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Continuous Peroxide Cross-linking of Low Density Polyethylene by Shear Head Method*

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ABSTRACT

There are many different methods for production of peroxide cross-linked polyethylene in the form of pipe, cable, sheet, etc. In this study shear head as a new approach method was applied for continuous cross-linking of low density polyethylene. The shear head was designed and constructed and coupled with a modular single screw extruder. The screws of shear head were Maddock, Egan and Troester with 0.4 mm gap. The highest increment in temperature of compound was around 30°C in shear head for Maddock screw. Cross-linking was confirmed by gel fraction and mechanical tests. The highest gel fraction was related to 2 wt% of dicumyl peroxide (DCP) and Maddock screw. With increasing of DCP the tensile strength and elongation-at-break increased. The highest increment in tensile strength belonged to samples with above 70% gel fraction (2 wt% DCP and Maddock screw). Due to stretching and chain orientation of polymer compound in shear head (by high speed rotation of screw in short die land) these properties increased continuously to high gel fraction (90 %). If this method is coupled with other commercialized methods, the efficiency of cross-linking reaction of low density polyethylene and the quality of product would improve. In such case the energy consumption would also be lowered and the length of the production lines would be considerably shortened from the current methods.

Key Words:
continuous cross-linking;
LDPE; dicumyl peroxide;
shear head; extrusion.

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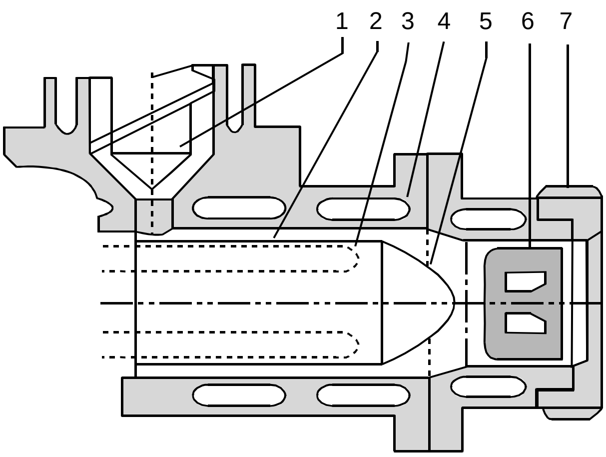
INTRODUCTION

Shear head, as an efficient method is not long which has been just commercialized for continuous vulcanization of elastomers. Making use of this method by itself or coupled with other methods (hot air, UHF, fluidized bed, etc.) have been reported [1-5].

At first, Krupp Company introduced shear head at the K 79 Plastic and Rubber Trade Fair and then it was developed by the Teichman Company [6-8].

Figure 1 shows the structure of the shear head schematically. By



Basic design of shear head: 1- extruder; 2- shearing gap; 3- mandrel heating; 4- jacket heating; 5- rotating mandrel; 6- die; and 7- union nut.

Figure 1. Schematic of shear head [5].

rotating the screw in shear head, the temperature of compound raises within a short time due to viscous heating generation by the applied shear stress between the screw and barrel of shear head .The temperature rise depends on the rotational speed, geometry of screw, rheological characteristics of the compound and the output (residence time). Temperature of the compound can increase from 1 to 100°C pertaining to adjustment of these parameters [9-12].

The most important characteristic of shear head is its own drive and function independent of the extruder screw. Controlling of temperature is very important in this method and using of PLC controller for the first time has been reported [13].

The aim of this study is to investigate the use of shear head for continuous cross-linking of low density polyethylene by organic peroxide. In general, the production of cross-linked polyethylene (by organic peroxides) in form of cables, pipes, heat shrinkable articles, etc. is carried out in a continuous operation and cross-linking reaction is completed along the long (100-150 m) production line. Shear head method coupling with other commercialized methods can lower the length of the production line as well as saving energy.

The whole apparatus was designed and constructed at Iran Polymer and Petrochemical Institute (IPPI) and could couple with any extruder by a simple adaptor.

EXPERIMENTAL

Materials

LDPE was the product of Bandar Imam Petrochemical Co, with LF0200 trade name, MFI = 2 g/10 min and density of and 0.918 g/mL.

Cross-linking agent was dicumyl peroxide from Hercules Co with Di-Cup 90 trade name, 98% purity and half-life time of 1 min at 180°C.

Instruments and Methods

The single screw extruder was modular with L/D=31, D=70 mm and six heating zones. The modular sections of screw were in 1D, 2D and 3D in length. This extruder was also constructed at IPPI.

The shear head system (L/D= 3, D= 70 mm) with choice of fitting three types of screw viz, Maddock, Egan, Troester and a slit die at the end of shear head was coupled with the above single screw extruder. Screws had three entrances and three exits with 0.4 mm gap. The difference between these screws is the helix angle of channels. The helix angels are 30, 70 and 90° for Egan, Troester and Maddock, respectively. The schematics of these screws are shown in Figure 2 [14-16].

