L.O.I and DSC analyses of antimony trioxide containing plasticised PVC as a function of processing method

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ABSTRACT
The correlation between the processing method and thermal properties of antimony trioxide containing plasticised PVC has been studied in this paper. Two processing methods included rolling and single screw-extrusion were used to produce PVC-ATO samples, and observe the effect of each method on the thermal properties limiting oxygen index (L.O.I) and differential scanning calorimetry (DSC) of the samples. The results obtained from the thermal tests showed that the extrusion method was better than the rolling method for L.O.I and DSC (gelation grade). This is due to the heat will distributed uniformly in the screw-extrusion method, which reduces thermal stresses in the final product.

Keywords: Processing method, Plasticised PVC, L.O.I, DSC, Gelation grade, ATO.

1. INTRODUCTION
There are several critical parameters (constant or variable) that control and any forming process. These parameters are: temperature, time, speed and pressure. These critical parameters are closely related, and directly affect the properties and product, the economic feasibility of the forming process, and its technical relevance to the formed material, in order to obtain the best properties, whether mechanical, thermal, chemical, etc. In addition to the above parameters, there is a parameter of no less importance, which is the human factor (worker), and the extent of its intervention in the forming process, and whether the process depends on it completely or not. Therefore, the worker efficiency will be also a critical parameter the properties of the final product. All these parameters must be taken into consideration in order for the forming process to be succeeded.
Polymers are known to be highly sensitive to heat due to their low melting points; therefore, any change in temperature will change its structural phases, and thus will change its qualities and properties. This change depends on the thermal range and the time period of heat exposure. Polyvinyl chloride (PVC) one of these thermally sensitive polymers; its properties are a function of its history [1-3]. In the forming processes of polymers, high temperatures are required, in order to increase their flowability and reduce the viscosity, thus, the shear stress will decrease. In addition, the forming processes differ in terms of the homogeneous thermal distribution on all formed area, and the stability of the heating and not effected by surrounding environment, which improves the quality of the product and reduces the deformations resulting from different temperatures between the parts of the same product.
In the rolling process, the heat distribution is not symmetrical on the surface of the roll, as it is in the center and on the sides, therefore, the distribution of heat varies from the center and the edges of the formed sample, affecting its dimensions, especially the thickness, and more importantly, the difference in the value of thermal stresses from one point to another for the same formed sample. Moreover, because the rolling is done manually and fully dependent on the efficiency of the human

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parameter and determining the exact time of the output of the product to ensure that it is not exposed to excessive temperatures. In the extrusion process, the temperature is better controlled by the presence of a number of heaters along the forming barrel, so the thermal distribution is regular throughout the specimen, and thus the final product is more homogenous in terms of heat distribution. Where the screw moves and flips the material automatically from the center of the barrel to its walls (the hottest) and so on to be extruded [4-6]. Fig.1 represents the heat distribution in the rolling and screw-extrusion processes.

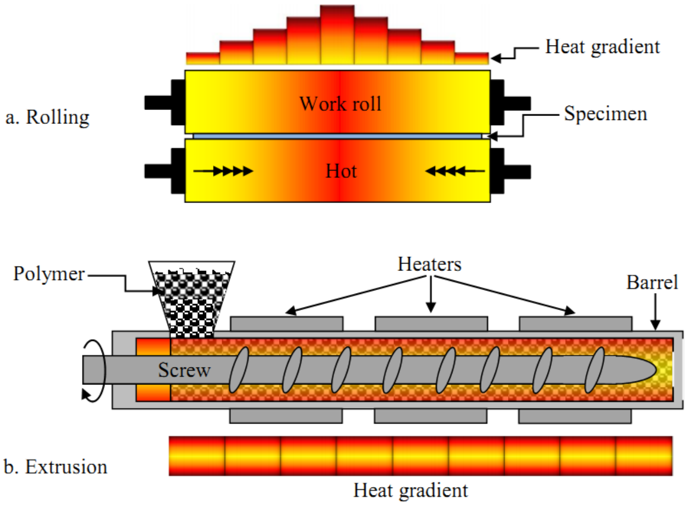

Fig.1: Heat distribution in (a) rolling and (b) screw-extrusion processes

2. MATERIALS AND METHODS

All work supplying of materials, sample production and tests were completed at the BorsodChem Zrt., Hungary; Laboratory of Vinyl Technology.

