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Effect of Nano-Refractory Bricks on the Morphological and Thermal Properties of PVC/LDPE Polymer Blend

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Abstract: In this study, the morphological and thermal properties of a blend consisting of 75% polyvinyl chloride (PVC) and 25% low-density polyethylene (LDPE), reinforced with nano-refractory bricks (NRB) at varying ratios (1%, 3%, 5%, and 7%), were prepared and investigated. The objective was to enhance the blend's thermal stability and surface structure homogeneity. The morphological structure of the prepared samples was analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The obtained images revealed that the nano-refractory brick particles remained predominantly within the PVC phase, resulting in an increased composite density without significantly affecting the LDPE phase. This suggests that the overall morphology of the composite is largely unaffected by the presence of the nano-refractory bricks. From a thermal perspective, thermogravimetric analysis (TGA/DTG) was conducted on all samples from room temperature up to 600 °C at a heating rate of 10 °C/min. FTIR and TGA results indicated that the decomposition onset temperature shifted to higher values due to the presence of nano-refractory bricks, with the most pronounced shift observed in the sample containing 3% reinforcement. Additionally, the rate of mass loss was reduced. These findings demonstrate that reinforcing the PVC/LDPE blend with nano-refractory bricks improves its performance, making it more suitable for applications that demand enhanced thermal and mechanical properties, such as those in the construction and electronics industries.

***Keywords**: Nano-Refractory Bricks, Low Density Polyethylene, Polymer, Thermal Properties.*

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I. INTRODUCTION

Polymeric materials such as polyvinyl chloride (PVC) and low-density polyethylene (LDPE) have garnered significant attention in recent decades due to their versatility, cost-effectiveness, and ease of processing. These polymers are extensively utilized across various industrial and commercial applications, ranging from packaging to construction and electrical insulation. However, despite these advantages, their poor thermal stability remains a critical challenge in industrial applications [1–3].

Blending PVC with LDPE combines the unique properties of both polymers, offering enhanced flexibility, durability, and processability. To further improve the thermal stability and morphological homogeneity of such blends, the incorporation of nanomaterials has emerged as a promising strategy. Due to their large surface area and unique physicochemical properties, nanoparticles can significantly influence the structure and performance of polymer composites, even at low concentrations [4].

Pospisil investigated the thermal, mechanical, and decomposition properties of various polymer blends. The findings indicated that PVC blended with LDPE can withstand processing temperatures up to 180 °C. However, when the temperature exceeds the melting point of PE and the PE content in the blend is high, PVC degradation becomes more pronounced [5].

Thongpin et al. [6] examined the decomposition behavior of PVC/PE blends in terms of decomposition temperature, polyene index, and glass transition temperature. Their findings suggested that the addition of a small amount of polyethylene could enhance the thermal stability of PVC's molecular structure. Between 2001 and 2004, several studies investigated the effects of polyethylene's molecular structure and the use of compatibilizers on the thermal and rheological properties of PE/PVC blends [5-7–8].

In recent years, the development of PVC-based nanocomposites with significantly enhanced properties has attracted considerable interest. For example, Wang et al. evaluated the impact of nanoclay on the thermal behavior of PVC using thermogravimetric analysis (TGA), demonstrating that the clay modified the degradation pathway of PVC [9]. However, other reports suggest that PVC/organic clay nanocomposites may exhibit lower thermal stability than pure PVC [10].

In this context, nano-refractory bricks—which possess excellent thermal resistance and mechanical strength—have emerged as potential reinforcing materials. Their incorporation into polymer matrices may enhance thermal behavior and structural integrity, making the resulting composites suitable for more demanding applications.

This research aims to investigate the effect of different concentrations of nano-refractory bricks on the morphological and thermal properties of PVC/LDPE blends. Through detailed analysis using scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR), this study seeks to elucidate the interactions between polymer phases and nanofillers and to assess the suitability of the resulting materials for applications in the construction and electronics industries.

