

PREPARATION OF NON-WOVEN FIBER MATS BY MIXTURE OF PVC AND EPOXIDIZED NATURAL RUBBER

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ABSTRACT

Eletrospun non-woven fiber mats prepared from ENR modified PVC were successfully fabricated at ambient temperature by electrospinning method. Liquid epoxidized natural rubber (LENR) was used because it is easier to handle compared to dried ENR. PVC was mixed with LENR based on 3 different ratios (9:1, 8:2 and 7:3). The effect of ENR on electrospinnability of PVC was investigated. The morphologies and thermal properties of the electrospun fiber mats were characterized and assessed using scanning electron microscopy (SEM), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The polymer solution concentration 16wt% formed a homogenous PVC/LENR electrospun fiber mats. SEM micrograph showed that the morphology and diameter of the fibers were mainly affected by the addition of natural rubber and weight ratio of the solution. The diameter of the fiber also decreased with increasing amount of LENR in the solution. Thermal degradation involved two-step degradation with the first degradation representing the dehydrochlorination of PVC to form polyene and followed by the decomposition of LENR and the polyene. Addition of LENR into the sample caused the T_g of electrospun fiber mats of PVC/LENR to shift toward lower temperature.

ABSTRAK

Tikar serat eletrospun bukan tenunan yang disediakan daripada ENR PVC diubahsuai telah berjaya direka pada suhu ambien dengan kaedah electrospinning. Cecair epoxidized getah asli (LENR) telah digunakan kerana ia lebih mudah untuk mengendalikan berbanding ENR kering. PVC adalah dicampur dengan LENR berdasarkan 3 nisbah yang berbeza (9:1, 8:02 dan 7:3). Kesan ENR pada electrospinnability PVC telah dikaji. Morfologi dan sifat haba daripada tikar serat electrospun telah dicirikan dan dinilai menggunakan pengimbasan elektron mikroskop (SEM), analisis gravimetrik terma (TGA) dan kalori pengimbasan kebezaan (DSC). Larutan kepekatan polimer 16wt% membentuk PVC /LENR tikar serat electrospun homogen. Mikrograf SEM menunjukkan bahawa morfologi dan garispusat gentian terutamanya terjejas dengan penggunaan getah asli dan nisbah berat daripada penyelesaian. Garispusat gentian juga menurun dengan jumlah yang semakin meningkat dalam LENR penyelesaian. Degradasi haba yang terlibat kemusnahan dua langkah dengan kemusnahan yang pertama mewakili menggunakan proses PVC untuk membentuk polyene dan diikuti oleh penguraian LENR dan polyene itu. Penambahan LENR ke dalam sampel yang disebabkan T_g tikar serat electrospun PVC / LENR untuk beralih ke arah suhu yang lebih rendah.

Keywords: electrospinning, epoxidized natural rubber, electrospun fiber

INTRODUCTION

Electrospun fibers have been classified as a new ‘class of non-woven’ as the fibers are collected in the form of fibrous web structure (Grafe & Graham, 2003). A method known as electrospinning is used to prepare the electrospun non-woven fiber mats. The fiber mats usually have diameter less than a micron and they are identified by higher surface-to-volume ratio compared to film and bulk fibres (Feng et al., 2009; Grafe & Graham, 2003; Nisbet et al., 2009; Ramakrishna et al., 2005; Ramakrishna et al., 2006; Sawicka & Gouma, 2006), small pores (Ramakrishna et al., 2005; Sawicka & Gouma, 2006) and light weight (Grafe & Graham, 2003). Because of these characters, electrospun fiber mats are used in a variety of applications such as filtration (Grafe & Graham, 2003; Gopal et al., 2006; Ramakrishna et al., 2005; Ramakrishna et al., 2006; Sawicka & Gouma, 2006), biomedical (Greiner & Wendorff, 2007; Ramakrishna et al., 2005; Ramakrishna et al., 2006; Sawicka & Gouma, 2006), electronic (Ramakrishna et al., 2005; Ramakrishna et al., 2006) and protective clothing (Greiner & Wendorff, 2007; Ramakrishna et al., 2005; Ramakrishna et al., 2006).

