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PROCESSING CONDITIONS AND THEIR EFFECT ON HOMOGENEITY OF PPVC STRUCTURAL CHARACTERISTICS

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ABSTRACT

The processing conditions involved in rolling and extrusion methods and their effect on the thermal behavior of plasticised PVC (PPVC) were studied in this article. Limiting oxygen index test (L.O.I) and differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FTIR), and scanning electron microscope (SEM) has been used to evaluate the structure and properties of extruded and rolled PPVC. The SEM and FTIR tests proved there was a significant structural difference found between extruded and rolled PPVC samples, such as the ratios of the elements carbon, hydrogen, and oxygen were different in the samples of both methods, which affected by the L.O.I test and differences in active groups obtained by FTIR analyses.

Keywords: structure homogeneity, PPVC, processing method, L.O.I, DSC, FTIR.

1. INTRODUCTION

Every processing method has its own characteristics and limitations which are affected by the conditions surrounding the process. These conditions control the efficiency of the processing method to achieve a certain work of high quality compared to other processes. When a certain process specified to polymeric materials in general and especially for polyvinyl chloride (PVC), the temperature will be the basic criterion determining the effectiveness and efficiency of the process, because the properties of polyvinyl chloride depend on its operational history so it is very sensitive to any change or irregularity in processing temperature [1-6]. As we know, the polyvinyl chloride processed in two main methods: hot rolling and hot extrusion, where the regularity of temperature is different due to the machine specifications. In the rolling process, thermal distribution varies along the length of the roll, where the temperature of roll will be the highest value in the centre and decreases in the direction of the sides, which negatively affects the properties and structure of the polymer processed in this method (see Figure-1,a). On the other hand, the heat is distributed regularly along the extruder barrel in the extrusion process, thus providing a balanced and suitable thermal environment in which the polymer can retain its properties during the processing resulting in homogeneous products in terms of structure and properties, as shown in Figure-1,b [7-9].

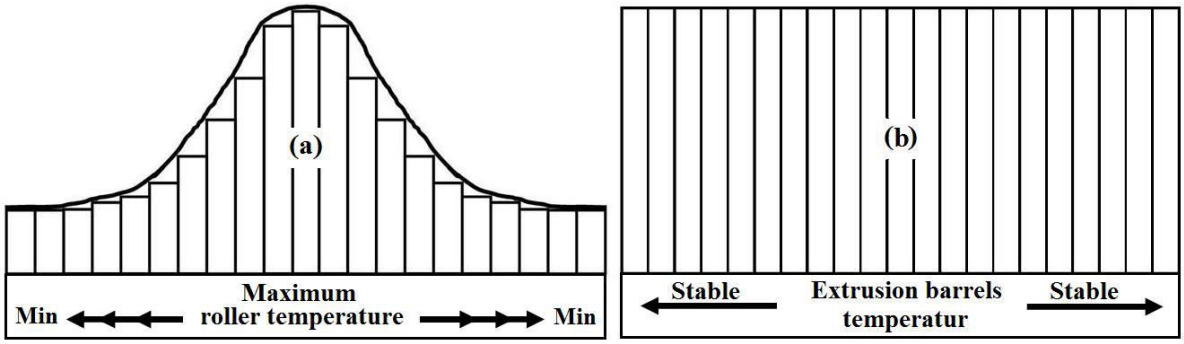

Figure-1. Heat distribution in (a) rolling, (b) extrusion.

There is also another reason for different characteristics by the process, where many studies have been proved that in any processing method there are residual stresses that will be formed in the final product regardless of the produced material type, and vary in concentration within the structure of the material according to the type of production process. Therefore, the material's resistance to the external conditions at these points where the stresses are concentrated will be at lowest values resulting in their failure under loads or temperatures less than expected [10-12].

2. METHODOLOGY

The main materials used shown in Table-1.

Table-1. Composition of batches.

Material	PVC basic formulation			
	PVC S-5070	DOP	Newstab-50	Wax-E
Content, pphr	100	70	1.5	0.3

Laboratory twin roll-mill type Schwabenthan 150U and Göttfert Extrusiometer 20 single screw laboratory extruder were used to fabricate Limiting oxygen index (L.O.I) samples according to ISO 4589-2 standard [13]. L.O.I test was done by Stanton Redcroft FTA flammability unit.