II. EXPERIMENTAL

➢ *Materials*

In this research, we used locally available polyvinyl chloride (PVC) in the form of green granules with a density of ($1.36 g/cm^3$). This plastic polymer is of great industrial importance due to its excellent properties, such as high flexibility and malleability, resistance to corrosion and rust, resistance to damaging factors such as water or high temperatures, light weight compared to metals, thermal insulation, good electrical resistance, sound insulation properties, and resistance to shock and vibration, among others. Low-density polyethylene (LDPE) from RasLanuf Company, product number (LLF-181HD), was also used. It is a colorless or gray transparent granule with a low density ($0.918 g/cm^3$). This polymer is characterized by high mechanical properties and good processability.

The nano-refractory bricks (51nm) used are a type of brick enhanced by the addition of nanomaterials. They consist of SiO_3 (40.91%), $MgCl_26H_2O$ (30%), and $Al_6Si_2O_{13}$ (29.09%), and feature improved physical and mechanical properties, along with higher thermal performance.

75% PVC was blended with 25% LDPE. Different weight percentages of nano-refractory bricks were then added to the mixture (1%, 3%, 5%, and 7%). To obtain a homogeneous mixture, final mixing was performed using a (HAAK MiniCTW) twin-screw extruder, set at (30 rev/min) and (180°C).

The mixture was air-cooled and then cut into small granules. Hot pressing then formed the granules into round films. This process was carried out by compressing (1.3g) of granules at (5bar) pressure, with a holding time of (10min), using a hydraulic press (Model: Sassuolo, Ceramic Instruments, Italy). The samples were characterized using various techniques.

III. MEASUREMENTS

➢ *X-ray Diffraction (XRD)*

The degrees of interference of nano-refractory bricks in the composite were evaluated by X-ray diffraction (XRD) analysis. X-ray diffraction (XRD) patterns were recorded at room temperature using a (PW 1800 X-ray diffraction device) from (M/s Philips NV, The Netherlands). The device utilized monochromatic (CuKα) radiation with a wavelength of ($\lambda = 1.5418$ Å), operating at (30kV) and (20mA). During testing, the diffraction angle **(2θ)** was set between (20° and 80°), with a scanning speed of (5°/min).

➢ *FTIR Studies*

Fourier transform infrared (FTIR) analysis was performed using an (IR Affinity-1) instrument within a wavelength range of (400–4000 cm^{-1}), at a scan rate of 4 and a resolution of (4 cm^{-1}).

➢ *Scanning Electron Microscopy (SEM)*

The morphological features of the samples were studied using, a (Philips FEG Quanta 250) field-emission scanning electron microscope (FE-SEM) equipped with a field-emission gun (FEI, Netherlands) was employed.

➢ *Thermal Property*

Thermogravimetric analysis (TGA) was conducted using a (Goloble MR Solution TGA BAXT-TGA101) to assess the thermal stability of the thermoplastic composite and enhance its properties. The analysis was carried out in a nitrogen environment, with a heating rate of (20°C/min), over a temperature range of (25–1584°C).

IV. RESULTS AND DISCUSSION

➢ *XRD Results*

The XRD patterns of pure PVC/LDPE and with different percentage of nano-refractory bricks are shown in Fig (1). X-ray diffraction pattern of pure PVC/LDPE (curves sp) shows a sharp peak at ($2\theta = 21.5^{\circ}$) with intensity (2656), which represents the level (110) and the prevailing trend.