Electrospinning starts when a high electrostatic voltage is applied on a drop of polymer solution which held by its surface tension at the tip of the syringe. At one point, the voltage will overcome the solution surface tension, which cause the surface of the liquid distorted and start to form a conical shape known as the Taylor cone. A stable liquid jet is ejected from the Taylor cone’s tip. While the jet move through the air, the solvent will evaporates leaving behind a fine electrospun fiber collected on the electrically grounded drum collector. The interaction between the external electric field and the surface charge of the liquid drop is the cause of the jet bent. Unlike commercial nonwoven fabrics, electrospun fiber mats have small pore size and larger specific surface area (Yuan et al., 2005).

Polyvinylchloride (PVC) was selected as the starting material for the preparation of electrospun membrane fibers due to the range of good properties such as excellent recoverability, chemical stability and wide usage (Rajendran & Uma, 2000). PVC’s major advantage is its compatibility with different kinds of additives which making it a highly versatile polymer. PVC electrospun fiber has been widely used in many fields as a high-efficiency fine particulate filter (Ding et al., 2013), polymer electrolytes (Cao et al., 2012), corrosion inhibitor (Elzatahry et al., 2012) and etc. Previously, Lee et al. (2002) studied the PVC electrospun fiber formation by electrospinning as a part of his study on the effect of mixed solvents. In addition, Gupta & Wilkes (2003) explored the possibility of side-by-side bi-component electrospinning with PVC and PVdF as the polymer blends.

PVC is known for its capability to form miscible blends with various high or low molecular weight polymers which perform as plasticizers (Varughese et al., 1989). This includes nitrile butadiene rubber (NBR), epoxidized natural rubber (ENR) and chlorinated polyethylene (CPE). Unique properties of ENR have made it as a suitable pair to blend with PVC. It has oil resistance, reduced air permeability, damping and wet grip compared to the synthetic rubber (Gelling, 1985). Previous research has proved that plasticized or stabilized PVC and ENR form miscible blends at any ratio (Varughese et al., 1989). PVC will be expected to give high tensile strength and good chemical resistance while ENR will act as a permanent plasticizer for PVC which gives good tear strength and enhance resistance against hydrocarbon oil.

MATERIALS AND METHODS

Materials and Chemicals

Low molecular weight polyvinyl chloride (PVC) was purchased from Sigma-Aldrich (M) Sdn. Bhd and epoxidized natural rubber was supplied by Guthrie Corp (M) Bhd.

Preparation of Liquid Epoxidized Natural Rubber

Liquid epoxidized natural rubber (LENR) was prepared by 150g of epoxidized natural rubber in toluene, in accordance with the technique as reported previously (Dahlan et al., 1999). The molecular weights of liquid epoxidized natural rubber (LENR) used as determined by gel permeation chromatography (GPC) were between 4.0×10^4 and 8.0×10^4 .

Preparation of The Electrospun Fiber Samples

PVC and LENR were mix based on ratio of 10:90, 80:20 and 70:30. The solutions were mixed and stirred thoroughly for 24 hours. Solution viscosities were determined by a rotational viscometer (Brookfield DV-II+ Viscometer) with a rotational speed of 10 rpm at 25 °C. A high voltage power supply (Kato Tech Co. Ltd.) was employed to supply the high voltage. The voltage used in this study was 16 kV. The distance between syringe's tip and collector drum was fixed at 15 cm. The solutions were loaded into 20mL syringe, and the inner diameter of needle was 1.2 mm.

Morphology

Scanning Electron Microscope (SEM) model FEI Quanta 400 with 500x and 2000x magnification were used for fiber membrane morphology examination. Studies performed in high vacuum mode and at a voltage of 20 kV. Samples coated with a thin layer of gold using the SC 500 sputter coater model in vacuum surrounding around 0.1 - 0.5 torr in the presence of an inert gas (Argon). SEM observations were conducted on samples of the fiber membrane from the top and the cross-section images. PVC electrospun fiber was used as a control to compare membrane with and without the addition of LENR. The diameters of the electrospun PVC/LENR fibers were measured directly from the SEM micrographs of fibers using Adobe Photoshop CS5 (Ruler Tool).

