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# Physical Properties of Flame Retardant Particulate Reinforced Thermoplastic Polymer Composites for Cold-Resistant Cable

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## Abstract

The demand for cold-resistant cable material is increasing due to the rapid increase in the development of devices that operate in a low temperature environment. Cold tolerance of a thermoplastic polymer largely depends on the type and content of about 20 or more additives used to make the polymer. The phenomenon of polymer hardening at low temperature can be classified into hardening by simple temperature effect, embrittlement at the glass transition temperature, and hardening by crystallization of polymers that tend to crystallize. In this study, a thermoplastic polymer having a low glass transition temperature, a flame retardant, and an additive were mixed to evaluate the mechanical properties of a thermoplastic polymer composite material for electric wires. It has been confirmed that mechanical properties and processability are determined depending on the additives and compatibilizers added, and this study is considered to be useful as basic data for optimization to meet the performance requirements of wires developed for low-temperature use.

## Keywords

Cold-resistant cable
Composite materials
Flame retardant
Thermoplastic polymer

## 1. Introduction

The increasing demand for polymers in industry and applications has led many researchers to conduct various studies to improve their mechanical properties and electrical shielding performance. For many years, polymers such as polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC) have been widely used as electrical insulation materials for power cables [1,2]. Among these, PVC is one of the most widely manufactured polymers in the world and is widely used in the power cable industry as an electrical insulation material for low- and medium-voltage cables due to its flame retardancy, excellent mechanical performance, and high stability at low temperatures [3]. However, since chlorine is a strong oxidizing agent, it easily reacts with organic molecules to produce a variety of chlorinated compounds, resulting in the production of organochlorine wastes (hazardous components of waste as defined in Annex I of the Basel Convention) and byproducts. Many of these chemicals also accumulate in ecosystems, including fish, wildlife, and humans, and are toxic even at low doses. The main product compounds, chlorinated dioxins and furans, are very dangerous compounds that can cause a variety of adverse health effects even at very low exposure levels, and their use has recently been restricted [4,5].

Thermoplastic elastomers (TPEs), which are replacing PVC wires, are materials with the elastic and mechanical properties of thermoset crosslinked rubber due to the melt processability of thermoplastic resins. TPEs are produced by a variety of processes such as extrusion blow molding, injection molding, vacuum forming, and calendering. TPEs exhibit the functional properties of conventional elastomeric materials, and Bhowmick *et al.* considered that the plastic acts as a continuous phase to enable melt processing of TPEs, while the dispersed rubber phase is responsible for the rubber elasticity and other elastic properties of the blend. Thermoplastic vulcanizates (TPVs) are a specific family of TPEs produced by dynamic vulcanization of immiscible blends of rubber and thermoplastic resins, i.e., selective crosslinking of the rubber during simultaneous melt mixing with the thermoplastic [6,7].

In recent years, the demand for cables used in low-temperature environments has increased due to the increasing number of ships operating in polar regions, such as icebreakers, and there is a need to develop cable materials with cold resistance. The cold resistance of polymeric materials is highly dependent on the type and content of about 20 types of additives that make up the rubber compound. Kim *et al* [7] prepared a rubber compound by compounding natural rubber (NR) with butadiene rubber (BR), which has a relatively low glass transition temperature, and compared the mechanical properties such as hardness and tensile strength with the glass transition temperature properties, and reported that the rubber compound with a lower glass transition temperature can improve the cold resistance performance. In order to develop a cable material with cold resistance, Sun *et al.* added various additives to PVC to produce a material that can be used in an environment of -50°C [8], and many other researchers have reported studies on improving mechanical and thermal properties through composites of rubber materials, nanoparticles, and fibers [9-12]. Considering the properties of polymers, composites of nanoparticles and polymeric materials have problems such as incompatibility between inorganic nanoparticles and organic polymers, and agglomeration of nanoparticles to form clusters, resulting in loss of beneficial effects. To overcome these problems, several studies have proposed surface functionalization of nanoparticles using appropriate coupling agents [13-15].