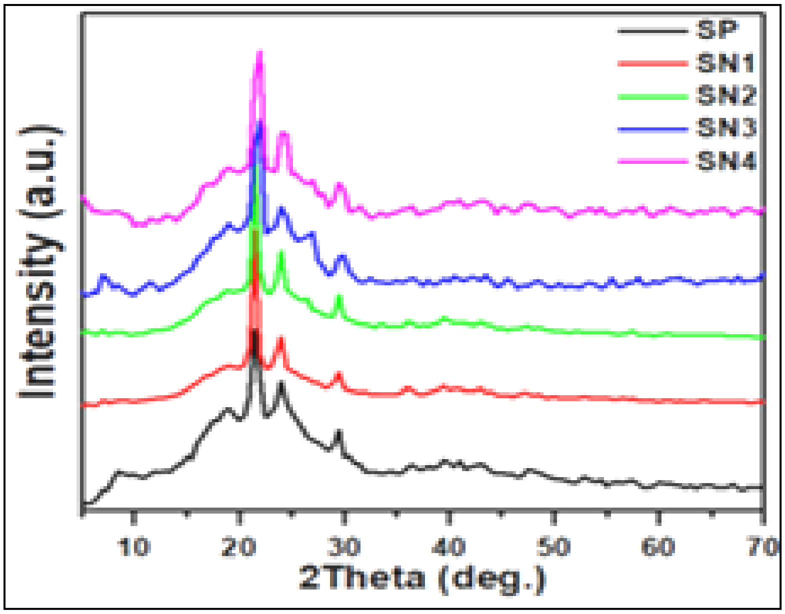

Fig 1. XRD Patterns of Pure PVC/LDPE and with Different Percentage of Nano-Refractory Bricks.

We find that this peak in the (curves SN1 and SN2), where the concentration of nano-refractory bricks (1% and 3%) appears at the same angle with an increase in intensity as well as peak width, which means that the nano-refractory bricks have been inserted into the crystal structure of the prepared composite. Also, when the intensity of the peaks increases, this typically indicates that the material has become more ordered at the atomic level, meaning increased crystallinity. Broadening of the peaks is typically associated with a decrease in crystal size, according to the Scherrer equation. Crystal stresses (such as those caused by defects or distortions in the crystal lattice) can also lead to broadening of the peaks. Whereas when the concentration of nano-refractory bricks increases to a concentration higher (5% and 7%) (curves SN3 and SN4), we find that this peak shifts to a higher angle ($2\theta = 22^{\circ}$) with a significant decrease in intensity and a significant increase in width. This indicates that the crystal sizes have become smaller, making the peaks wider and less pronounced. Internal stresses resulting from defects in the crystal lattice also broaden the peaks and decrease their intensity. There is also a change in chemical composition (phase or composition change) that shifts the peaks to higher angles, indicating a contraction of the crystal lattice, indicating the introduction of smaller ions into the lattice. which is in agreement with the decrease in the distance between the interlayer's.

➢ *FTIR Study*

Figure (2) shows the Fourier transform infrared (FTIR) spectra of the pure polymer blend sample (PVC/LDPE). The FTIR spectrum of the pure sample (SP) exhibits several distinct absorption bands at specific wave numbers. A broad absorption peak appears at 3271 cm^{-1}, indicating the dilatant stretching of the strong hydrogen bonds (O–H). Two adjacent, intense peaks are also observed at wave numbers 2846 cm^{-1} and 2916 cm^{-1}, attributed to the symmetric and asymmetric stretching vibrations of the C–H bonds, respectively. A weak absorption peak at 1735 cm^{-1} is attributed to the carbonyl group (C=O) stretching vibration. An additional C–H bond stretching vibration was observed at wave number 1265 cm^{-1}, and its bending vibrations at 1018 cm^{-1} and 617 cm^{-1}, while C–H bond vibrations were observed at 717 cm^{-1}. The wobble and sway vibrations of this C–H bond appear at 717 cm-1. Peaks occurring between 450 and 500 cm^{-1} are attributed to the presence of metal oxides, such as aluminum and magnesium.