Also Mettler Toledo DSC823e instrument was used to complete the differential scanning calorimetry test (DSC) with 30°C-240°C temperatures range according to ISO 11357 standard [14].

The scanning electron microscopy (SEM) was used to evaluate the structure of plasticised PVC (PPVC) basic and modifiers formulation processed by rolling and extrusion processes before done L.O.I. test. The SEM device type Carl Zeiss EVO MA10 was used to complete the SEM test.

The Fourier transform infrared spectroscopy (FTIR) was used to detect the effect of processing on active groups for PVC. Bruker Tensor 27 FTIR spectroscope was used for this purpose.

3. RESULTS AND DISCUSSIONS

The Results obtained from limiting oxygen index test are illustrated in Figure-2, where we note from this figure that the best results were those obtained from the extrusion process due to stable processing conditions (temperature, pressure, and time). Since the properties and composition of PPVC depends on its history, any irregularity in the conditions of the processing (especially temperature and time) will lead to deterioration of properties and forming heterogeneous structure as shown in Figure-3 and Figure-4 which represent the energy-dispersive X-ray spectroscopic micro-analyser (EDS) of the sample fabricated by extrusion and rolling respectively, where the electron microscopy proved that there are a real differences between the two samples structures fabricated by rolling and extrusion where the basic elements ratios of carbon, hydrogen, and oxygen were lower and irregular distribution in the rolling samples than in the samples of extrusion method. The reason for this is that the rolling temperature is irregular along the length of the roll, which causes the concentration of the elements to varying from one point to another depending on the amount of heat that was exposed during the rolling. In the extrusion process, the final form of the product is formed at a single stage so that a long period inside the extrusion barrel so it will maintain its properties. The standard limiting oxygen index is rounded to nearest whole number, but according to our experience the reproducibility of the test is well better than ±0.2 %, usually ± 0.1%, therefore the difference measured is significant.

The chemical structure of the PPVC (extruded and rolled) was determined by FTIR technique as shown in Figure-5. From this figure we can see that there is a real difference between peaks values for the same material "PPVC" but different processing method, where the C–H stretching vibration bond was formed at the 2958 cm^{-1} to 2859 cm^{-1} peaks range (high energy region) accompanied by forming aliphatic chains (–CH_2– and –CH–) at bonding vibrations at peaks range 1461cm^{-1} to 1426cm^{-1}. The peaks range extends from 1121 cm^{-1} to 1039 cm^{-1} corresponds to the link C–O–H or C–O–R (alcohols or esters); while the distinctive band at the peak 1269 cm^{-1} is due to a large amount of CH-OH groups. Also, the peak 1720 cm^{-1} refers to carbonyl functional groups. The main difference in FTIR analysis is the appearance of the peaks 1599.60 cm^{-1} to 1579.95 cm^{-1} extruded and rolled PPVC and its disappearance from the rolled PPVC, this peak corresponds to the link C=C (alkene) and the carbon-carbon double bond consists of one sigma bond and one pi bond also it strong. So the properties of PPVC processing by extrusion was better than processing by rolling [15, 16]. The gelation grade is also affected by the processing method as shown in Figure which represents differential scanning calorimetry measurement for extruded and rolled PPVC; where it is observed that the gelation grade for extruded polyvinyl chloride is 78% at 177°C and 73% at 173°C for rolled polyvinyl chloride. This behavior is due to the fact that the structure of polyvinyl chloride is subject to significant changes during the rolling process. Initially, it is rolled at 170°C into plates; these plates are then pressed to the desired thickness at 175°C. Therefore, the structure of polyvinyl chloride is overstressed, resulting in early yields at a lower temperature than in the extruded product.

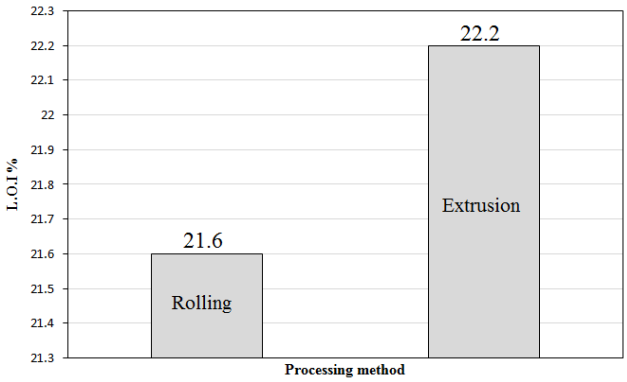

Figure-2. Limiting oxygen index (L.O.I) test results for extruded and rolled PPVC.

