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Effects of curing conditions on the properties of the dynamically cured EPDM/HDPE blends

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SUMMARY

Effects of curing conditions on the properties of the dynamically cured blends of the high density polyethylene (HDPE) and ethylene-propylene-diene terpolymer (EPDM) were studied. The blends were prepared using a curing die where EPDM was cured with dicumyl peroxide (DCP) in the presence of HDPE at different shear rate. The pressure drop for the constant flow rate across the curing die increased with increasing DCP concentration and EPDM content and decreased with increasing shear rate in curing die. The melt viscosity obtained by Capillary Rheometer increased with increasing DCP concentration for all compositions and decreased with increasing shear rate in curing die. The flow behavior index decreased with increasing DCP concentration and increased with increasing shear rate in curing die. The mechanical strength increased with increasing DCP concentration. The morphology of the blends was investigated by the scanning electron microscope (SEM).

INTRODUCTION

In recent years, polymer blends which were prepared by the dynamic curing process have been studied and several papers(1-15) and patents (16-21) have been published. The dynamic curing is the process of curing rubber under shear.

The dynamically cured polymer blends are known to be composed of small gel particles (microgel) of rubber(16) and possess important processing advantages(2) since the blends can be fabricated by the usual thermoplastic processing technologies such as extrusion and injection molding due to the characteristic morphological feature even with the presence of the crosslinked rubber as one component. The crosslinked rubber in the other hand imparts improvement of the mechanical properties, hot oil and solvent resistance,etc(22,23).

There are several factors affecting the structure and properties of the dynamically cured blends. The structure and properties will be determined by the composition(24,25) of the rubber and plastic components, and by the concentration of the curing agent, and the shear rate(10,26) during the curing reaction.

In previous studies concerning the dynamic curing, the dynamically cured blends were prepared by adjusting the rotating speed of the mixer during curing reaction in a roller mixer(3-5) or Banbury mixer(6,7). It is difficult to investigate the effect of the shear rate on the properties of the dynamically cured blends quantitatively using the above experimental equipments. But it is possible to examine the effect of shear rate quantitatively using appropriate shearing device.

In this paper, the effect of the quantitative shear rate, DCP concentration, and HDPE/EPDM composition on the morphology, rheological and

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mechanical properties of the dynamically cured HDPE/EPDM blends were studied using curing die device. The processing characteristics during the continuous curing reaction was also investigated.

EXPERIMENTAL

Materials

The materials used in this study are shown in Table 1. The high density polyethylene(HDPE) and the ethylene-propylene-diene terpolymer (EPDM) with ethylidene norbornene(ENB) as a termonomer are commercial products. Dicumyl peroxide(DCP) was used as the curing agent.

Table 1.
Materials and Their Characteristics

Materials	Characteristics	Source
HDPE	MFI 0.8 density 0.956	E308 (Korea Petrochem.)
EPDM	E/P=51/49 ENB type	Royalene 521 (Uniroyal)
DCP	Granule type	Concord

Dynamic Curing Equipment

The arrangement of the dynamic curing equipment is shown in Fig.1. It consists of a single screw extruder (C.W.Brabender Type 2003) with barrel diameter of 19mm, L/D ratio of 20:1 and the compression ratio of 3:1 attached with the curing die with barrel diameter of 19mm, die length of 150mm, and die gap width of 2.5mm. The polymer melt is sheared in the curing die gap by the rotation of the smooth mandrel driven by DC motor (3HP). Temperature controller is connected with electrical heater on the barrel of the curing die in order to maintain the curing temperature. Melt pressure during the dynamic curing is measured by the melt pressure transducer (Dynisco TPT 484-3M-6/18, 0-3000 psi) which is installed at the extruder-end for the investigation of the processing characteristics.