In this study, flame retardant particles were added to the base polymer produced by blending elastomer blends with cold resistance to produce composite materials, and the flame retardant properties and mechanical strength, such as tensile strength, of the wires were evaluated by using various additives.

## 2. Experimental method

In order to manufacture composites with cold-resistant properties, we used polymers such as olefin block copolymer (OBC), polyolefin elastomer (POE), PE, polyolefin-based elastomers (PBE), TPV, etc., with low-temperature glass transition temperature (Tg) to compensate for low-temperature brittleness by manufacturing commercially available thermoplastic elastomer blend compositions, and for this purpose, we tried to secure low-temperature flexibility by blending materials with cryogenic Tg and adjusting the soft and hard phases. In addition, Refos65, $Mg(OH)_2$, a commercial flame retardant, was used to impart flame retardant properties to the composition for wires, and various functional additives such as $CaCo_3$, Zeosil175GR, and silicon oil were used to improve mechanical strength such as tensile strength.

To secure the dispersibility of the thermoplastic particle reinforced composites, the resin and base polymer were firstly melted and dispersed according to the characteristics of each thermoplastic composition, and then the compound was formulated at a temperature of 120–150°C using a sealed mixing machine, a kneader (Moriyama, Japan), and then kneaded using a roll-mill, and then melted and dispersed at a temperature of 150–180°C.

The dispersed compositions were prepared in pellet form using a plastic injection molding machine and extruder, and then flat plates of 3 mm thickness each were prepared using a compression press at 155 degrees for 10 minutes.

Mooney viscosity was measured in accordance with ASTM D 1646. Tensile strength was measured in monolithic specimens in accordance with ASTM D 638, and tear strength was measured in accordance with ASTM D 624. Each specimen was evaluated by measuring the average value of five or more specimens. The tensile and tear strengths were measured at room temperature using a Universal Test Machine (DUT-500CM, Daekyung Engineering, Korea). The load cell was a 50 kN cell, and the crosshead speed was measured at a speed of 300 mm/min.

The flame retardant properties were evaluated using the limiting oxygen index (LOI), which is the minimum volume content of oxygen in an oxygen-nitrogen mixture required for a polymer sample to ignite and burn for three minutes without being extinguished. The test apparatus consists of an igniter, a gas supply part consisting of oxygen and nitrogen gas cylinders, a combustion part including a combustion cylinder made of heat-resistant glass, and a measurement part consisting of a flow meter and a gas mixer. A mixture of oxygen and nitrogen gas is injected from the bottom of the combustion cylinder at a constant flow rate and burned by igniting a sample hanging vertically on a sample hook located at least 100 mm above the top of the combustion cylinder. The minimum flow rate of oxygen and nitrogen required for the sample to continue burning for at least 3 minutes or for the sample to ignite and have an inherent combustion field of at least 50 mm, is determined.

If the oxygen flow rate at that time is $[O_2]$ (l/min) and the nitrogen flow rate corresponding to this flow rate is $[N_2]$ (l/min), the oxygen index is obtained as OI (O. I.) = $[O_2] \times 100 / ([O_2] + [N_2])$. The larger the OI (O. I.) value, the more flame retardant it is.

## 3. Results and discussion

To improve the cold resistance of the flame retardant particle reinforced thermoplastic polymer, the glass transition temperature was measured by differential scanning calorimetry (DSC) for the base polymer candidate material. Prior to compounding, specimens of the base polymer alone were made to evaluate basic properties such as tensile strength, hardness, and tear strength, and the results are shown in **Table 1**. As a result of evaluating the tensile strength of various types of polymers such as OBC, POE, PE, PBE, and TPV, low density polyethylene (LDPE)5321 specimens prepared with PE-based base polymer showed the highest properties, and it was confirmed that the tensile strength of the same type of polymer varies depending on the content of co-polymer. Comparing the Tg values to evaluate the cold resistance performance, it was found that Infuse9107 of the OBC series had the lowest glass transition temperature, while the propylene-based elastomer had a higher glass transition temperature. The densities of all the base polymers were similar, ranging from 0.86 to 0.93 g/cm$^3$.