Thermal Analysis (TGA & DSC)

TGA Q500 TA Instruments model was used to determine the temperature resolution and the percentage weight loss of samples at a given temperature. Sample undergoes degradation during the analytical run. Fiber membrane samples were analyzed at heating rate of 10 °C per minute to a temperature range from room temperature up to 800 °C. Sample weight used in this analysis is 3 mg. The ratio of the different natural rubber gives different temperature resolution. PVC electrospun fiber membrane was also used as a control. DSC Q20 TA Instruments was used in order to determine the change of electrospun fiber's T_g . Samples used were 2.5 mg and the heating rate for this analysis was 10 °C/min. The analysis was done in ambient temperature under dry nitrogen atmosphere.

RESULTS AND DISCUSSION

Spinnable Concentration

One of the most important parameter in electrospinning process is concentration. In our study, continuous PVC/LENR fibers were successfully electrospun from the PVC/LENR solutions in THF with concentration of 16 wt%. For the lower concentration of PVC/LENR solution, only droplets of the solution were formed on the collector when the solution concentration was set from 10-13 wt%. Figure 1 shows the SEM micrographs of lot continuous fibers with beads and some fiber segments obtained when the concentration was increased to 14 wt% and 15 wt%. The formation of beaded fibers had been studied widely (Lee et al., 2002). They were referred as "by products" often formed in electrospinning process. It was studied that the formation of beaded fibers is connected to the instability of the jet sample solution, surface tension and solution viscosity (Entov & Shmaryan, 1997).

On the other hand, the electrospinning process becomes difficult for higher concentration of PVC/LENR solution. When the concentration was set to 17 wt% and 18 wt%, fibers with bigger bead were formed (Figure 2). Furthermore, with the solution concentration higher than 16 wt%, high viscous fluid balls could be gathered at the tip of the needle due to the solvent volatilization. As a result, no fibers could be formed on the collector, no matter how high the voltage was applied on the PVC/LENR solutions. Similar observation occurred when the amount of LENR added exceeded 30% in the PVC/LENR solution. Hence, the spinnable concentration of PVC/LENR solution in electrospinning is 16wt% with the maximum percentage of 30%.

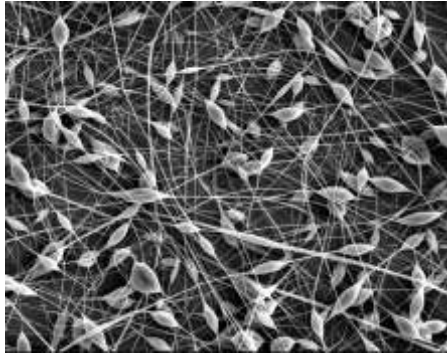


Figure 1: Effect of lower concentration of PVC/LENR solution

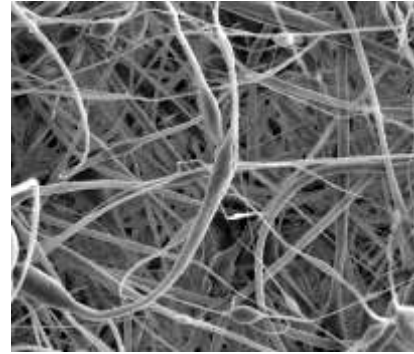


Figure 2: Effect of higher concentration of PVC/LENR solution

Viscosity of Polymer Solutions

Hsiao et al. (2002) had reported that the sample solution concentration or the viscosity was one of the most important variables controlling the electrospun fiber produced. Thus the effect of the LENR on the sample solution and hence on the electrospinning was investigate. Figure 3 shows the relationship between the spinnable concentrations and the sample solution viscosities of PVC and PVC/LENR solutions. The viscosities of PVC/LENR decreased from 235 cP to 95 cP with the increase of the LENR from 10 wt% to 30 wt%.