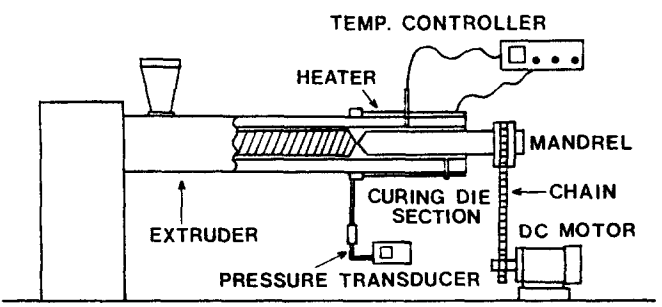


Fig.1 Dynamic curing equipment

Preparation of Blends

The EPDM and DCP were mixed in a 3x7 inch two roll mill(Farrel co.) at roll temperature of 50°C for 5 min. The amount of DCP was varied from 0 to 1.33 phr based on the amount of EPDM. The EPDM/DCP mixture and HDPE were

blended with compositions of 10, 15, 25, and 50 wt.% EPDM by the two roll mill at roll temperature of 140°C for 5 min. in order to prevent the curing reaction during blending period. The unreacted HDPE/EPDM/DCP blends were cut into small pieces using the laboratory crusher. The blends were extruded and fed into the curing die. The temperature of the extruder was controlled at 130°C (heat zone 1), and 140°C (heat zone 2). The temperature of the curing die was controlled at 200°C for the curing reaction. The melt flow rate was 5 g/min. and the average residence time was 3.2 min. in the die. The shear rate in the curing die was controlled by adjusting the rotating speed of the mandrel as 10, 50, 100, and 200 rpm which were corresponding to the shear rates ($\dot{r}_d$) of 3.8, 14.7, 29.3, and 58.6S^{-1}, respectively. The shear rate was calculated by considering the extrusion shear rate and rotational shear rate simultaneously(27). The extrudates were cooled in the air and were cut into small pieces once again for the measurement of the properties.

Measurements

The rheological properties were measured with a Capillary Rheometer (Instron Model 3211) in the shear rate($\dot{r}_w$) range of 3.5-350.5 S^{-1} at 200°C. The length and the diameter of the capillary were 5.0925 and 0.1275 cm, respectively. The diameter of the reservoir was 0.9525 cm and the entry angle was 90°. The L/D ratio of the capillary was about 40, and the end effects were considered negligible(10).

The mechanical properties were measured with tensile tester (Instron Model 4202) with the crosshead speed of 100 mm/min at room temperature. Average values of ten measurements were taken. The tensile specimens were prepared by injection molding with dimension following ASTM D683-77a. The temperature of the injection molder (Newbury HV1-25ARS) was controlled at 150°C (rear zone), 190°C (front zone), and 160°C (nozzle). The injection pressure and the injection time were 1750 psi. and 4 sec., respectively.

The morphology of the cryogenically fractured surfaces of the blends was observed using the scanning electron microscope (SEM)(JEOL JSM-35CF). Fractured surfaces were coated with gold for the microscopy.

RESULTS AND DISCUSSION

Rheological Properties

Fig.2 shows the effects of DCP concentration and shear rate in curing die($\dot{r}_d$) on the melt viscosity(η_a)-shear stress(τ_w) relation obtained by Capillary Rheometer for the dynamically cured 50:50 HDPE:EPDM blends. η_a increased with increasing DCP concentration due to the formation of higher chemical crosslinks in EPDM and decreased with increasing $\dot{r}_d$ due to the formation of the smaller segregated microdomain of the crosslinked EPDM gels(10,26). η_a at constant τ_w decreased with $\dot{r}_d$ at higher DCP concentration more rapidly. It seems that the changes in morphology during the dynamic curing under different shear rates are larger at higher DCP concentration.

Fig.3 shows the effects of DCP concentration and $\dot{r}_d$ on η_a-τ_w relation for the dynamically cured 85:15 HDPE:EPDM blends. η_a increased with increasing DCP concentration and decreased with increasing $\dot{r}_d$. In contrast to 50:50 HDPE:EPDM blends, η_a of 85:15 HDPE:EPDM blends is lower at the same DCP concentration because the dispersed EPDM phase has higher viscosity than the continuous HDPE phase. In case of 1.33 phr DCP concentration, η_a is found to be influenced very much by $\dot{r}_d$. Thus we can see the effect of $\dot{r}_d$ on η_a is more sensitive as the DCP concentration increases.