The shear head had two heating zones and a water cooling system around the barrel. For monitoring of temperature in shear head two thermocouples were inserted; one could be operated at the end of extruder and the other just before the die. The cooling system could be activated in two options: automatically (under control of thermocouples) and manually for emergency conditions.

Four levels of DCP, viz. 0.25, 0.5, 0.75 and 2 wt % prepared as a 10 wt% master-batch in LDPE. Feeding of DCP master-batch was carried out at the end of the fifth zone of extruder by Engelhard (model KDE-Gl-100E) vibration feeder.

Figure 2 shows the screw arrangement of the extruder. Temperature profile of extruder was 120,125,130,135, 140°C and for shear head it was 135 and 140°C at the beginning of experiments.

The rotational speed of screw in the extruder was maintained constant. Attempt was made to acquire constant residence time in the shear head by adjusting its rotational speed for all samples. In this respect the residence time for all samples was kept about 45 s, which was estimated by using of a colour master-batch method.

Gel fraction of cross-linked polyethylene was determined according to ASTM D-2567 and tensile properties of samples were determined according to

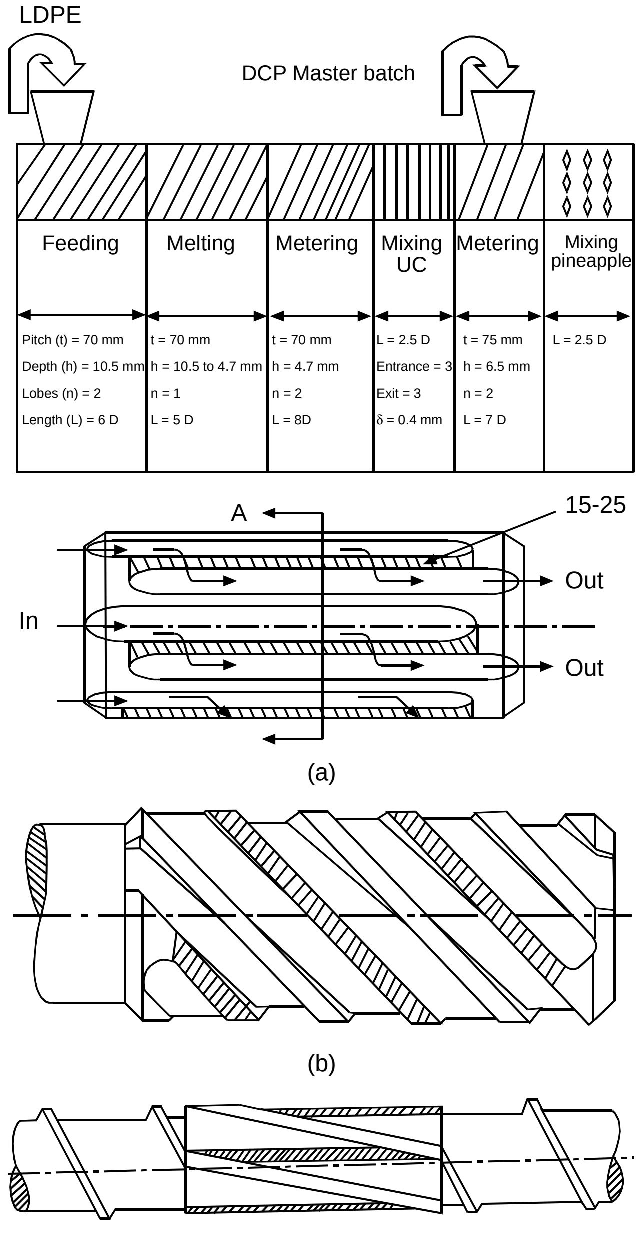


Figure 2. Screw arrangement in single screw extruder and schematics of: (a) Maddock, (b) Egan, and (c) Troester.

ASTM D-638.

Figure 3 shows the shear head system coupled with the single screw extruder.