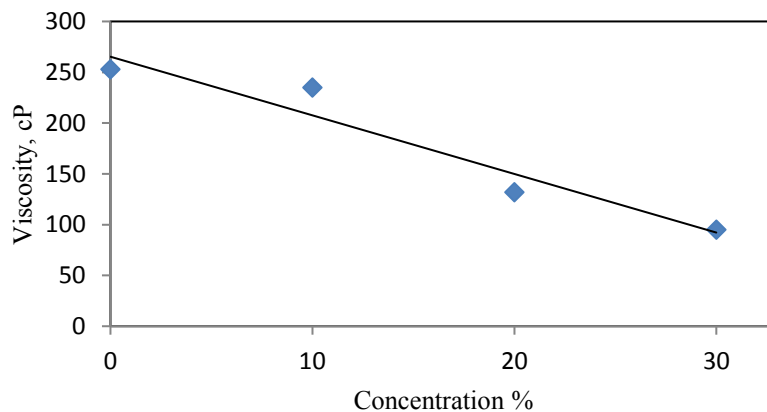


Figure 3: Solution viscosity as a function of LENR solution concentration

Effect of ENR on Fiber Morphology

The SEM micrographs and range of size distributions of the electrospun PVC/LENR fibers with different percentage of LENR are shown in Figure 4 (cross section) and Figure 5. The size distribution of each electrospun PVC/LENR fibers was measured and averaged from a sample of 50 fibers. The addition of LENR was found to change the morphology of the electrospun fibers. PVC electrospun fiber mats have a larger gap between the fibers compared to PVC/LENR fiber mats (Figure 4). Addition of LENR caused the number of

fiber to increase although the volume of polymer solution used was unchanged. Low molecular weight of ENR caused the viscosity of the solution to decrease and flow rate to increase (Theron et al., 2004). Hence, the fiber size is decreasing. Increasing number of fibers cause the gap between the fibers also decreasing. From the Figure 5, the average fibers diameter of PVC is about 7-9 μ m. As the LENR increasing, the fibers become smoother and smaller. The average fibers diameter of 90:10 PVC/LENR, 80:20 PVC/LENR and 70:30 PVC/LENR are about 3-5 μ m.

Thermal Properties Analysis

Samples were prepared in different compositions such as 90/10, 80/20 and 70/30 to PVC and LENR. All the samples were subjected to thermogravimetric analysis and the data were analyzed for the effect of epoxy content of ENR on the degradation pattern of PVC. Thermogravimetric traces of PVC, 90:10 PVC/LENR, 80:20 PVC/LENR and 70:30 PVC/LENR are given in Figure 6 (a)-(d). For all samples, a two-stage degradation pattern is observed. In case of PVC, the first stage begins at 202 $^{\circ}$ C and ends at temperature round up to the nearest whole number 326 $^{\circ}$ C and 267 $^{\circ}$ C (Table 1). This resembles to a weight loss of round up to 63% which is attributed to the expulsion of HCl molecules leaving behind a long polyene chains. The second stage of degradation begins at 360 $^{\circ}$ C and ends at 469 $^{\circ}$ C with a peak temperature of 415 $^{\circ}$ C. At this stage, thermal degradation of the polyene chains take place which yield volatile aromatic and aliphatic compounds by the intramolecular cyclisation of the conjugated sequences (Wypych, 1985).