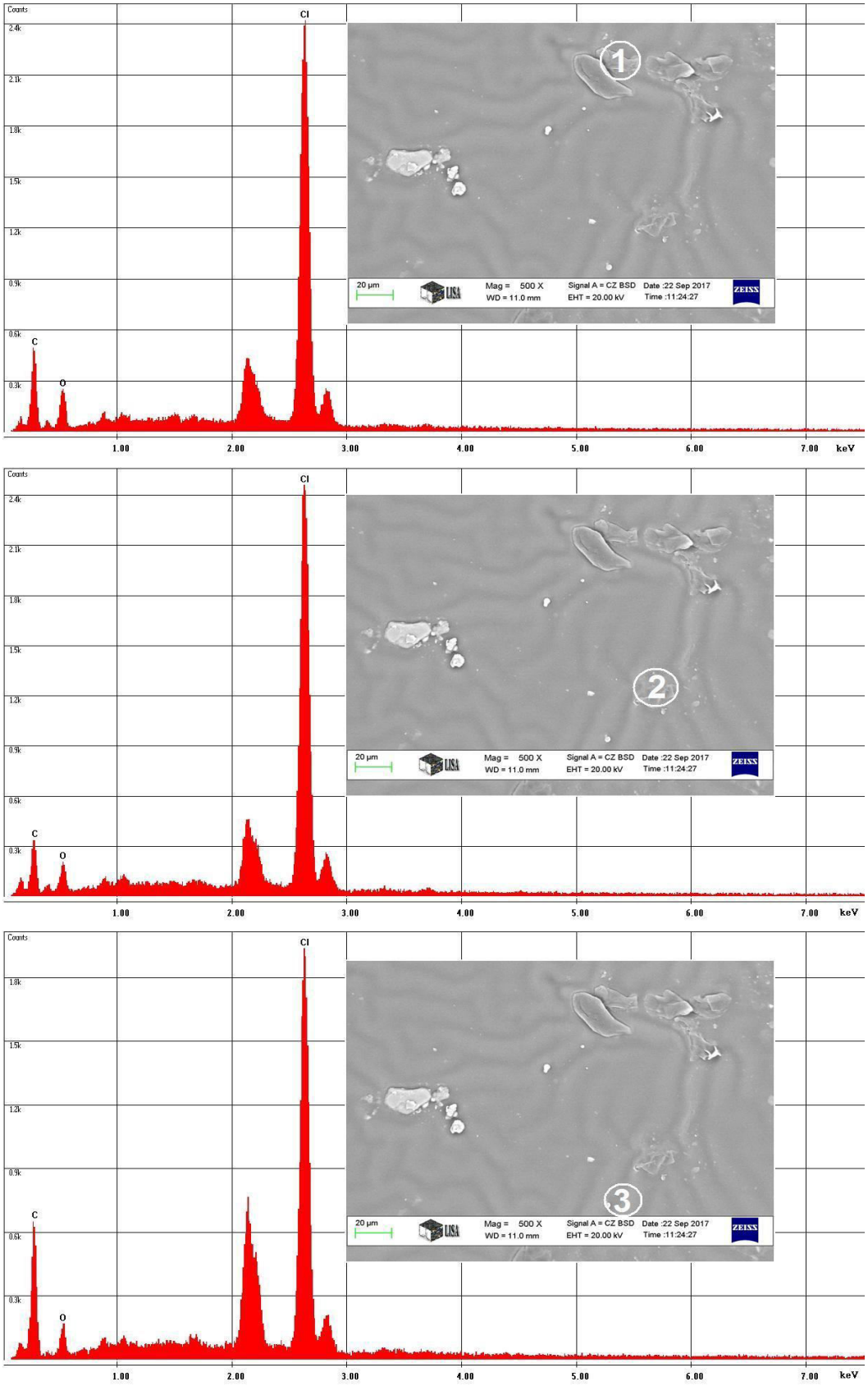

Figure-3. Energy-dispersive X-ray spectroscopic micro-analyser (EDS) of extruded PPVC.