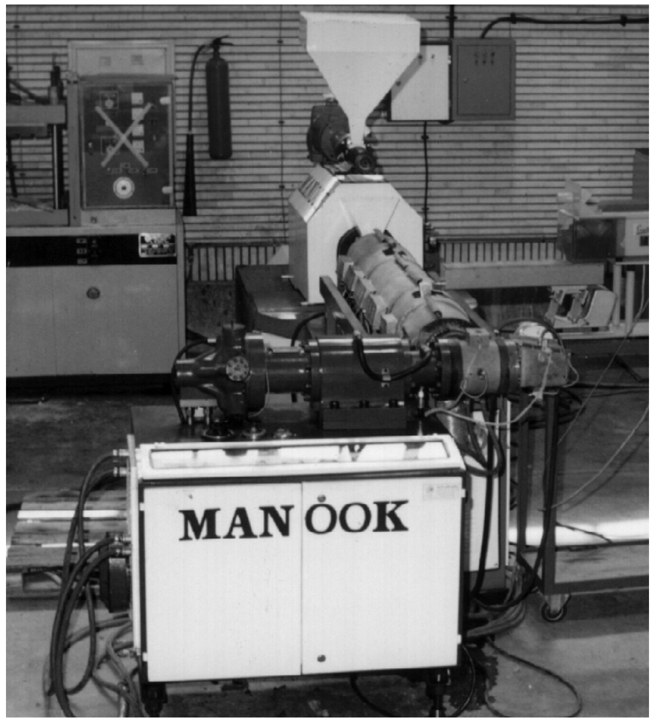


Figure 3. Shear head coupled with single screw extruder.

RESULTS AND DISCUSSION

Gel Fraction

The results from gel fraction experiments (Table 1) confirmed that cross-linking has been carried out in the shear head system. It is obvious that the gel fraction increases with increasing of DCP concentration due to higher amounts of formed proxy radicals. Samples prepared with Maddock screw showed higher gel fractions, because of its geometry and the higher shear generated. The highest increment in temperature (ca. 30°C) was observed with the Maddock screw. The increments in temperature in the shear head are shown in Table 2.

During the experiments, the die pressure was very high because of the high viscosity of cross-linked melt compound. Hence the system adjustment and working on samples with 2 wt% DCP was difficult. In such cases, we had to stop the experiments and clean the shear head off the highly cross-linked solid material.

Table 1. Gel fraction of samples with three screw types.

Screw types	Maddock				Egan				Troester			
DCP (wt%)	0.25	0.5	0.75	2	0.25	0.5	0.75	2	0.25	0.5	0.75	2
Gel fraction (%)	19	24	37	90	17	20	35	90	17	22	30	90

Table 2. Temperature increasing for three types of screw.

Screw types	Maddock				Egan				Troester			
DCP (wt%)	0.25	0.5	0.75	2	0.25	0.5	0.75	2	0.25	0.5	0.75	2
Increasing of temperature (°C)	20	23	26	34	17	19	22	26	19	21	24	29

When the gel fraction increased to 45% and higher amounts by changing of shear head parameters, the fluency of melt was disturbed and the appearance of output was impaired.

Tensile Properties

Figures 4-6 show the tensile strength for three types of screw in the shear head at room temperature and machine direction. In the same screw, with increasing of DCP, tensile strength increased. The highest increment in tensile strength belonged to samples with above 70% gel fraction (2 wt% DCP and Maddock screw). It should be noticed that the rate of increasing of tensile strength versus gel fraction in peroxide cross-linking method is less than silane and irradiation methods. However, the increase in tensile strength is attributed to the large number of cross-links tightening the chains together [17].

Figures 7-9 show the elongation-at-break of samples prepared with various screws in the shear head versus DCP concentration. It is observed that by increasing gel fraction, elongation-at-break increases.

In spite of previous publications, reporting that the elongation-at-break reaches its peak value at about 70% gel content and then it decreases, in our experiments, however, the increment trend of elongation-at-break continues up to high gel fractions (90%) [18-19].

This trend may be assigned to molecular orientation of polymer in transverse machine direction occurring in shear head section due to high rotational speed of screw in the barrel of shear head being maintained and unrelaxed in passing the short die land. Stretching the sample, cut along the ribbon, perpendicular to chain orientation direction causes disruption of chain folds and their re-orientation in the direction of the applied force, consequently giving rise to high elongation-at-break with respect to unoriented or oriented sample stretched parallel to the chain backbone [20].

On the other hand cross-linking occurs in the melt condition of peroxide method and the cross-linking

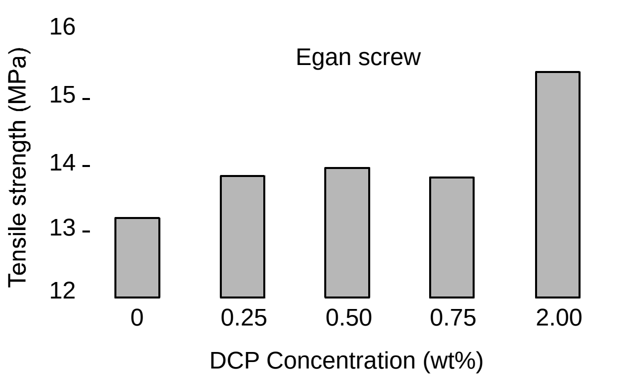


Figure 4. Tensile strength of samples prepared by Egan screw.