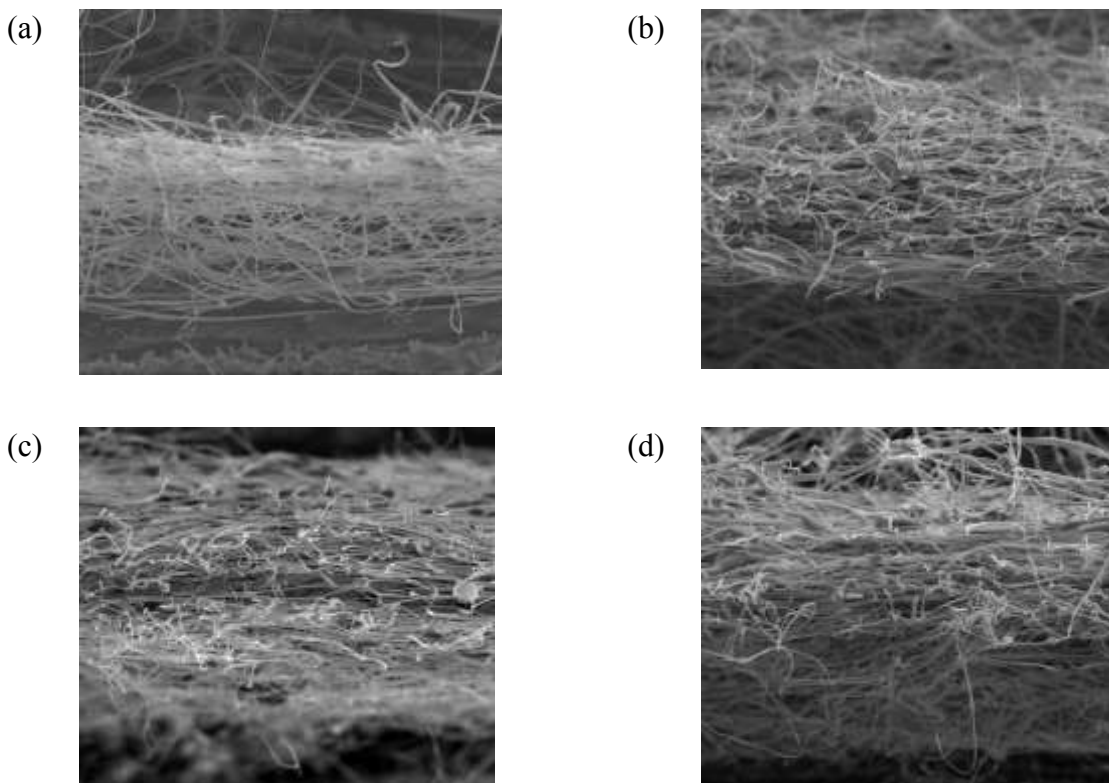
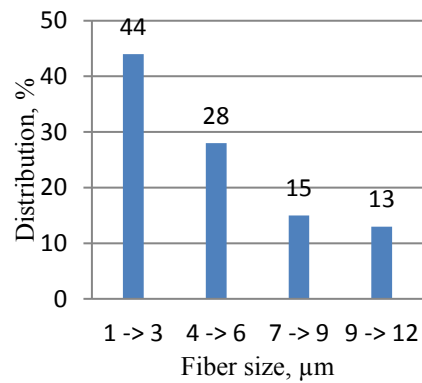
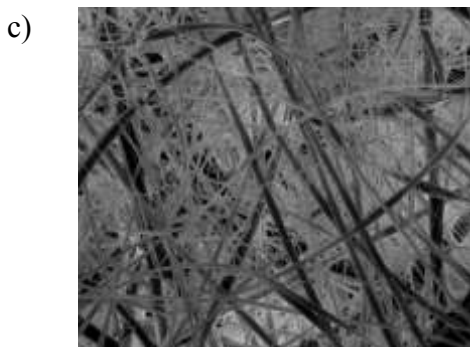
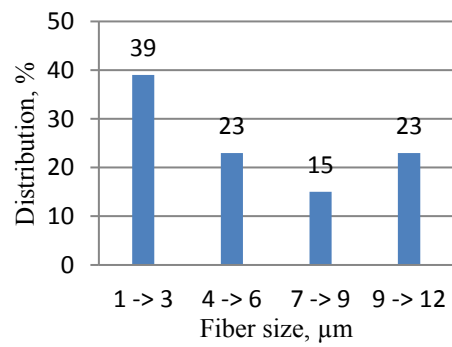
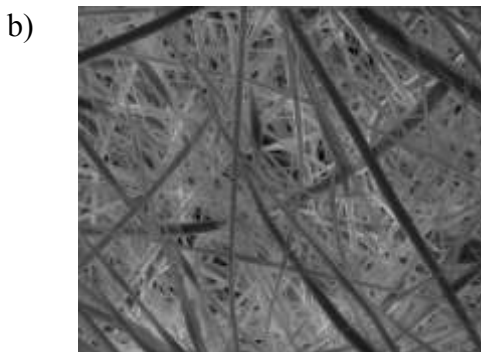
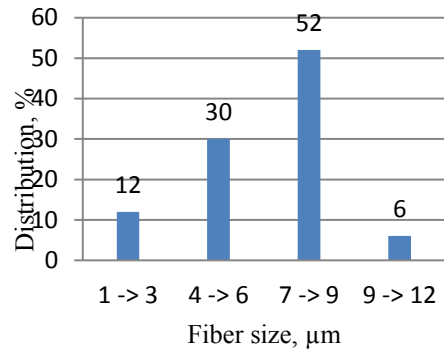
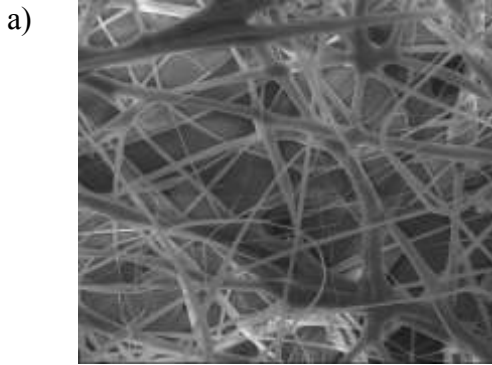