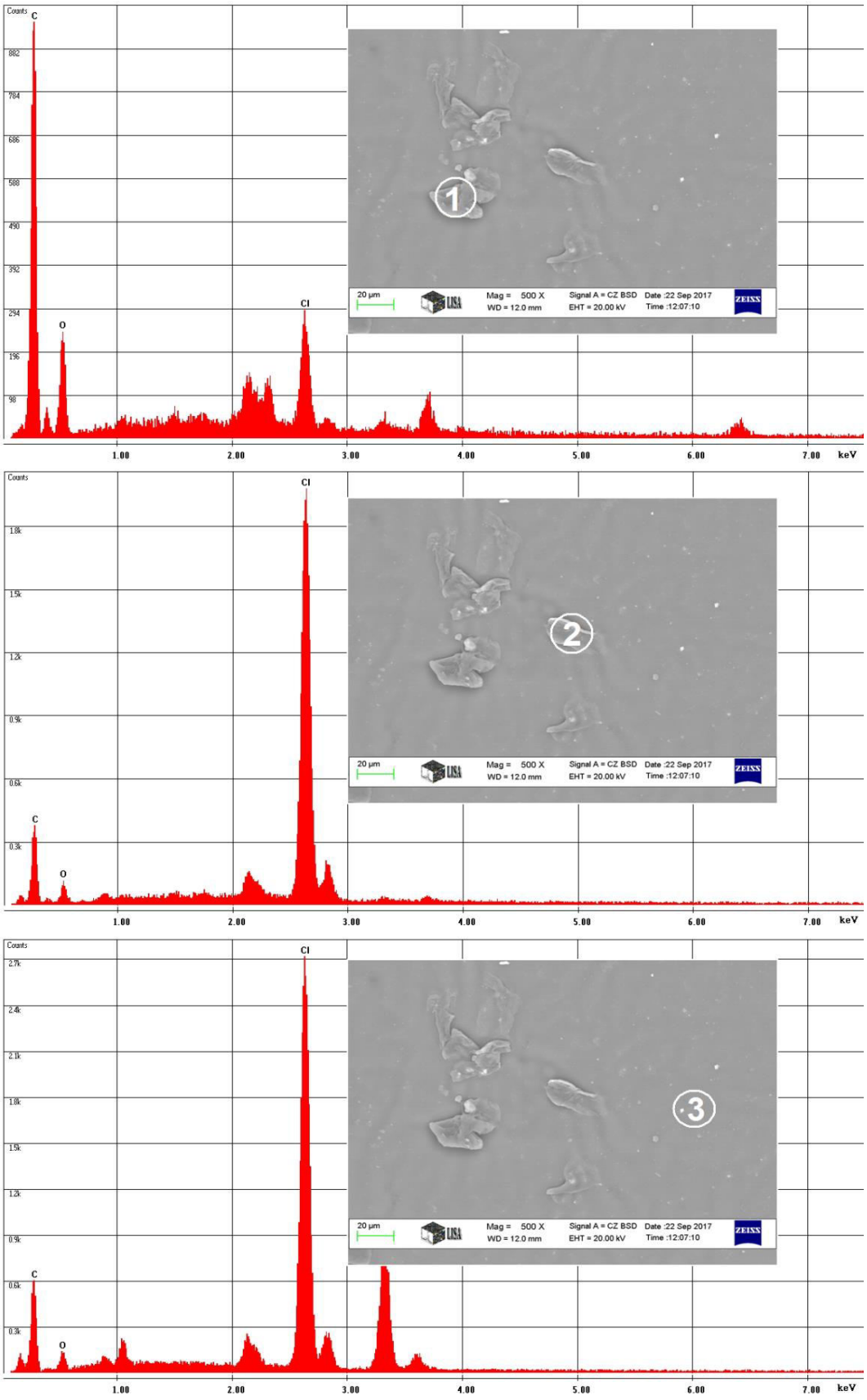

Figure-4. Energy-dispersive X-ray spectroscopic micro-analyser (EDS) of rolled PPVC.

