

Study on Influencing Factors on Properties of Injectional Compounds Based on Polyethylene and Silica from Waste Materials

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Abstract

In this study, silica from waste materials - rice husk (silica TT) and byproduct of quartz stone grinding (silica TA) - modified with bis (3-ethoxy propylsilane) tetrasulphide (TESPT) were characterized. Their particle sizes are mostly under 30 μm , quite suitable for plastic filling. Some factors influencing the properties of injectional compounds based on HDPE/LDPE blend and silica from waste materials were carried out. It was found that the processing conditions which including maximum temperature of 190-200 $^{\circ}\text{C}$ and screw speed of 50-100 rpm are suitable for stable compound properties. Processing aid additives ratios such as stearic acid/zinc stearate and PE wax/paraffinic oil affect mostly compound melt flow index, but HDPE/LDPE ratio strongly affects both melt flow index and mechanical properties of compounds: change HDPE/LDPE ratio from 90/10 to 60/40 decrease tensile from 15.2 MPa to 12.5 MPa, bending strength from 15.5 MPa to 10.6 MPa while melt flow index decrease almost twice but elongation at break increase from 34.4% to 72.2%. Also, using PE-g-MA as a compatibilizer may remarkably enhance the mechanical properties of compounds: the PE-g-MA content of 0.8-1.0 (%wt) increases tensile, bending strength, and impact resistance of compound by about 10-30% in comparison with the compound without PE-g-MA.

Keywords: Injectional compounds, polyethylene, waste silica, compounds, processing conditions.

1. Introduction

Compounds from polyethylene (PE) are one of the materials most used for injection techniques due to their advantages such as low cost, easy processability excellent dielectric properties, resistance to chemicals, low water absorption,... [1-2]. However, PE shortcomings include not very high tensile strength or lack of necessary rigidity [2]. Hence, PE compounds particularly injectional often filled with reinforcement fillers, one of which is silica.

Although silica does not remarkably enhance the tensile strength of plastic materials it may improve thermal resistance, abrasive resistance, and modulus as well. Due to the mentioned properties, silica is one of the most applied reinforced fillers until now.

Although commercial silica is used popularly by far, but silica prepared from agricultural and industrial waste began to attract attention. One example is silica from rice husk, an agricultural waste. Rice husks may contain up to 20% amorphous silica which might be converted into crystal form - cristobalite by suitable thermal treatment [3]. Under controlled burning conditions, amorphous silica of high quality such as fine size, and large surface area, may be prepared [4]. By controlled combustion followed by the sol-gel technique, nanosilica from rice husks was prepared for gravity chromatography [5]. Also, silica from rice husk may be used to enhance the rigidity of

fibrocement [6], for dye absorption [7] or in the lithium-ion cell [8]. Another type of wasted silica is one prepared from the by-product of quartz stone grinding. This silica has high purity with SiO_2 content more than 90% and its size is suitable for plastic filling [9].

It should be mentioned that besides the reinforcing effect of plastic and rubber, the utilization of wasted silica has a positive effect on environmental protection. For example, the application of silica from rice husks will contribute to reducing the waste of rice husks that reaches 6-8 million tonnes per year in Vietnam [10].

In this article some factors influencing preparation and properties of injectional compounds based on PE blend and wasted silica from by-products of quartz stone grinding (silica TA) and rice husk (silica TT) will be studied and discussed.

2. Experiments

2.1. Materials

HDPE MK910 from SK Chemical, Korea, MFI 20g/10 min (190 $^{\circ}\text{C}$, 2.16kg)

LDPE 7050 from Aquate, Kuwait with MFI 2g/10min (190 $^{\circ}\text{C}$, 2.16kg)

Stearic acid SA1838 from Wilmar, Indonesia.

Table 1. Compound composition

Chemicals	HDPE	LDPE	SiO ₂	Acid stearic	Zinc stearate	Paraffin oil	PE wax	PE-g-MA
Content, % wt	58.16	14.54	20	1	1	2.25	2.25	0.8

Table 2. Temperature regimes for compound preparation

Temperature zones	1	2	3	4	5	6	7	8	9	10
Regime I, °C	150	160	170	175	180	180	175	170	165	160
Regime II, °C	160	170	180	185	190	190	185	180	175	170
Regime III, °C	170	180	190	195	200	200	195	190	185	180
Regime IV, °C	180	190	200	205	210	210	205	200	195	190

Zinc stearat AZT271 from Allbright, Malaysia.

PE wax 620F from Harvest Europe, China.

Paraffinoil 600N from Beekei, Korea.

All these chemicals are of technical grade

Wasted silica from the by-product of quartz stone grinding of Vitcostone company (Vietnam) with SiO₂ content 98%.

Wasted silica from rice husks: Vietnamese origin and purified in Center of Polymer Composite and Paper, HUST, with SiO₂ content not lower than 93%.

2.2. Compound Composition

The basic composition of the compound is presented in Table 1.