2.1. Materials

1. Polyvinyl chloride (PVC) type Ongrovil® S-5070 as a matrix material with (100 pphr). PVC produced and supplied by BorsodChem Zrt., Hungary.
2. Dioctyl-phthalate (DOP or DEHP) as plasticizer was added with (70 pphr). This plasticizer was produced by the Czech Republic company DEZA, a. s. CO., Valašské Meziříčí.
3. Calcium-Zinc type Newstab-50 heat stabilizer has been added with (1.5 pphr). This stabilizer was produced by Betaquímica CO., Barcelona, Spain.
4. Wax-E type Licowax® E as lubricant which produced by Swiss company Clariant International Ltd, was added with (0.3 pphr).
5. Antimony trioxide (ATO) with chemical symbol (Sb_2O_3). has been added with (0-5) wt.%.

All of the materials were supplied by BorsodChem Zrt.

2.2. Mixing Process Preparation of Samples

The samples were produced according to international specifications and standards, where the L.O.I samples were according to the ISO 4589-2 standard, and DSC samples were produced according to the ISO 11357 standard. Two batches from PVC with ATO additives were prepared and used as follows:

1. The first batch prepared by a laboratory two roll mill type Schwabenthan, with forming temperature 170°C, 21 rpm and 24 rpm for front roller and back roller speeds respectively, and rolling time was 5 min. In the beginning the samples were made in the form of sheets with dimensions as sheets with 0.4 -0.6 mm thickness, and then formed by a hydraulic press of the desired shape according to operating conditions 300 and 20 bar pressure at 175 °C temperature.
2. The extrusion machine type Göttfert was used to prepare the second batch, where the material extruded to the desired shape in one step by Ø 20 extruder rod diameter at uniform pressure, compression force and temperature. The temperatures range of the machine heaters were 140, 150, and 160 °C at uniform rate.

2.3. Thermal tests

1. L.O.I test: The Stanton Redcroft FTA flammability unit was used to complete this test.
2. DSC test: Mettler Toledo DSC823^{e} instrument was used to finish this test for gelation grade (G.G) measurement. The temperature range was 30 °C-240 °C; the heating rate 20°C/min.

3. RESULTS AND DISCUSSION

Fig.2 represents the limiting oxygen index of plasticised PVC vs. ATO additives for extrusion and rolling samples respectively. The optimum L.O.I increment is obtained with extrusion samples because the operating conditions (temperature, pressure, and time) are controlled uniformly and these results prove that the L.O.I is a process-dependent property, and this is being proved for the first time. Also, we can observed from this figure that the limiting oxygen index of PVC increased with ATO additions, This increase is direct, as the percentage of ATO increased the value of L.O.I will increase. Also, the percentage of oxygen which the PVC samples needs to burn will increase. This behavior due to the ATO absorbed heat and there will be phase transformations in its internal structure. This represents endothermic process which decreased surface temperature which will prevent fire propagation.

Gelation grade (G.G) of PVC considered a critical factor during processing to get optimum properties for certain application. From the DSC measurement results shown in Fig.3 and Fig.4 for extrusion and rolling processes respectively, where we observe the clear stability in the gelation temperature in extrusion process accompanied by a regular increase in the gelation grade, but this state is exactly the opposite in rolling process, where the gelation grade is very unstable as well as gelation temperature. This behavior is due to the distribution of heat during the forming process, where the distribution is regular in extrusion and variable in rolling. On the other hand, we noted that the average values of the gelation grade will increase with ATO additions.

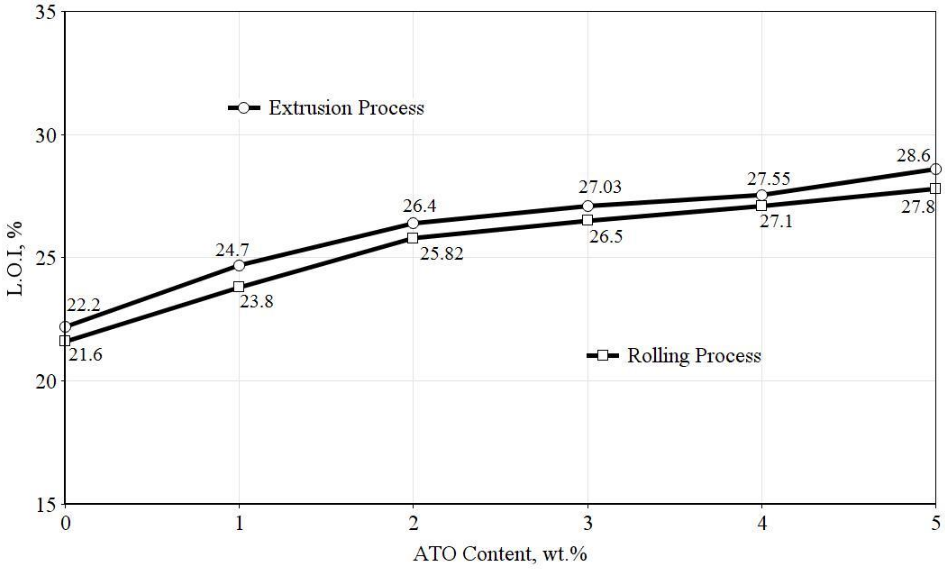

Fig.2: Limiting oxygen index of plasticised PVC vs. ATO additives processed by rolling and extrusion