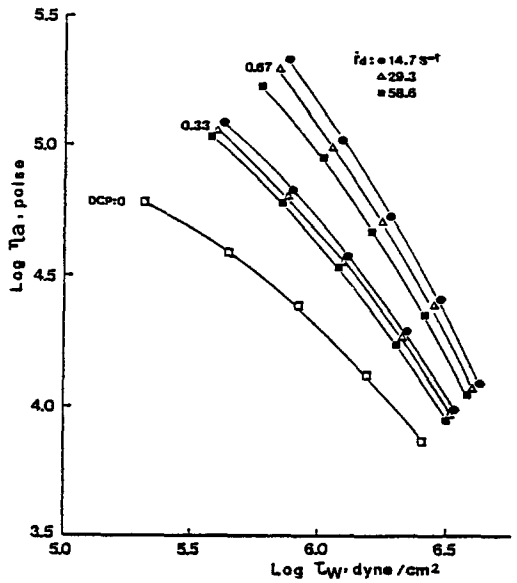


Fig.2. Effects of DCP concentration and shear rate in curing die $\dot{\gamma}_d$ on viscosity-shear stress relation for the dynamically cured 50:50 HDPE:EPDM blends at 200°C (□:linear blend).

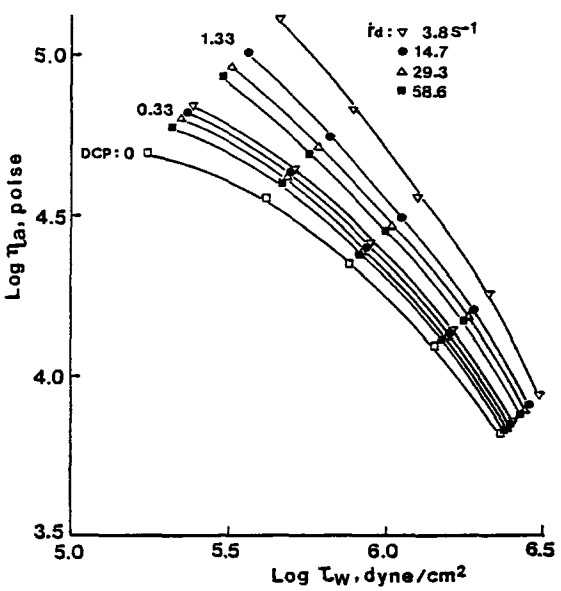


Fig.3. Effects of DCP concentration and shear rate in curing die $\dot{\gamma}_d$ on viscosity-shear stress relation for the dynamically cured 85:15 HDPE:EPDM blends at 200°C (□:linear blend).

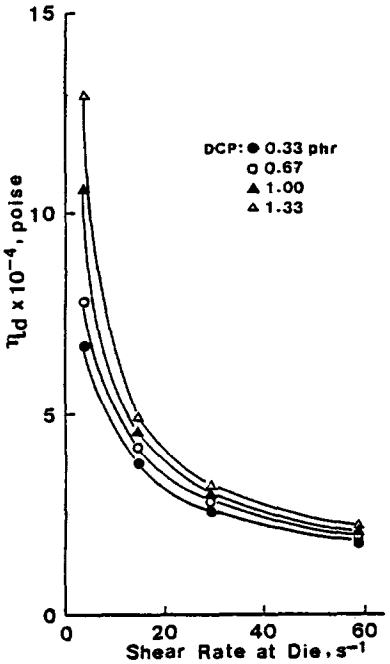


Fig.4.Effect of DCP concentration and $\dot{r}_d$ on viscosity in curing die for the 85:15 HDPE:EPDM blends at 200°C.

Fig.4 shows the effect of $\dot{r}_d$ on η_{ld} for 85:15 HDPE:EPDM blends. η_{ld} was estimated by calculating the viscosity obtained by Capillary Rheometer at $\dot{r}_w$ which was corresponding to $\dot{r}_d$. The reduction in η_{ld} during the curing reaction is more prominent in the lower $\dot{r}_d$ range for all DCP concentrations. It indicates that the formation of the continuous three-dimensional network is constrained effectively even at low $\dot{r}_d$.