To optimize the formulation of thermoplastic composites for wires used in low-temperature environments, low-temperature flexibility was evaluated by adjusting the soft and hard phases of a mixture with a low-temperature Tg. In addition, various flame retardants were added to impart flame retardant properties, and various additives were evaluated for flame retardancy of the wires. Four types of base polymers were selected based on the results in **Table 1**. **Figure 1** shows the results of the mechanical property evaluation to select the base polymer prior to the evaluation of the blending properties by adding compatibilizer agents and additives. Each test specimen was divided into PBE series and POE series polymers. Reofos-65 and magnesium hydroxide were added as flame retardants to improve the flame retardant performance, and Zrosil 175GR and PEG4000 were added as additives to prepare the compounds. Zeosil 175GR was added to improve mechanical strength and PEG4000 was used as a coupling agent to improve compatibility with the composite base. Four types of highly resistant thermoplastic compounds were prepared by mixing various compositions, and the proportions and additives are shown in **Table 2**. In terms of single polymers, the specimens prepared with Vistamaxx 6202 as the base polymer showed the highest tensile strength and Mooney viscosity, and the specimens with LC565 showed the lowest tensile strength and Mooney viscosity. On the other hand, the 6202/3980FL specimen with a 7:3 blend of Vistamaxx 6202 and 3980FL showed superior mechanical properties compared to the other specimens in all properties, suggesting that blending the base polymers in appropriate proportions can result in elastic material compositions with higher mechanical properties compared to the use of single polymers. The compression molding of all compositions was good, and the tensile strength was relatively low for the compositions with POE as the base polymer. Base polymers Vistamaxx 6202 and 3980FL, which showed the highest mechanical properties, were used in a ratio of 7:3 and 3:7 to make base polymers, and the compound materials blended with additional compatibilizer products and additives were evaluated, and the results are shown in **Figure 2**.

The reason for producing specimens with blends of Vistamaxx was to create a high-strength base polymer by blending high-strength polymers and to improve the tensile strength of the compositions by varying the type and content of compatibilizers. A-type and B-type specimens were prepared using Vistamaxx 6202 and 3980FL in a ratio of 7:3 and 3:7, respectively. In A-type, silicone rubber and Lotryl35BA40 were added as additional additives, and silicone rubber was designated as S and Lotryl35BA40 was designated

**Table 1.** Mechanical properties of the base polymer through compound formulation

| Properties | Infuse 9107 | LC565 | LC670 | LDPE5321 | Vistamaxx 3980FL | Vistamaxx 6202 | KEPA1150 |
|---|---|---|---|---|---|---|---|
| Hardness (A type) | 63 | 57.3 | 70 | 96.3 | 92.6 | 69 | 66.3 |
| Density (g/cm$^3$) | 0.881 | 0.875 | 0.870 | 0.927 | 0.890 | 0.886 | 0.866 |
| Tensile strength (MPa) | 2.91 | 1.04 | 5.5 | 6.91 | 4.43 | 1.72 | 1.93 |
| Elongation (%) | 1005 | 726.59 | > 1000 | 114 | 471 | 477 | 592 |
| Tear strength (k·Nm$^{-1}$) | 33.44 | 24.19 | 38.78 | 96.17 | 93.33 | 35.31 | 41.78 |
| Tg (°C, by DSC) | -62.59 | -56.27 | -55 | -24.36 | -18.14 | -28 | -52.37 |
| Major component (Material classification) | OBC | POE | | PE | PBE | | TPV |