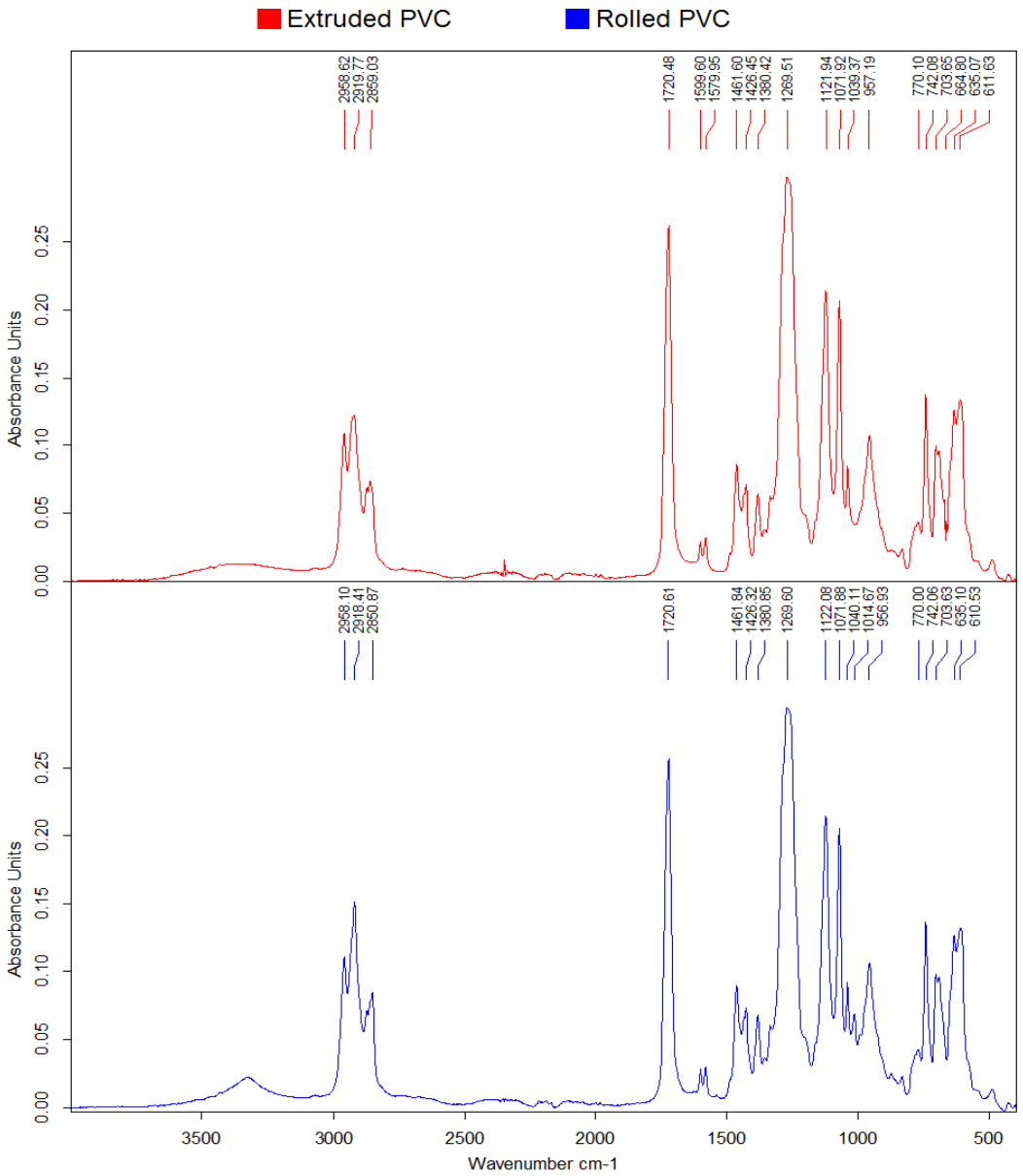

Figure-5. Fourier transform infrared spectroscopy (FTIR) for extruded and rolled PPVC.

Table-2. FTIR analysing results for extruded PPVC.