Fig.5 shows the effect of $\dot{r}_d$ on the pressure drop required for the constant flow rate across the curing die for 85:15 HDPE:EPDM blends. The pressure drop increased with increasing DCP concentration due to the increase of chemical crosslinks and decreased with increasing $\dot{r}_d$. The blends of higher DCP concentration under higher $\dot{r}_d$ exhibit lower pressure drop than the blends of lower DCP concentration under lower $\dot{r}_d$ and have better mechanical properties due to the increased degree of chemical crosslinks. This is the characteristic advantage of the dynamic curing process.

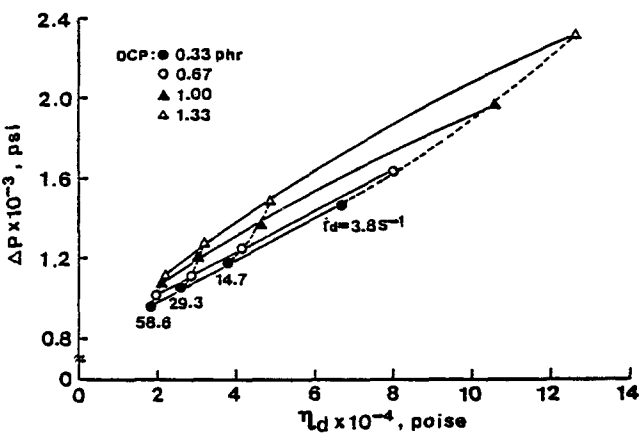
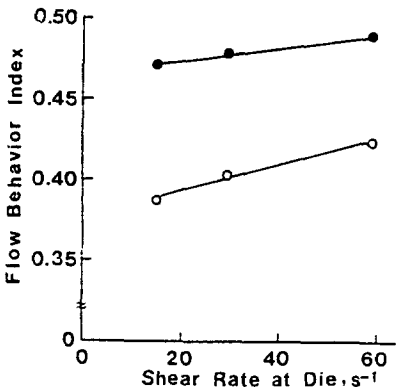


Fig.5. Effect of $\dot{r}_d$ on the pressure drop and viscosity in curing die for the constant flow rate across the curing die for the 85:15 HDPE:EPDM blends at 200°C.

Fig.6 shows the effect of $\dot{r}_d$ on the flow behavior index for 50:50 HDPE:EPDM blends. The flow behavior index is defined by d(log shear



stress) / d(log shear rate) and was calculated by regression analysis of the values of shear stress and shear rate obtained by Capillary Rheometer. The flow behavior index increased with increasing $\dot{r}_d$ due to the changes in morphology. The increase rate with higher DCP concentration is higher than lower DCP concentration. This is also due to the change in morphology.

Fig.6. Effect of $\dot{r}_d$ on flow behavior index for the 50:50 HDPE:EPDM blends at 200°C [DCP conc.(phr);(●) 0.33 ; (○) 0.67].

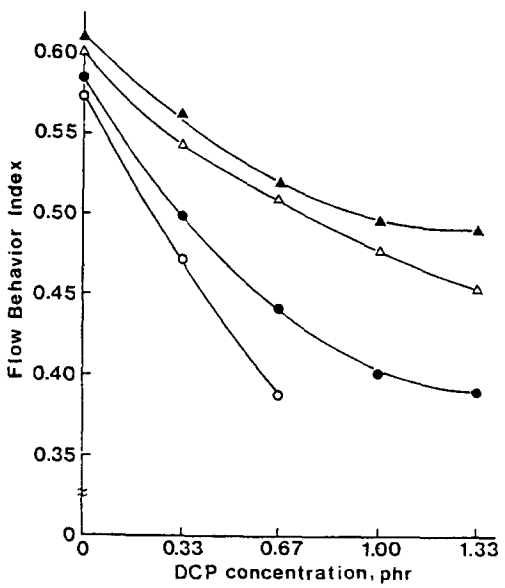


Fig.7 shows the effect of DCP concentration on flow behavior index at constant $\dot{r}_d$ for HDPE/EPDM blends. The flow behavior index decreased with increasing DCP concentration for all composition due to the decrease of the mobility of polymer chain from the higher molecular weight in the microgel as the DCP concentration is increased. The flow behavior index decreased with the increase of EPDM content.

