1. Introduction

Thermoplastic Elastomer Vulcanizates (TPEV) prepared by dynamic vulcanizing process [1], is the material which combine the elasticity of thermo-set rubber with the processibility of thermoplastics. TPEV is cost effective for its good processibility and eco-friendly for its recyclability. TPEV has more advantages of chemical resistance due to chemical cross-linking compare with general polymer which has no chemical cross-kinking.[2~4]

For these reasons, TPEV is rapidly and widely replacing vulcanized rubber such as NR, CR, EPDM, etc., and flexible PVC in various automotive parts applications. Recently, this requirement of replacement is expanded to foam area. But, several trials to developing TPEV foam could not show satisfied result. The foam ability of TPEV is very poor because of its unique morphology and low melt strength. [5] TPEV is composed of a large volume fraction of oil extended vulcanized EPDM which is impossible to foaming and a small volume fraction of polypropylene which is very difficult to foaming due to crystallinity. Also oil which is migrated to polypropylene from EPDM in TPEV system decreases melt strength of polypropylene.

In this study, for improvement foaming processibility, two kinds of new ideas were introduced. The first is the introduction of high melt strength polypropylene (HMSPP), Homo-Polypropylene, PP-g-MAH as compatibilizer (supplied from Honam petrochemical Corp.)[7,8], EPDM, paraffin oil, clay and nano-clay (Cloisite®) which is contained dimethyl dihydrogenatedtallow quaternary ammonium as organifier, and X-linking agent (SP-1045) was used.

2. Experimental

2.1 Materials

High melt strength polypropylene (HMSPP), Homo-Polypropylene, PP-g-MAH as compatibilizer (supplied from Honam petrochemical Corp.)[7,8], EPDM, paraffin oil, clay and nano-clay (Cloisite®) which is contained dimethyl dihydrogenatedtallow quaternary ammonium as organifier, and X-linking agent (SP-1045) was used.

2.2 Sample preparation

The TPEV/clay nanocomposite was prepared by dynamic vulcanization process using a Brabender Plasti-Coder mixer. The temperature of the mixer was 180 °C. The rotor speed was maintained at 120 rpm for 20 minute. The scheme of each process is given in Fig.1.

2.3 Extrusion Foaming

Extrusion foaming was carried out with Hakke Rheomix single screw extruder(screw
diameter: 19mmØ, L/D: 28) which is fitted with gear pump, static mixer and strand die as Fig.2. In all foaming test, CO₂ was used as physical blowing agent, and Hydrocerol was optionally used as inorganic chemical blowing agent and nucleating agent.

![Extrusion foaming Equipment](image)

Fig.2. Extrusion foaming Equipment

2.4 Characterization

2.4.1 Cross-linking degree
Cross-linking degree in this study is defined as

\[
\text{Cross-linking degree} = \frac{\text{cross-linked EPDM}}{\text{Total amount of EPDM}} \tag{1}
\]

Cross-linking degree of TPEV/clay nanocomposites is measured by boiling xylene insoluble method. Non-cross-linked polymer such as polypropylene and EPDM in case of TPEV can be solved in boiling xylene but cross-linked EPDM cannot be solved. Total amount of EPDM is decided from formulation.

2.4.2 Clay dispersion
Degree of filler dispersion was evaluated using a TEM images and XRD was conducted to measure the d-spacing between clay in PP matrix.

2.4.3 Melt tension & Melt strength
Melt tension was evaluated using Rheotens. Extruded strand was obtained from Brabender single screw extruder. Melt strength behavior was evaluated by molten Rheometer.

2.4.4 Foaming cell analysis
Several methods of evaluation were carried out for extruded TPEV foam. Density was measured for calculation of expansion ratio. Observation of cross-section of extruded strand foam using optical microscope is carried out for evaluation of cell distribution.

3. Results and Discussion

3.1 Cross-linking degree
Cross-linking degree of TPEV is very important property because this property directly influence on not only physical properties such as surface hardness, tensile strength, and permanent set property but also processibility, oil resistance, and etc. Fig.3. shows patterns of surface hardness and tensile strength of data with cross-linking degree. Two physical properties are increase with cross-linking degree linearly.