Figure 4: SEM micrographs of cross section for membrane mats of: (a) PVC, (b) 9:1 PVC/LENR, (c) 8:2 PVC/LENR and (d) 7:3 PVC/LENR

Table 1: Thermogravimetric data for electrospun fiber of PVC and PVC/LENR

Sample	1 st stage		2 nd stage	
	Peak temperature	Weight loss (%)	Peak temperature ($^{\circ}$ C)	Weight loss (%)

	(°C)			
PVC	267.39	62.81	415.17	27.51
PVC 90:10 LENR	240.86	55.32	409.42	32.44
PVC 80:20 LENR	242.58	52.89	404.01	37.24
PVC 70:30 LENR	243.58	49.20	399.33	42.76



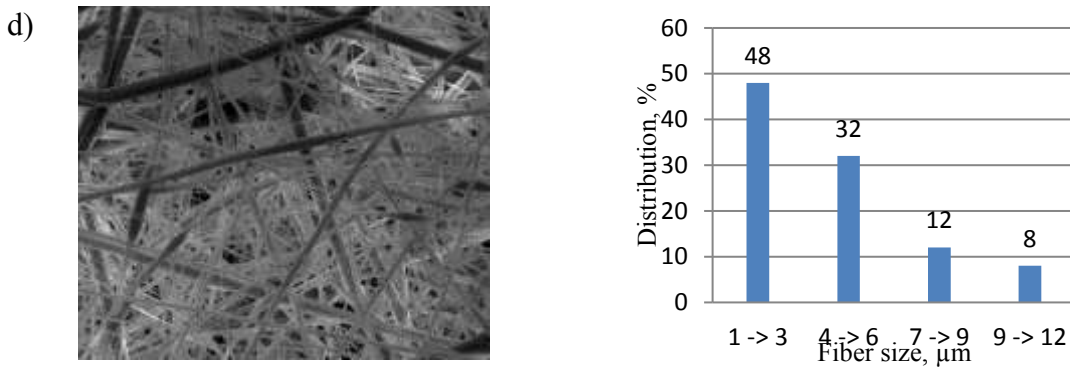


Figure 5: SEM micrographs and fiber size distribution of: (a) PVC, (b) 90:10 PVC/LENR, (c) 80:20 PVC/LENR and (d) 70:30 PVC/LENR