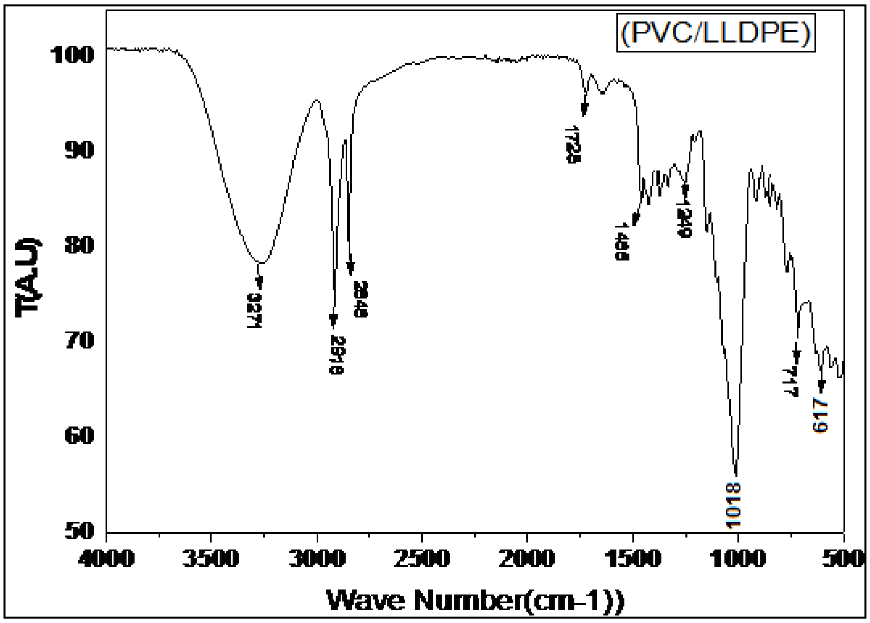

Fig 2 (FTIR) spectra of the pure polymer blend sample (PVC/LDPE).

Figure (3) also shows the FTIR spectra of polymer samples treated with different nano-refractory brick concentrations (PVC/LDPE/ PVC/LDPE/Nano-refractory bricks), represented by the symbols SN1, SN2, SN3, and SN4, which correspond to increasing filler concentrations. All spectra exhibit characteristic absorption bands similar to the pure sample, with notable differences in the intensity, position, and width of some peaks due to the incorporation of nano-refractory bricks. In particular, the absorption peak at 3271 cm¹ shows a decrease in intensity with increasing nano-refractory brick concentrations. This decrease in intensity is attributed to the participation of hydroxyl groups on the nano-refractory brick surface in hydrogen bonding and cross linking interactions with the polymer matrix. Furthermore, the shift in the hydroxyl absorption bands from 3271 cm^{-1} in the pure sample (SP) to 3232 cm^{-1} in the sample with the highest filler content (SN4) provides further evidence of the formation of hydrogen bonds between the nano-refractory brick surfaces and the polymer chains. Awal et al. [11] reported similar observations, finding that the incorporation of filler into the polypropylene composite resulted in a shift of the hydroxyl group to lower wave numbers, along with an increase in the intensity of the C-H stretching region.