**Table 2.** Composition table of compounds for selection of cold-resistant base polymers

| Number | Base polymer | | | | Flame retardants | | Additives | | |
|---|---|---|---|---|---|---|---|---|---|
| | Vistamaxx 6202 | Vistamaxx 3980FL | POE LC565 | POE LC670 | Refos65 | Grafted $Mg(OH)_2$,[1)] | $CaCo_3$ | Zeosil 175GR | Silicon oil, KF96 |
| 6202 | 100 | - | - | - | 10 | 70 | 20 | 10 | 1 |
| LC565 | - | - | 100 | - | 10 | 70 | 20 | 10 | 1 |
| LC670 | - | - | - | 100 | 10 | 70 | 20 | 10 | 1 |
| 6202/3980FL | 70 | 30 | - | - | 10 | 70 | 20 | 10 | 1 |

[1)]Grafted $Mg(OH)_2$ is a surface-treated flame retardant with a silane coupling agent.

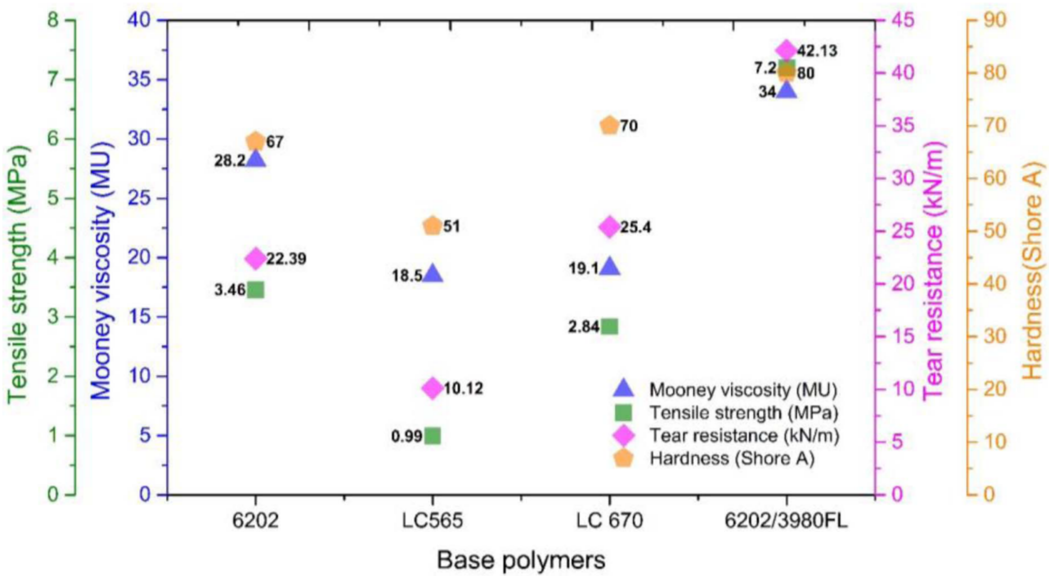


**Figure 1.** Mechanical properties of basic compounds depend on the polymer types

as L in the graph. In B type, Reofos-65 was added as an additional flame retardant without any additional additives, and Lotryl35BA40 was added as the same as the compatibilization agent, and they were labeled R and L, respectively, in the graph. The silicone additive was used to improve process ability in addition to flame retardancy, and silica, a reinforcing additive, was used to improve the mechanical strength of the composition. In the A-type specimen, the Mooney viscosity increased with the addition of the compatibilizer agent, but the tensile strength, tear strength, and flame retardant performance decreased, while the addition of silicone rubber decreased the Mooney viscosity, tensile strength, and tear strength, but slightly improved the flame retardant performance. In the B-type specimen, the Mooney viscosity, tensile strength, and tear strength decreased with the addition of additional flame retardant, but there was no significant change in flame retardant performance, and only the Mooney viscosity increased slightly with the addition of compatibilizer agent, and the tear strength and tensile strength properties tended to decrease. This shows that the process ability of silicone rubber with compatibilizer agent is improved due to the decrease in pattern viscosity, but due to the decrease in tensile strength and tear strength, optimal formulation is required to meet the design value of the material when manufacturing elastic material compositions for wires. In addition, it was confirmed that the flame retardant performance of existing flame retardants decreases when the compatibilizer agent is used alone, so when using Lotyl35BA40 compatibilizer agent, it is judged that the use of additional flame retardants and the amount of flame retardant should be optimized to prevent the decrease in flame retardant performance.