Compounds were prepared by twin screw extruder machine Leistritz (Germany) with the following temperature regimes in Table 2, with various screw speeds such as: 50, 100, 150, 200 rpm accordingly. The compounds were then pelletized into 3.5 - 4 mm pellets by a pelletizer machine.

2.3. Testing Methods

Melt flow index (MFI) was defined according to ASTM D1238 on Tinius Olsen MP933 (USA)

Tensile strength and elongation at break were conducted according to ASTM D638 on Instron 5582 - 100KN (USA) with a crosshead speed of 10 mm/min at 25 °C and RH 70%.

Bending strength was conducted according to ISO 178:1993 on Instron 5582 - 100KN (USA) with a crosshead speed of 10 mm/min at 25 °C and RH 70%.

The particle size distribution was carried out by laser scattering method using Laser scattering particle size distribution analyzer LA-960 Horiba (Japan)

Silica particle morphology was observed by Scanning electron microscopy (SEM) instrument Hitachi TM4000 Plus (Japan).

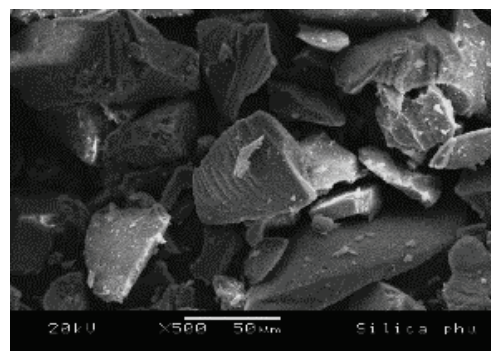
The melting temperature of the compound was carried out by differential scanning calorimetry method by DSC250 of TA Instrument (USA).

3. Results and Discussion

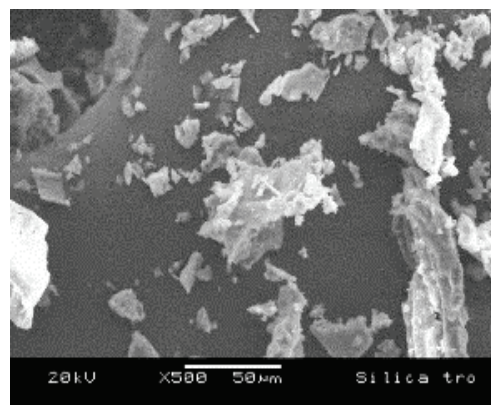
3.1. Characterization of Wasted Silica

Two types of wasted silica from byproducts of quartz stone grinding (silica TA) and from rice husk (silica TT) were characterized.

In Fig. 1, the particle morphology was presented through SEM images



a



b

Fig. 1. SEM images of wasted silica: a. Silica TA; b. Silica TT

One can see in Fig. 1 that the silica TT particles have a rather uniform shape, but easily gather to form aggregates. On the contrary, silica TA particles have a bigger size, mainly under 50 μm , but are less aggregated together.

Table 3 shows that after modification with TESPT, wasted silica particles have a size mainly under 30 μm , which is quite suitable for plastic filling. Moreover, the finesse of silica TA is higher than that of silica TT more than 90% of silica TA particles are of the size under 30 μm .

Table 3. Size distribution of silica particles before and after modification

a. Silica TA

Size range, μm	Cumulative content, %wt	
	Before modification	After modification
<10	23.98	44.50
<20	56.44	80.14
<30	74.18	92.21
>30	100.00	100.00

b. Silica TT

Size range, μm	Before modification	After modification
Overall	5-150	4-50
D>50%	10-50	8-30

3.2. Properties of the Compound Containing Wasted Silica

To evaluate waste silica as a possible filler for injectional compounds, some properties of compounds containing silica TA and silica TT were roughly examined. Table 4 presents the characteristics of the compound which was prepared with composition in Table 1.

From Table 4 one can see that compounds with both silica TA and silica TT have almost the same processing possibility and they are suitable for injection technique with MFI higher than 13 g/10min. Tensile and bending properties are also the same for compounds. However, the impact resistance of compounds containing silica TA is higher in comparison with silica TT. This may be due to the finer particle size of silica TA (Table 3).

Table 4. Properties of compound based on PE blends and wasted silica

Properties	Compound with silica TA	Compound with silica TT
Melt flow index, g/10min	13.93	13.75
Tensile strength, MPa	13.3	13.0
Elongation at break, %	27.5	28.0
Bending strength, MPa	11.0	10.8
Impact resistance, kJ/m ²	4.5	3.3

3.3. Factors Affect on Technological Properties

The technological possibility of plastics is evaluated through their melt flow index (MFI). Hence the factors affecting MFI will be studied for evaluation of the technological properties of the compound.