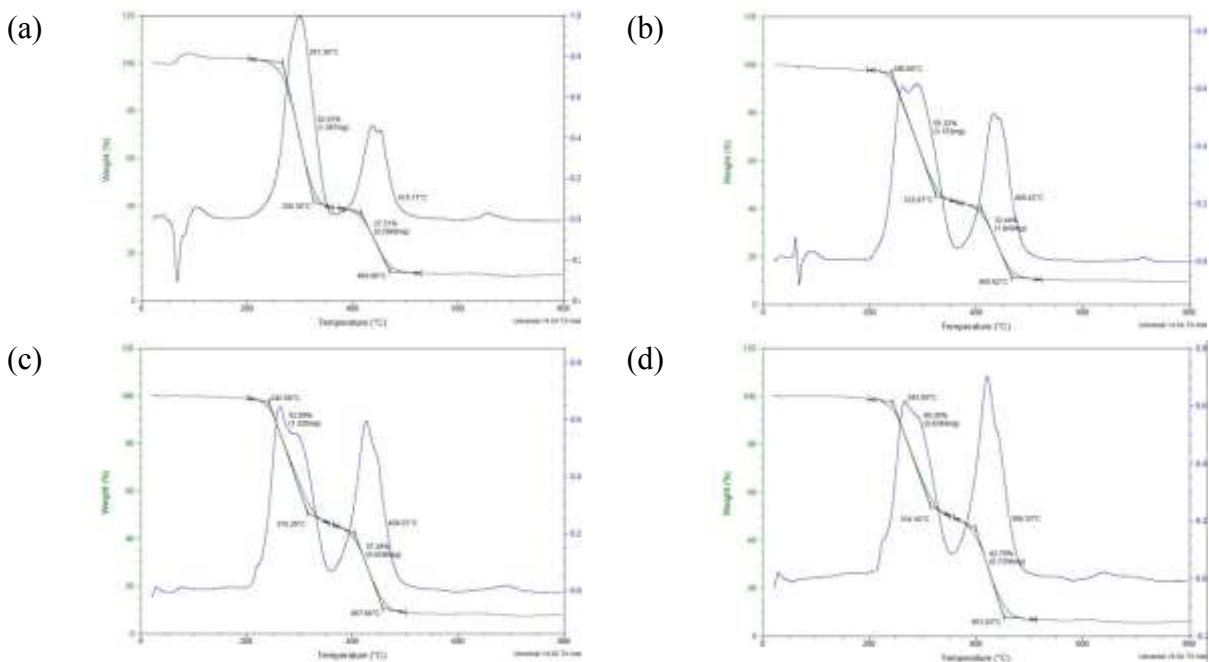


Figure 6: Thermogravimetric curves of : (a) PVC, (b) 90:10 PVC/LENR, (c) 80:20 PVC/LENR and (d) 70:30 PVC/LENR

Compared to PVC sample described above, peak temperature of the first stage degradation of PVC/LENR series occurs at lower temperatures, which seem to be increasing with the LENR content of the sample. An increase from 240 °C to 242 °C is observed as the LENR content is increased from 10% to 20% and remains around at 243 °C at 30 %. The weight loss after the first stage degradation was found to be 55%, 52% and 49% respectively. It is to be recognized that the mass loss undergoes a decrease as the LENR content is increased in the sample, which indicates the stabilizing effect on PVC. However, the second stage degradation occurs as before. It is known that epoxy group absorbs hydrogen chloride (Figure 7), and thereby stalling its catalytic activity for further dehydrochlorination of the PVC (Penn, 1971).

DSC thermograms of the electrospun fiber mats of PVC/LENR blends are shown in Figure 8. The analysis was carried out to determine the change of T_g between PVC and PVC/LENR electrospun fibers. For pure PVC, the T_g was 61 °C (Table 2). When the percent of LENR is increased, the T_g shift towards lower temperature which is from 55 °C to 47 °C. According to Biju et al. (2007), a miscible system was formed due to high epoxy content in LENR which enhanced the miscibility of PVC/LENR blend. Hence, the LENR act as plasticizer caused by the oxirane group, which add the element of complementary dissimilarity to the non-polar component (Olabisi, 1975).