To improve mechanical properties and cold resistance, the base polymer was prepared by blending Infuse9107, an OBC series with a low glass transition temperature (-62.59°C) in a ratio of 7:3 with LDPE. Compounds were prepared under the same conditions as Type A in **Figure 2** to evaluate mechanical properties. In **Figure 3**, it can be seen that the Mooney viscosity decreases with the silicone rubber additive, unlike the conventional Vistamaxx blended specimen. The flame retardant performance decreased with the addition of the compatibilizer, but the flame retardant property increased when the compatibilizer and silicone rubber were used simultaneously, and the tensile strength decreased when the compatibilizer and silicone rubber were used. The tear resistance of the compound blended with LDPE5321 and Infuse9107 decreased slightly when the compatibilizer and silicone rubber were used, but there was no significant difference, thus it is not considered to have a significant effect on the tear resistance.

In **Figure 4**, Infuse9107, a TPO-based polymer with the lowest glass transition temperature, and KEPA1150, a TPV-based polymer, were added to the base polymer in a ratio of 7:3. Similar to the results for LDPE5321, the pattern viscosity tended to decrease with the addition of silicone rubber additives and Lotryl35BA40. The tensile strength decreased slightly with the addition of silicone rubber and Lotryl35BA40, but the tensile strength characteristics did not change significantly with the change in the amount of additives and compatibilizers.

From the previous mechanical property evaluation results, it can be seen that the highest tensile strength