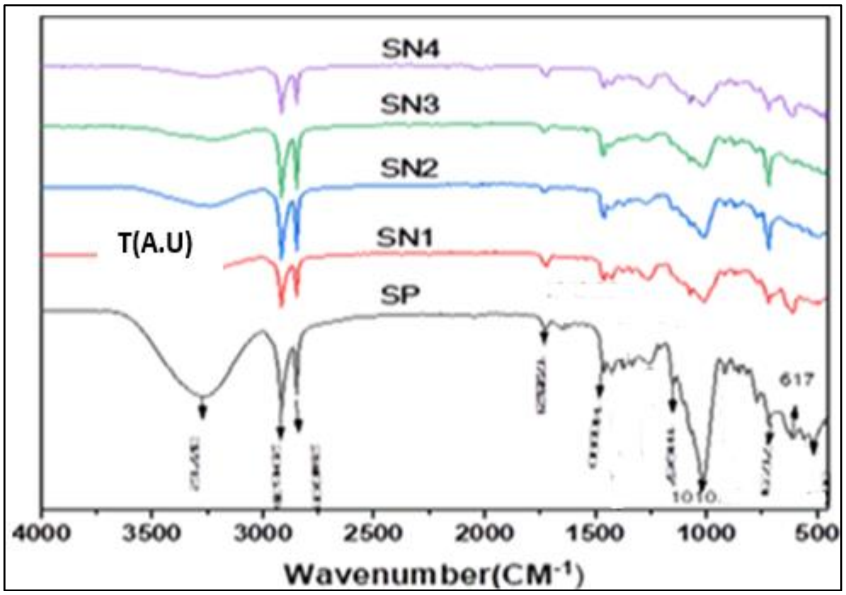

Fig 3 FTIR spectra of (PVC/LDPE /NRB) contents

Other absorption bands in the spectra of the nanocomposites samples (SN1, SN2, SN3, and SN4) remained at wave numbers similar to those of the pure sample; however, an overall decrease in peak intensity was observed. This decrease is attributed to potential interactions or interferences between the functional groups of the polymers and the surfaces of the nano-refractory bricks, leading to a decrease in the number or mobility of vibrational modes. Alternatively, these changes may result from modifications in the physical structure of the polymer composite, such as increased crystallinity or restricted chain mobility.

- *SEM Studies*

To evaluate the surface topography and composition of the prepared polymer samples, a scanning electron microscope (SEM) was used. Figure (4) shows electron micrographs of various fractured samples. These images show that the polymers are largely immiscible; however, the miscibility improves with increasing nano-refractory bricks content. The micrographs also show that the nano-refractory bricks particles are mainly located within the polyvinyl chloride (PVC) phase, while the low-density polyethylene (LDPE) phase remains largely unaffected. This indicates that the incorporation of nano-refractory bricks does not significantly alter the overall morphology of the composite, maintaining the inherent properties of LDPE. Furthermore, increasing the concentration of nano-refractory bricks within the PVC can be beneficial, enhancing the mechanical and thermal properties of the composite without compromising the elasticity of the LDPE. This phase-specific enhancement enables the development of composite materials with a fine balance of properties.