Table 2: DSC data for electrospun fiber of PVC and PVC/LENR

Sample	T _g (°C)	T _m (°C)
PVC	61.78	152.32
PVC 90:10 LENR	55.07	148.01
PVC 80:20 LENR	52.51	148.56
PVC 70:30 LENR	47.47	146.18

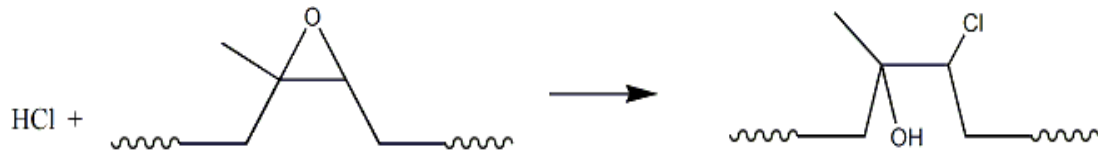


Figure 7: Epoxy group absorbs hydrogen

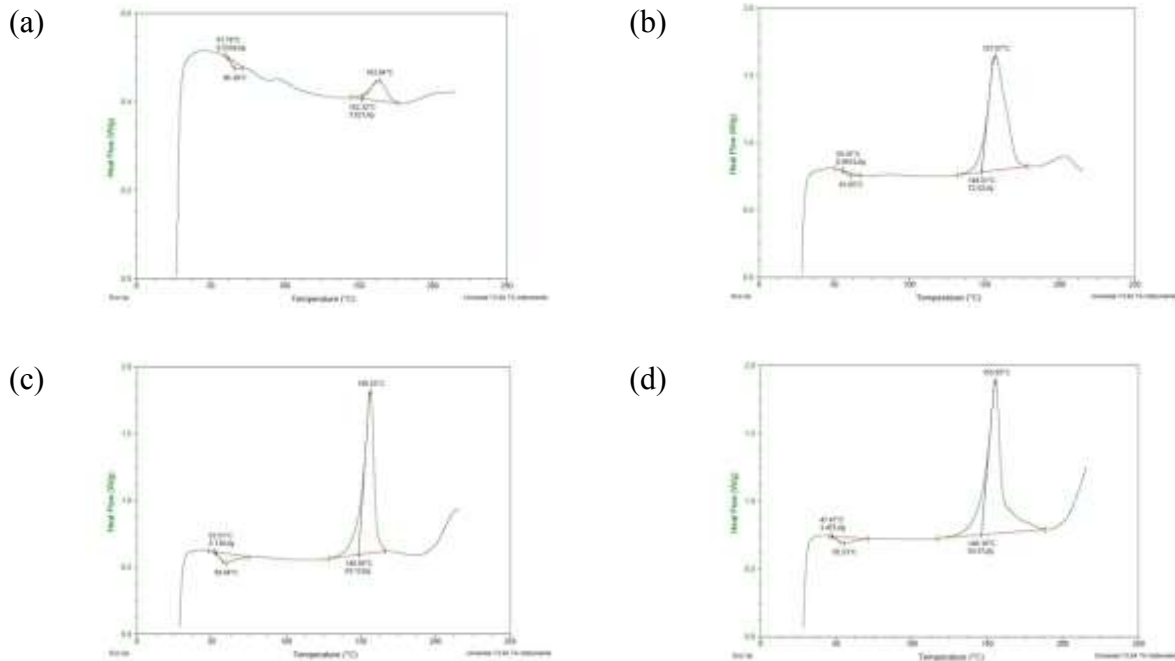


Figure 8: DSC thermograms of electrospun fiber mats of: (a) PVC, (b) 90:10 PVC/LENR, (c) 80:20 PVC/LENR and (d) 70:30 PVC/LENR

CONCLUSIONS

The PVC/LENR fibers were successfully produced by electrospinning. The spinnable concentration of the PVC/LENR solution was 16 wt%. Higher solution concentration caused the formation of spindle like fiber and lower concentration caused the formation of with a lot high degree of beads. The diameter of the electrospun fiber and degradation temperature decreases with the addition of LENR.

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