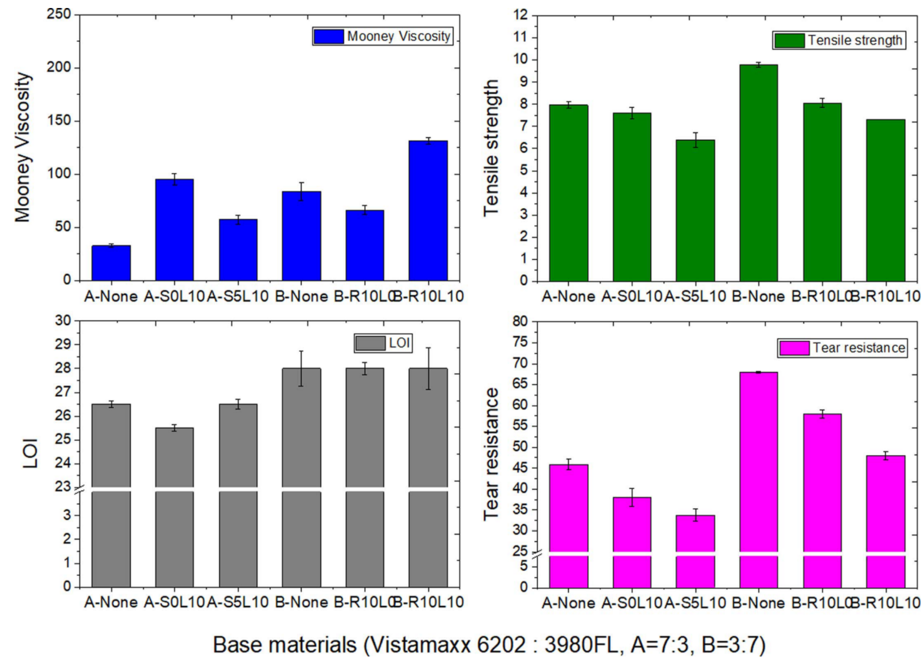


**Figure 2.** Mechanical properties as a function of compatibilizers and additives of mixed Vistamaxx resin

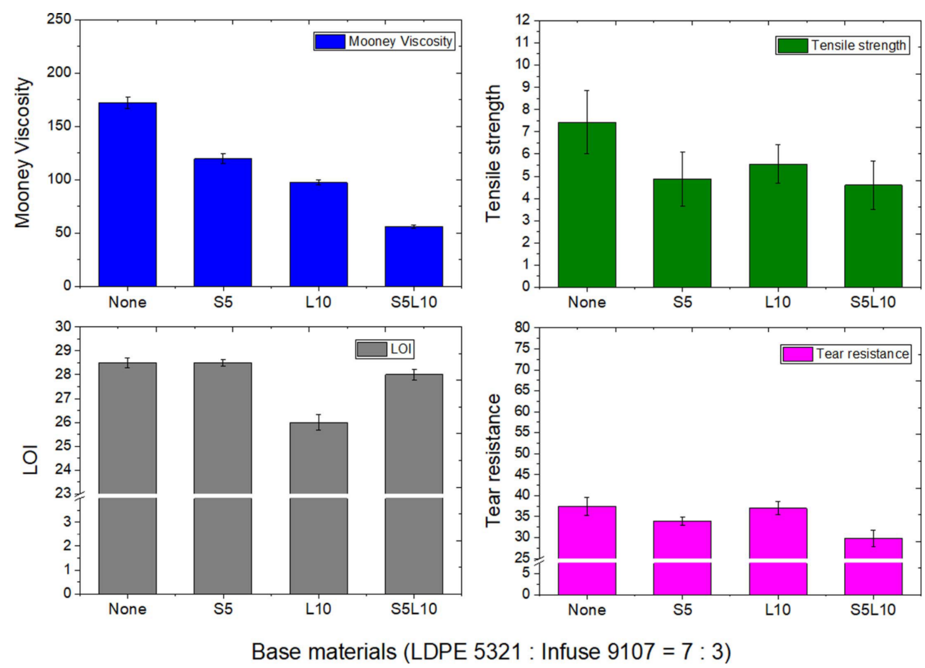


**Figure 3.** Mechanical properties by adding compatibilizers and additives to the base polymer mixed with LDPE5321 and Infuse9107 in a ratio of 7:3

properties were obtained for the base polymer blended with Vistamaxx 6202 and 3980FL at 3:7. The relatively higher tensile strength of the 70% Vistamaxx 3980FL than the 70% Vistamaxx 6202 test specimen suggests that Vistamaxx 3980FL has superior mechanical properties when blended with additives such as solvents, flame retardants, and additives. However, the evaluation results in **Table 1** show that the glass transition temperature of Vistamaxx is relatively high, suggesting that its cold resistance at low temperatures is poor. Therefore, in the composition formulation, Vistamaxx 3980FL, which has excellent mechanical strength, was used as a base, and high density polyethylene (HDPE), which is known to have excellent low-temperature embrittlement properties, was added to prepare the composition, and the results of evaluating the properties are shown in **Figure 5**. In **Figure 2**, Reofos-65, which plays a role in improving flame retardancy, was added at 10 phr (parts per hundred rubber), and the amount of additive was reduced by half, unlike other specimens.

