-15/PEGDE and PVC/PEO/CB-15 conductive films, respectively. This was due to the addition of PPy which is intrinsic conducting polymer along with CB plus incorporating PEGDE improves the electrical conductivity of the PVC/PEO conductive films. At lower content of conductive fillers exhibits the distance of conductive fillers particle is very broad and the conducting pathways are discontinuous within PVC/PEO matrix and may lead to low conductivity. Low amount of conductive filler was dispersed to homogeneous matrix which would not change the conductivity until the conductive films are highly loaded that the aggregates would be in contact with each other. For PVC/PEO/PPy-15/PEGDE conductive films, the principle of electric conduction in the addition of PPy particles acted upon inter-chains of PVC/PEO matrix to lead the pyrrole with heterocyclic molecules to transform the pyrrole molecular structure into an electron transfer polypyrrole complex.

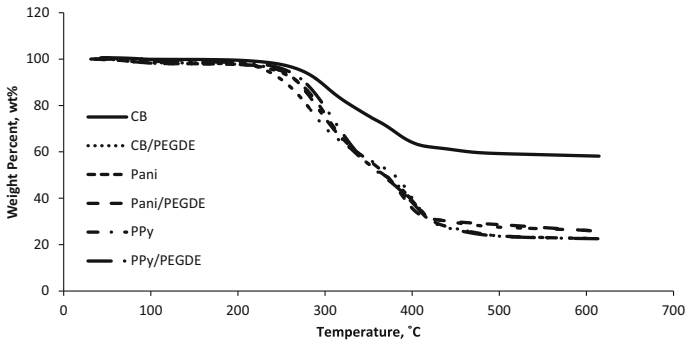
### Thermogravimetric analysis (TGA)

Figure 5 shows the typical thermal degradation curves of PVC/PEO/CB-15, PVC/PEO/CB-15/PEGDE, PVC/PEO/PAni-15, PVC/PEO/PAni-15/PEGDE, PVC/PEO/PPy-15 and PVC/PEO/PPy-15/PEGDE conductive films with similar filler loading. Table 2 shows the temperature at 5 % weight loss, peak decomposition temperature and residual mass for PVC/PEO/CB-15, PVC/PEO/CB-15/PEGDE, PVC/PEO/



**Fig. 4** Effect of conductive fillers and the addition of PEGDE on the electrical conductivity of PVC/PEO conductive films





**Fig. 5** TGA thermogram curves of PVC/PEO conductive films with conductive fillers and the addition of PEGDE

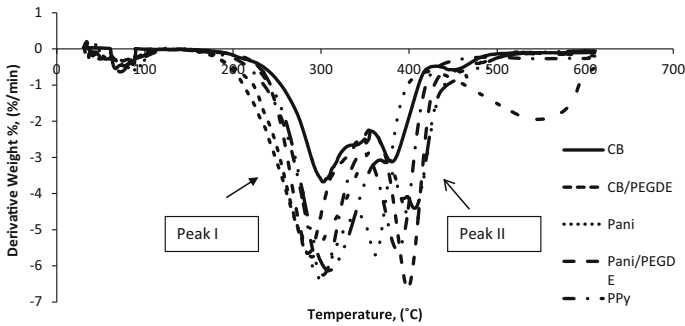
**Table 2** Data for  $T_{-5}$  wt%, decomposition temperature, and residual mass of PVC/PEO conductive films with type of conductive fillers and PEGDE

Conductive films	$T_{-5}$ wt% (°C)	Decomposition (°C)		Residual mass (%)
		Peak I	Peak II	
PVC/PEO/CB-15	268.32	296.89	373.8	58.37
PVC/PEO/CB-15/PEGDE	365.02	297.57	358.15	22.60
PVC/PEO/PAni-15	232.97	279.25	394.7	24.43
PVC/PEO/PAni-15/PEGDE	249.31	282.55	392.96	22.57
PVC/PEO/PPy-15	249.33	302.2	381.30	22.69
PVC/PEO/PPy-15/PEGDE	256.59	300.97	401.24	22.54

$T_{-5}$  wt% temperature at 5 % weight loss

PAni-15, PVC/PEO/PAni-15/PEGDE, PVC/PEO/PPy-15 and PVC/PEO/PPy-15/PEGDE conductive films. The result finding that a PVC/PEO/CB-15 conductive film gives the highest thermal stability with residual mass around 58.37 %. This was due to the addition of carbon black which gives rise to catalyzed cyclization and significantly increases their thermal stability. Figure 5 shows that the addition of PPy clearly decreases the thermal degradation of PVC/PEO/PPy-15/PEGDE conductive film. The thermal degradation of PVC/PEO/PPy-15/PEGDE conductive films shows the PPy particles acts as conducting filler in the PVC/PEO blend which the PPy particles randomly formed aggregation within the PVC/PEO blend chain. Thus, it hindered the molecular cyclization lead to decrease thermal degradation [11]. Ouyang et al. [12] stated that the decrease of the thermal stability for PVC/PPy conductive composites is caused by the degradation of the surface region of the PPy layer. This was due to the PPy is one of intrinsic conductive polymers that are not stable at elevated temperatures in the presence of oxygen.

Figure 6 shows the DTG curves for PVC/PEO conductive films with various types of filler at 15 wt% and addition of PEGDE. From the Fig. 5, it can be clearly seen that the peak decomposition temperature of all conductive films shows the



**Fig. 6** DTG thermogram curves of PVC/PEO conductive films with conductive fillers and the addition of PEGDE

changes in thermal decomposition temperature with different filler loading and addition of PEGDE. The two peaks of degradation phenomena/modes are significant in the present work as the first DTG peak may represent the decomposition of the PVC/PEO while the second peak represents the breakdown of conductive fillers.

## Conclusion

The conductive films in this research project were produced by mixing poly (vinyl chloride) and poly (ethylene oxide), forming PVC/PEO blends. The PVC/PEO/CB-15 showed higher tensile strength followed by PVC/PEO/PPy-15/PEGDE, PVC/PEO, PVC/PEO/CB-15/PEGDE, PVC/PEO/PPy-15, PVC/PEO/PAni-15/PEGDE, PVC/PEO/PAni-15 conductive films. The highest modulus of elasticity was shown by PVC/PEO/CB-15/PEGDE conductivity films compared to the others. Besides, the electrical conductivity results exhibited PVC/PEO/PPy-15/PEGDE conductive films had the highest electrical conductivity, followed by PVC/PEO/PAni-15, and PVC/PEO/PPy-15 conductive films with the lowest electrical conductivity.

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