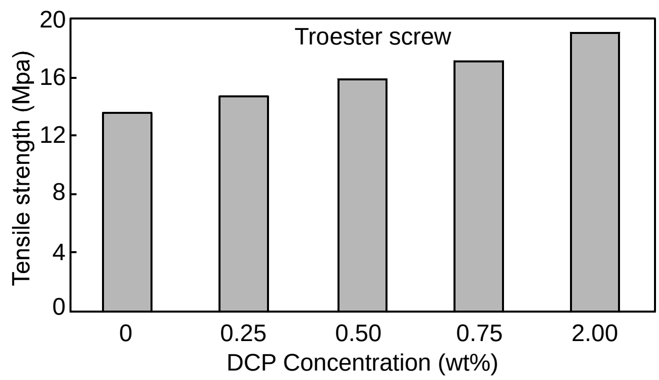


Figure 5. Tensile strength of samples prepared by Troester screw.

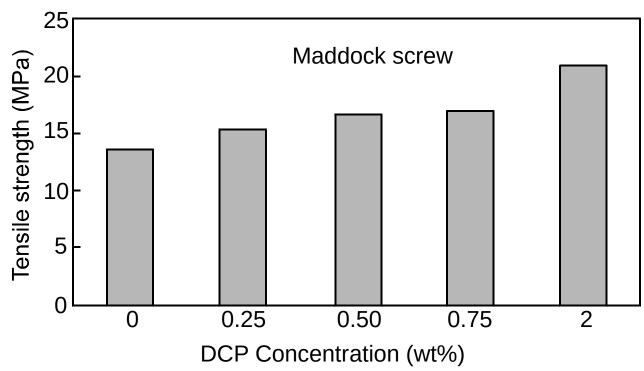


Figure 6. Tensile strength of samples prepared by Maddock screw.

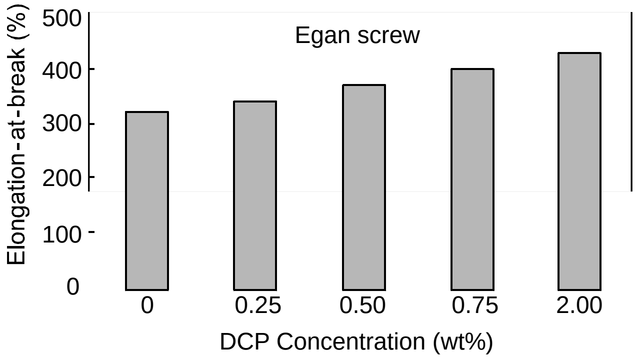


Figure 7. Elongation-at-break of samples prepared by Egan screw.

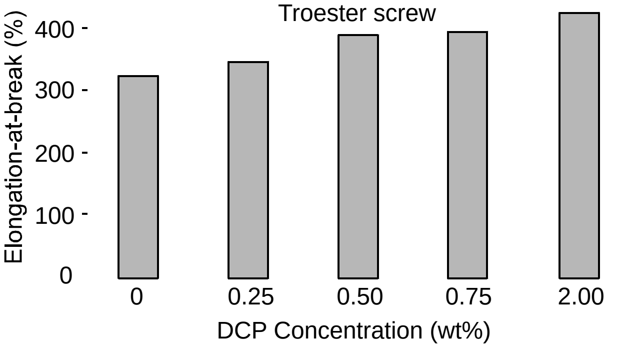


Figure 8. Elongation-at-break of samples prepared by Troester screw.

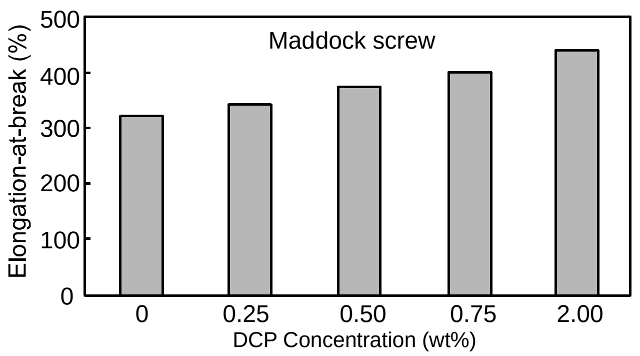


Figure 9. Elongation-at-break of samples prepared by Maddock screw.

bonds distribute evenly and randomly compared to other methods.

CONCLUSION

The gel fraction and mechanical properties tests the confirm the occurrence of continuous peroxide cross-linking of polyethylene by the shear head assembly constructed and employed. The highest gel fraction is related to sample of 2 wt% DCP with Maddock screws in shear head which produced the highest viscous dissipation energy. Obtaining products with good appearance at high gel fraction (above 45%) is difficult. It seems that when this method is coupled with other commercialized methods, the efficiency of cross-linking reaction and the quality of product would improve as well. In such case the energy consumption would also be lowered and the length of the production lines would be considerably shortened compared to the current methods.

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