Fig.7. Effect of DCP concentration on flow behavior index for the HDPE:EPDM blends [(○) 50:50; (●) 75:25 ; (△) 85:15; (▲) 90:10] at 200°C ($\dot{r}_d$;14.7 S^{-1})].

Mechanical Property

Fig.8 shows the stress-strain curves for the dynamically cured 85:15 HDPE:EPDM blends at constant $\dot{r}_d$. The mechanical strength increased with increasing DCP concentration while the elongation at break decreased. The tensile strength at DCP concentration of 1.33 phr is about twice as much as compared with that of the linear blend.

Morphology

Fig.9 shows SEM micrographs of the dynamically cured 85:15 HDPE:EPDM blends at DCP concentration of 1.00 phr extruded through the capillary at 116.8S^{-1}. The crosslinked EPDM domains are finely dispersed in HDPE matrix. It is seen that the size of microgel domains of EPDM is reduced from about 0.3-0.5 μm to 0.1-0.2 μm as the shear rate at curing die increases from 3.8 S^{-1} to 29.3 S^{-1}. For this reason, the dynamically cured HDPE/EPDM blends can be processed with low viscosity using the thermoplastic processing technology.

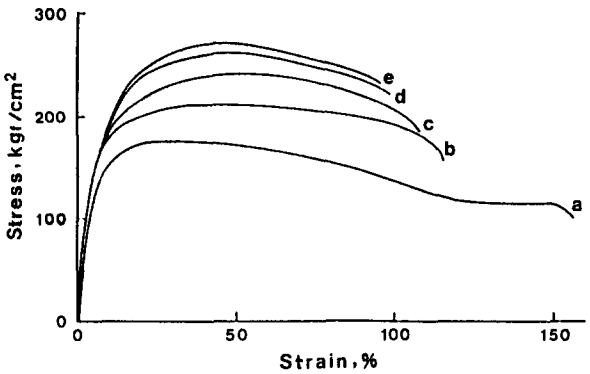


Fig.8. Stress-strain curves for the dynamically cured 85:15 HDPE:EPDM blends [DCP conc.(phr):(a) 0 (b) 0.33 (c) 0.67 (d) 1.00 (e) 1.33] ($\dot{r}_d$;29.3 S^{-1}).

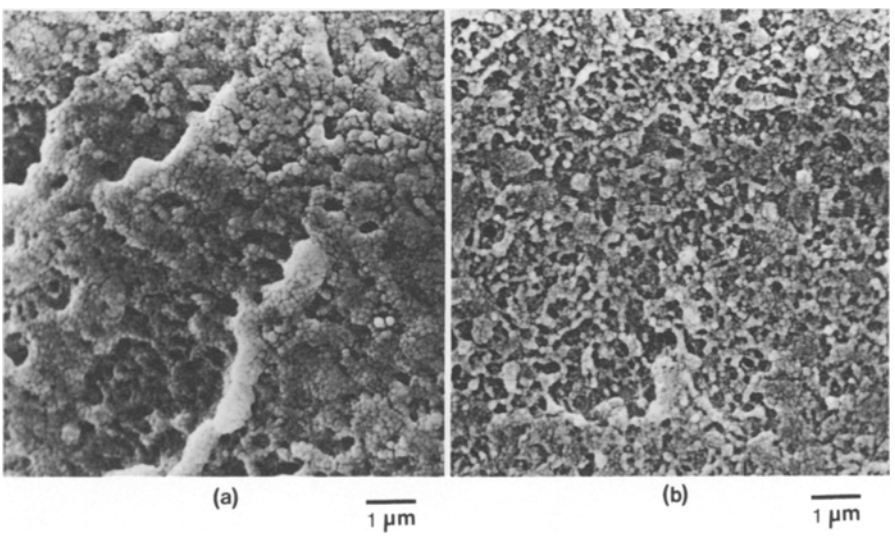


Fig.9. SEM micrographs of the dynamically cured 85:15:1.00 HDPE:EPDM:DCP blends [(a) $\dot{r}_d$;3.8 S^{-1} (b) $\dot{r}_d$;29.3 S^{-1}].

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