![Surface hardness and tensile strength](image)

Fig.3. The surface hardness and the tensile strength of composites as a function of cross-linking degree

3.2 Clay dispersion
Fig.4. shows the XRD pattern for TPEV/clay nanocomposites using Cloisite 15A and Cloisite 20A respectively. In terms of the degree of dispersion, nanocomposite having 1% Cloisite 20A shows the best dispersion. Fig.5. TEM images of each process having 5% of organoclay are shown. In process 1, organoclays are located in the whole region of cross-linked EPDM and PP matrix. In process 2, organoclays are in PP phase mainly but rarely EPDM phase. In process 3, organoclay can be found in only PP phase.
3.3 Melt tension & Melt strength

Melt tension of each composite was measured by Rheotens for prospecting relevance as foaming materials. As a result, melt tension also increased with content of filler as Fig.6 (a). Especially, composite with organoclay shown 1.5 times higher melt tension compare with other fillers. In Fig.6 (b), the melt tension of four composites using 2 types of polypropylene and 2 types of organoclays is given. The composite with HMSPP and Cloisite 15A shown the highest melt tension, and the composite with conventional PP and Cloisite 20A was lowest. From this phenomenon, HMSPP and organoclay seems to give some synergy effect each other in terms of melt tension. Melt strength behavior of composite with combination of 2 types of PP and types of organoclay are given in Fig.6 (c) and (d). In case of composite with conventional PP, melt strength was also increased with filler contents. From these results, the combination of HMSPP and Cloisite 15A was used mainly in further study such as preparation of TPEV/clay nanocomposites and extrusion foaming test.

Fig.4. The XRD patterns of TPEV/clay composite (a) with Cloisite 15A, (b) with Cloisite 20A

Fig.5. TEM micrographs of TPEV/clay composites with Cloisite®20A prepared by process 1, process 2 and process 3 (Content of organoclay: 5%)

Fig.6. (a) melt tension of PP/fillers composite, (b) melt tension of PP/organoclay composite, (c) melt strength of PP/clay composite and (d) melt strength of HMSPP/clay composite
3.4 Foaming cell analysis

The optical microscope images of cross-section of extruded foam are provided Fig. 7. The expansion ration of extruded foam with HMSPP TPEV/clay nanocomposite is from 1.8 to 3.3 times. This could be achieved by using a HMSPP TPEV/clay nanocomposite with the combination of HMSPP and nanocomposite using organoclay, but conventional TPEV. Form of extruded foam with CO₂ flow rate of 0.5 ml/min has more expansion ratio than 0.5 ml/min. The coalesced big cells were found on the foam with 0.75 ml/min of CO₂ flow rate. In case of using Hydrocerol has more expansion ration caused by cell nucleating and has better cell distribution. In terms of die temperature, in case of 160℃ showed the highest expansion ration and the best cell distribution.[9] The expansion ratio changes of extrusion foam with each die temperature are shown in Fig. 8.

![Fig.7. The optical microscope images of extruded foam using 1% of NaHCO₃ as blowing agent (a) Conventional TPEV, (b) HMSPP TPEV and (c) HMSPP TPEV/Clay nanocomposite](image)

![Fig.8. Expansion ratio of extruded foam with HMSPP TPEV/clay nanocomposite as a function of die temperature](image)

4. Conclusion

TPEV/clay nanocomposite using organoclay with 3 different processes were prepared. The cross-linking degree, morphology, surface hardness, tensile properties, melt tension and melt strength were investigated. Nanocomposites with Cloisite 20A showed somewhat bigger d-spacing compared to Cloisite 15A. The nanocomposites with 1% organoclay shows better dispersion compared to with 3% organoclay. Conventional TPEV showed poor foaming processibility. HMSPP could give the improving effect of foaming processibility, and well dispersed organoclay could give the more nucleating and stabilizing capabilities. In terms of the content of organoclay, the TPEV/clay nanocomposite with 3% of Cloisite 15A was better 5%, because the collapsed and coalesced cells were found in the TPEV/clay nanocomposite with 5% of Cloisite 15A. Hydrocerol can improve the expansion ratio and cell distribution remarkably. In terms of die temperature, expansion ratio curve showed the mountain shape which has the top at 160℃.

As a result of TPEV/layered silicate nanocomposite evaluation, Cloisite 15A could give better mechanical properties and bigger d-spacing. TPEV/clay nanocomposites can give more advantage of weight reduction which is a key issue in automotive parts applications because of fuel efficiency. The mechanical properties of TPEV/layered silicate nanocomposite using small amount (3 wt%) of MMT was similar to general TPEV using large amount(11%) of Kaolin clay as reinforcement. It can give advantages of weight reduction and specific foaming processibility caused by the volume fraction increasing of thermoplastic components. HMSPP was used to TPEV/layered silicate nanocomposite instead of general polypropylene for improvement of foamability. This new TPEV, HMS TPEV/clay nanocomposite has shown the higher melt strength behavior and better extrusion foaming processibility than general TPEV. As a result of extrusion foaming test, remarkably improved foam in terms of cell density, cell distribution and expansion ratio compare with the foam made from general TPEV.
References