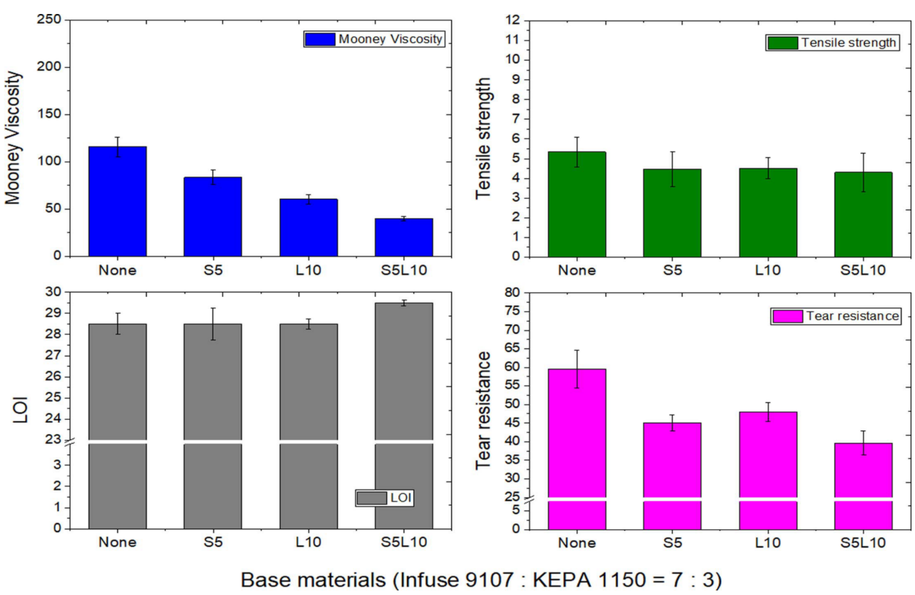


**Figure 4.** Mechanical properties by addition of compatibilizer and additive on the base polymer mixed with Infuse9107 and KEPA1150 in a ratio of 7:3

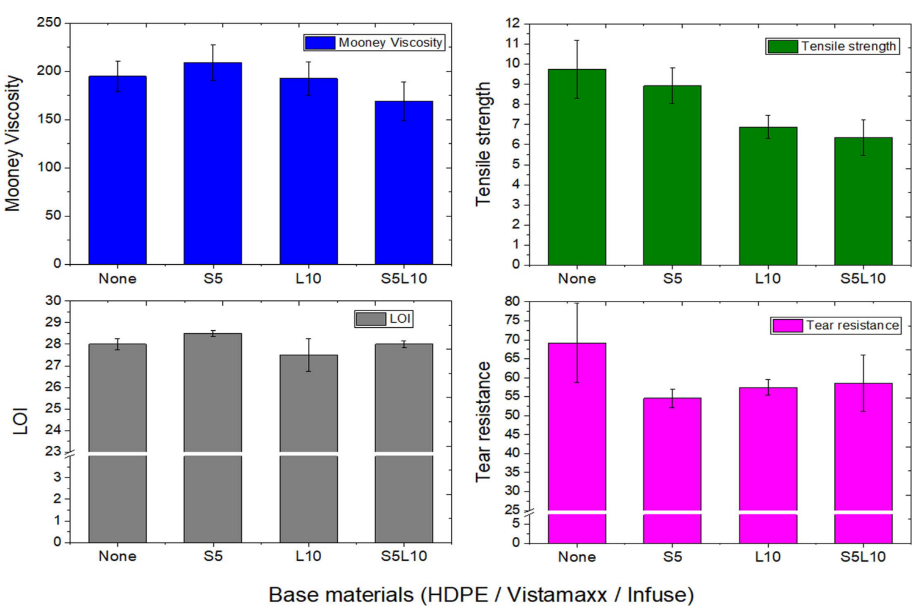


**Figure 5.** Comparison of mechanical properties of flame retardant-added thermoplastic composites mixed with various types of base polymers