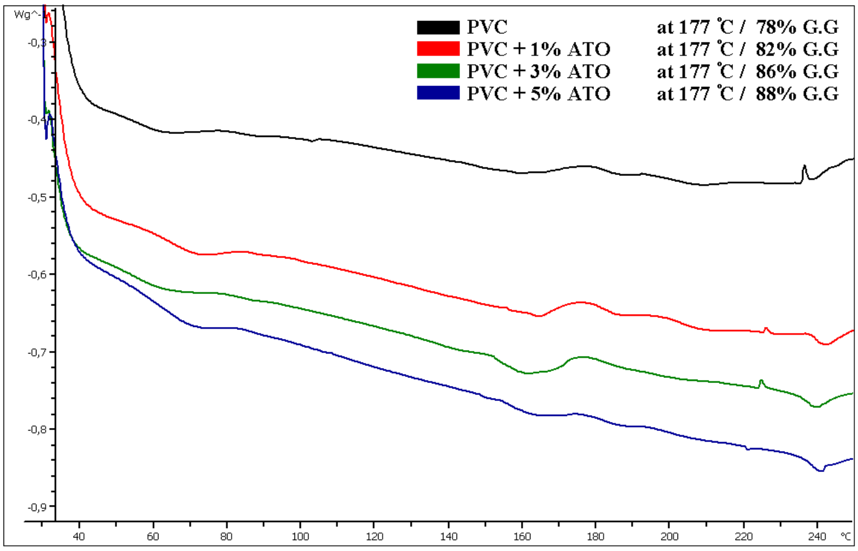

Fig.3: DSC traces of ATO containing plasticised PVC processed by screw-extrusion

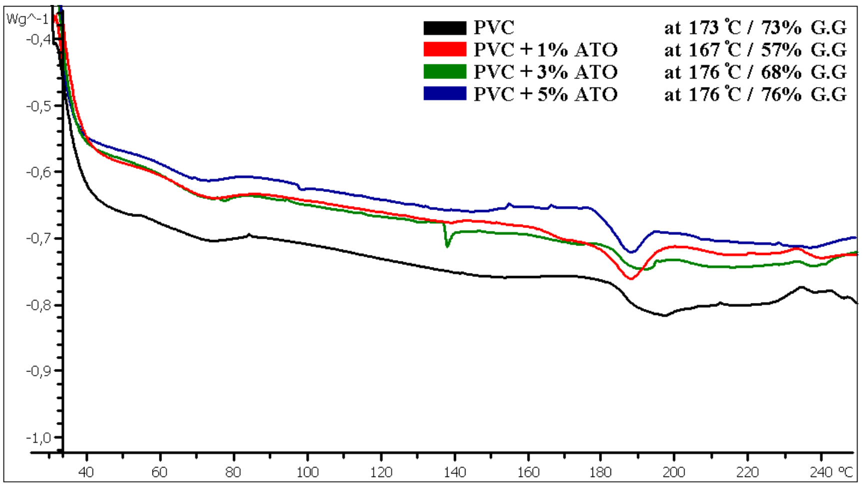

Fig.4: DSC traces of ATO containing plasticized PVC processed by rolling

4. CONCLUSIONS

1. L.O.I and gelation grade determined by DSC are process-dependent properties.
2. The best results of L.O.I, obtained by extrusion process, because the process is fully systematic in terms of the distribution of heat and pressure, better than rolling.
3. The gelation grade was better and more regular in the case of extrusion process accompanied with temperatures stability (177ºC), but in the case of rolling process, is clearly fluctuating with the change in the temperatures range of gelation.
4. As an additional indicator, ATO additives improve thermal properties for both processes, and the ratio of improvement depends on the percentage of ATO addition. The gelation grade of PVC will increase uniformly once the ATO is added in case of screw-extrusion, but in rolling was irregular.
5. Reduced thermal gradient was observed after the addition of ATO that had not been published in the literatures before.

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