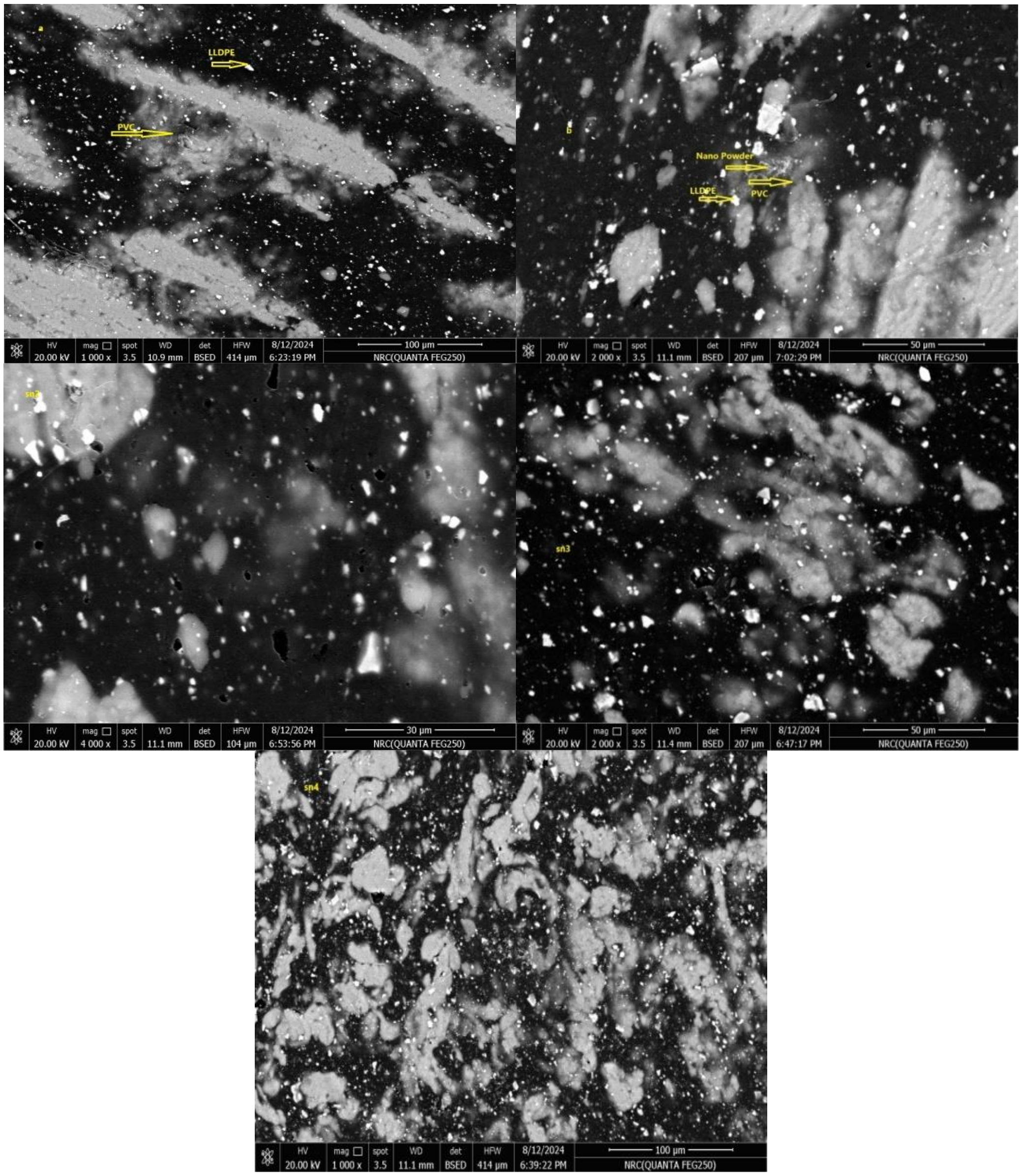

Fig 4 SEM of the Blends with Different NRB Contents.

- *Thermogravimetric Decomposition: TGA-DTG*

Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) tests were performed on all prepared samples, from room temperature up to 600 °C, at a heating rate of 10 °C/min. Figures (5) illustrate the DTG-TGA curves for the pure PVC/LDPE blend and the samples modified with various concentrations (1%, 3%, 5%, and 7%) of nano-refractory bricks (NRB). These curves reveal that the thermal decomposition proceeds through four distinct stages. Table (1) presents the initial decomposition temperatures (T_i), the maximum decomposition temperatures (T_m), and the final decomposition temperatures (T_f), along with the weight loss percentages (wt%) for each of the four stages. In the **first stage**, a notable increase in the onset decomposition temperature (T_i) was observed, rising from 48 °C for the pure sample to 85 °C for the NRB-filled samples. This increase was accompanied by a reduction in weight loss of up to 7%. The highest T_i was recorded for the sample containing 1% NRB. This stage typically corresponds to the decomposition of unstable components or moisture evaporation, with water dissociating into H_2 and O_2 gases around 100 °C [ ]. The **second stage** is characterized by a sharp weight loss starting at approximately 237 °C and ending near 354 °C. The dominant process in this stage is the dehydrochlorination of the polymer chains, resulting in HCl release [ ]. The highest Ti in this stage was 288 °C for the pure sample, which decreased to 271 °C as the NRB content increased to 7%. Despite this reduction, the weight loss decreased from 62% to about 50%, indicating that the incorporation of NRB improves resistance to HCl elimination and enhances the thermal stability of the PVC component.

During the **third stage**, a gradual weight reduction was observed between 357 °C and 397 °C, with minimal mass loss. This stage is attributed to the decomposition of PVC residues remaining after HCl removal [ ]. The **fourth and final stage** showed a broader and less steep degradation profile, occurring between 395 °C and 550 °C, with up to 34% weight loss. At this stage, the decomposition of polyethylene begins around 400 °C, releasing various gases and hydrocarbons (Abdullah et al., 2013).

The final decomposition temperature (T_f) increased to 550 °C for the sample containing 1% NRB, compared to 489 °C for the pure blend. However, increasing the NRB content beyond 3% resulted in a decline in thermal stability. These findings suggest that incorporating low concentrations (1% and 3%) of nano-refractory bricks significantly enhances the thermal stability of PVC/LDPE blends.

Table (1) Presents the Initial Decomposition Temperatures (T_i), the Maximum Decomposition Temperatures (T_m), and the Final Decomposition Temperatures (T_f), Along with the Weight Loss Percentages (wt%) for each of the Four Stages.