Positive Number	Active Group
(3641.60) cm^{-1}	OH
(2873.94) cm^{-1}	CH
(2513.25) cm^{-1}	C-H
(1994.40-1793.80) cm^{-1}	C = O
(1618.28) cm^{-1}	C = C
(1450.47) cm^{-1}	$-CH_2$
(1192.01-1105.21) cm^{-1}	C–O-H or C–O-R
(931.62-659.66) cm^{-1}	= CH

Table-3. FTIR analysing results for rolled PPVC.

Positive Number	Active Group
(3429.43-3070.68) cm^{-1}	OH
(2956.87-2872.01) cm^{-1}	CH
(2729.27) cm^{-1}	C-H
(1728.22) cm^{-1}	C = O
(1600.92-1579.70) cm^{-1}	C = C
(1463.97) cm^{-1}	$-CH_2$
(1379.10) cm^{-1}	$-CH_3$
(1286.52) cm^{-1}	CH-OH
(1163.08-1039.63) cm^{-1}	C–O-H or C–O-R
(954.76-754.17) cm^{-1}	= CH

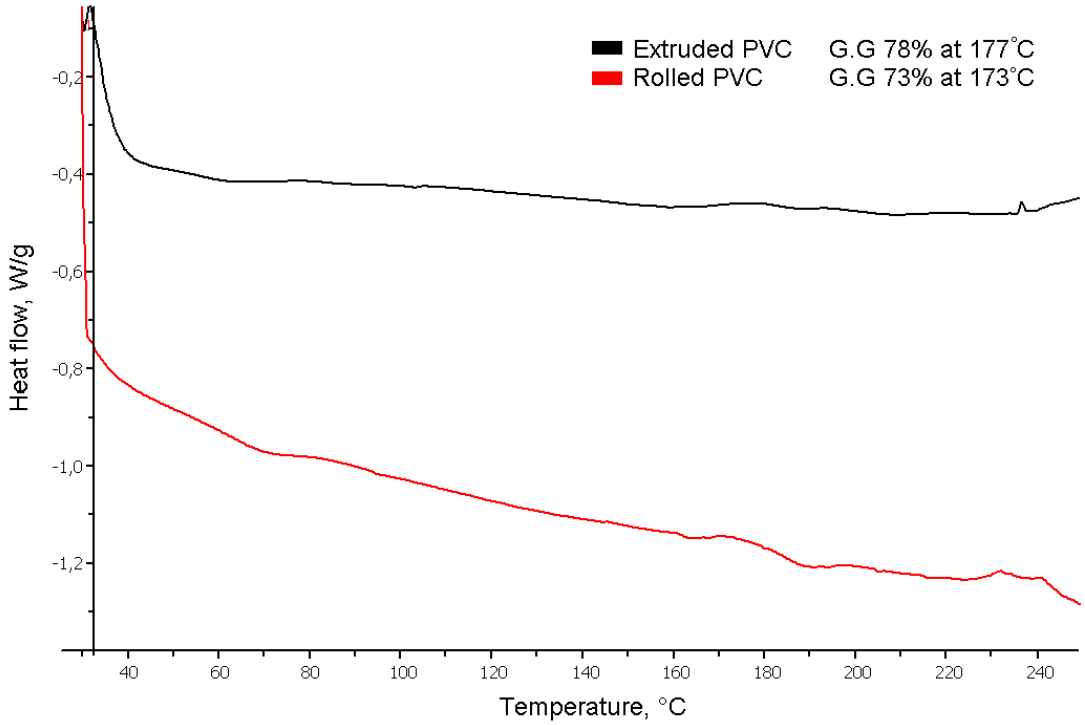

Figure-6. Differential scanning calorimetry (DSC) measurement for extruded and rolled PPVC at same testing conditions (30 °C-240 °C temperatures range and 20 °C/min heating rate).

4. CONCLUSIONS

The obvious difference in the composition of extruded and rolled PVC obtained by scanning electron microscopy and Fourier transform infrared spectroscopy proves that microstructure depends on the process and therefore this thing is what affects the properties being measured which is like a sequence and can be called process dependent structure-properties. The optimum results were obtained from the thermal tests limiting oxygen index and differential scanning calorimetry were with extruded polyvinyl chloride, where the structure of polyvinyl chloride was more homogenous in terms of processing conditions, because it was produced in a single step (by extrusion only) so the residual stresses were less than rolled and thus less stressed.

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