Two types of HDPE, F600 and M690, were used and blended with Vistamaxx 3980FL and Infuse9107 to make the base polymer compositions. The compositions of HPDE F600, Vistamaxx 3980FL, and Fusabond N525 in a ratio of 3:6:1 were named HFV, and the compositions of HPDE M690, Vistamaxx 3980FL, and Fusabond N525 in a ratio of 3:6:1 were named HMV, and the compositions of HPDE F600, Vistamaxx 3980FL, Infuse9107, and Fusabond N525 in a ratio of 2:3:3:2, and HPDE M690, Vistamaxx 3980FL, Infuse9107, and Fusabond N525 in a ratio of 2:3:3:2 were named HFV and HMV, respectively. The specimens with HDPE showed high mechanical properties overall, but the Mooney viscosity was also high, which is considered to be difficult to process. In addition, the tensile strength and flame retardant properties of the test specimens with Infuse9107 were degraded, thus it is not suitable as a material for wires that require high strength and high flame retardancy. It was found that the tensile strength of the composite was generally higher as the content of the material with high inherent tensile strength in the base polymer increased. However, the tear strength of the composites decreased in relation to the compatibilizer agent. This is believed to be due to the fact that the bonding reaction did not occur uniformly when the base polymer and the compatibilizer agent were compounded, and it is thought to be due to the effect of the uneven reaction caused by the added components such as flame retardants. As a result of measuring the glass transition temperature of the composites of various combinations used in this study, it was found that the glass transition temperature of the composites composed of the same content of base polymer did not change significantly due to the added components such as compatibilizer agents. Therefore, the graph is shown in **Figure 6** as the measured average of the glass transition temperature according to the type of base polymer. In the glass transition temperature measurement results, we can see that the glass transition temperature of the test specimen containing a lot of Infuse series polymer, which showed a low glass transition temperature in the results of polymer alone, is lower. In particular, the glass transition temperature of the composite of Infuse and KEPA was the lowest. It is recommended that the material design should be based on polymers with low glass transition temperature for materials at low temperatures.

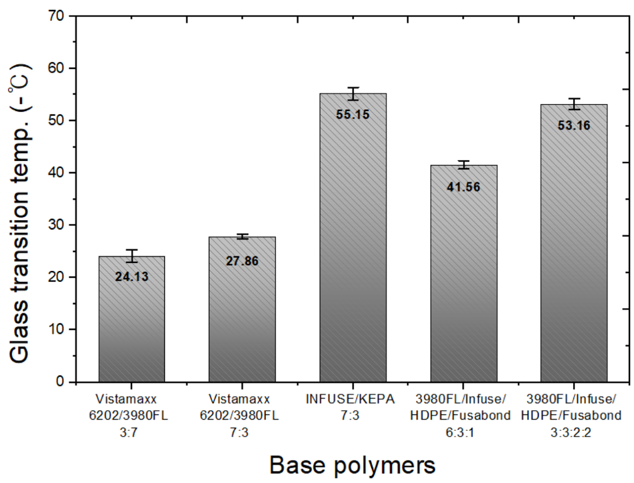


**Figure 6.** Glass transition temperature of composite materials with different base polymer compounds

However, it is expected that the composites blended with Infuse and KEPA will have relatively low mechanical properties, limiting the range of applications. On the other hand, if a high-strength material is mixed with a polymer with a low temperature range, it is expected that a cable material with high strength and a low glass transition temperature above a certain level can be obtained. Therefore, for the application of cold-resistant cables, it is expected that the material formulation design is required according to the design requirements for the temperature and stress to which the cable material is exposed.

## 4. Conclusion

In this study, thermoplastic elastomers with low glass transition temperature were evaluated using various additives to impart flame retardant properties to marine wires and improve mechanical strength such as tensile strength by blending elastomer blend compositions, and the following conclusions were obtained.

(1) It was confirmed that the mechanical properties such as tensile strength, tear strength, processability, and flame retardancy change depending on the use of compatibilizers agents and additives. It was confirmed that securing dispersibility and uniformity in the preparation of the compositions has a great influence on the realization of the properties of the optimal compositions, and it is considered necessary to optimize the appropriate use and amount of additives.

(2) Excellent tensile strength and other properties were obtained in the compositions using HDPE-based polymers, but due to the high Mooney viscosity, a mixture of Vistamaxx 6202 and Vistamaxx 3980FL as a base polymer is thought to be suitable as a flame retardant composition for wires.

(3) The results of this study can be used as a basic research for resin formulation design for cold-resistant cable application, and it is expected that cold resistance and required design mechanical properties can be satisfied through composite materialization of resin with low embrittlement temperature, and resin and additives with high strength.

(4) Although we have completed the verification of composite compositions with glass transition temperature below -50°C, we plan to conduct further research on the application of flame retardant compositions for wires in environments with lower temperatures and the correlation of glass transition temperature with the composition and content of low-temperature materials.

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## Disclosure statement

The authors declare no conflict of interest.

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