Sample	**1ststage**			**2nd stage**				**3rd stage**				**4th stage**			
	T_i	**T_f**	**wt%**	**T_i**	**T_m**	**T_f**	**wt%**	**T_i**	**T_m**	**T_f**	**wt%**	**T_i**	**T_m**	**T_f**	**wt%**
pur	48	220	14.4	237	288	354	62	357	377	397	5	398	456	489	16
1%	85	215	7.3	234	284	352	50	356	378	392	15	395	460	550	22
3%	70	227	7.6	226	288	355	50	366	389	404	7	408	469	533	34
5%	62	222	17	229	280	353	52	364	381	392	8	397	458	494	21
7%	76	226	11	234	271	261	51	240	363	400	9	403	461	498	26

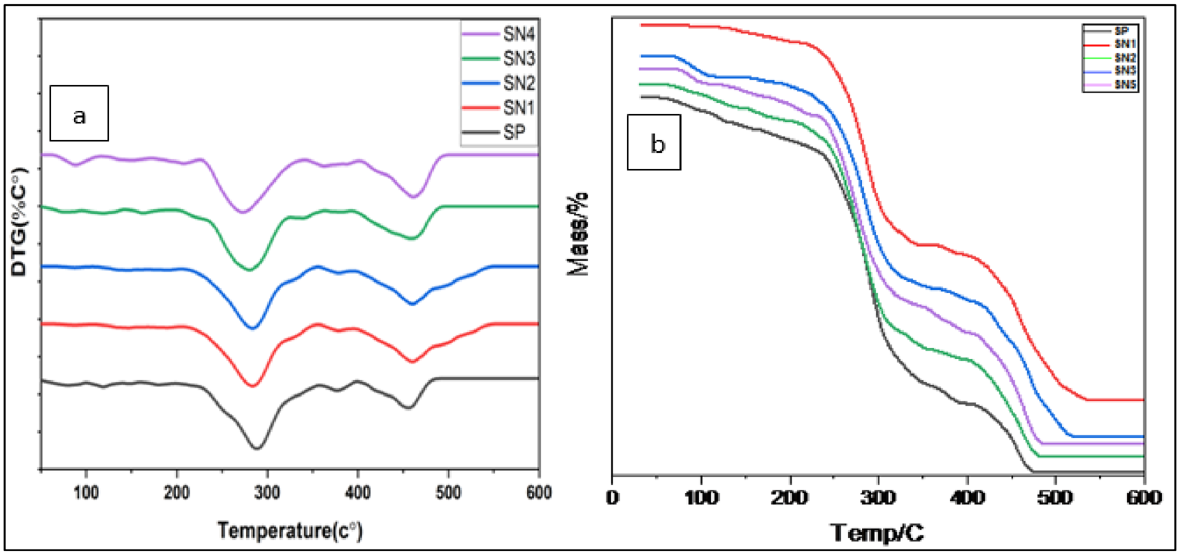

Fig 5 Illustrate the DTG (a) and TGA (b) Curves for the Pure PVC/LDPE Blend and the Samples Modified with Various Concentrations (1%, 3%, 5%, and 7%) of Nano-Refractory Bricks (NRB).

V. CONCLUSIONS

The solution mixing method was successfully used to prepare blend composites of polyvinyl chloride (PVC) and low-density polyethylene (LDPE), reinforced with varying concentrations of refractory nano-blocks (NRB). The prepared samples were comprehensively characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA/DTG).

X-ray diffraction results confirmed the successful incorporation of NRB into the crystalline structure of the composite. SEM images showed increased miscibility between the polymer components with increasing NRB content, indicating uniform dispersion of the nanofillers within the polymer matrix.

FTIR analysis revealed absorption bands similar to those of the pure blend, with significant changes in intensity, position, and bandwidth upon addition of NRB, indicating the presence of physical and/or chemical interactions between the composite components.

TGA/DTG results indicated a significant improvement in the thermal stability of PVC/LDPE blends with the incorporation of low concentrations of NRB (1% and 3%), highlighting the potential of these nanocomposites for use in applications requiring high temperatures.

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