3.3.1. Effect of technological conditions

In technological conditions, the two most important factors are the temperature regime and screw speed of the twin-screw extruder machine.

a. Temperature regime

Compounds were prepared with various temperature regimes (Table 2) and screw speed of 100 rpm. The properties of the obtained compound are presented in Table 5. For comparison, some mechanical properties of compounds are also introduced.

As results from Table 5, temperature regimes I and II are not applicable for the preparation of injectional compounds. In regime I, the temperature is not high enough which leads to constable melting of plastic and repeated jam at the outlet from the machine.

Table 5. Properties of compounds obtained in various temperature regimes

Properties	Temperature regimes			
	I	II	III	IV
Pelletization	Difficult	Easy	Easy	Difficult
Tensile strength, MPa	11.7	13.0	13.6	12.4
Elongation at break, %	22.5	26.4	27.8	25.2

On the contrary, temperatures in regime IV are too high, which causes the decrease of melted plastic viscosity and makes the exit stream discontinuous. Hence, only temperature regimes II and III are applicable for the preparation of injectional compounds from PE. Note, that regime III is preferable because the obtained compound has better mechanical properties.

b. Screw speed

Screw speeds of 50, 100, 150, 200 rpm at temperature regime III were studied. Their effect on the MFI of compounds is illustrated in Fig. 2.

Fig. 2 shows, the higher the screw speed, the wider the MFI dispersion: at speed 50 rpm, the MFI values of 5 measurements were in range 12.5-15 g/10min. However, when the screw speed reaches 200 rpm, the MFI range is 11-18 g/10 min. This may be explained by that, at high screw speed, the

increasing internal pressure in the extruder chamber leads to silica and PE resin being pushed out quickly and do not have enough time to be mixed well. As a result, the obtained compound is not homogeneous enough and MFI values are varied at measurements.

3.3.2. Effect of processing aid additives

Processing aid additives used for the preparation of injectional compounds in this study are stearic acid, zinc stearate, paraffin oil and PE wax. From them, stearic acid and zinc stearate are used mainly for enhancement of filler dispersion, and paraffinic oil and PE wax - as lubricants.

In this study, the total content of stearic acid - zinc stearate is 2 %wt, and PE wax - paraffin oil is 4.5 %wt (Table 1) according to the receipt from Phale Plastic Joint Stock Company. Fig. 3, 4 and 5 show the effect of the stearic acid - zinc stearate ratio on compound properties.

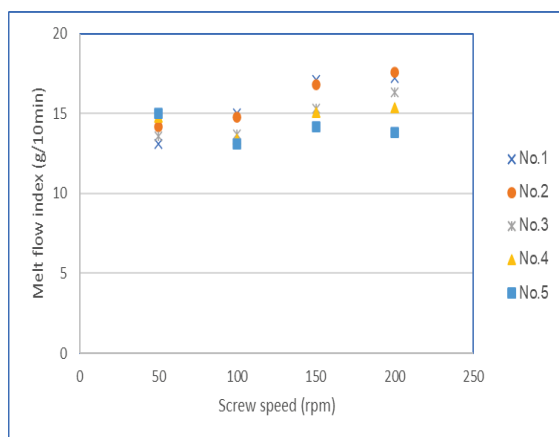


Fig. 2. The effect of screw speed on compound MFI

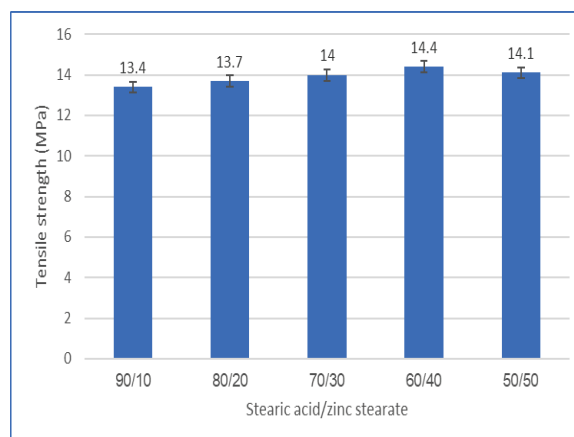


Fig. 4. Effect of stearic acid/zinc stearate ratio on compound tensile strength (PE wax - paraffinic oil content is 4.5 %wt)

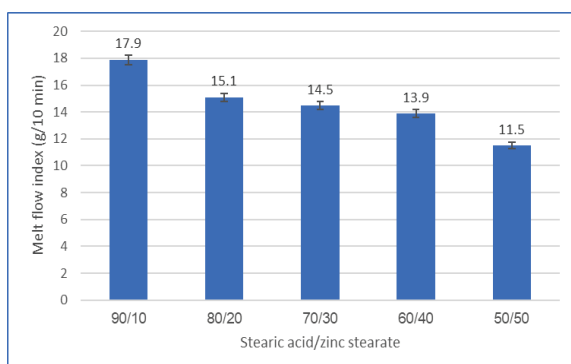


Fig. 3. Effect of stearic acid/zinc stearate ratio on compound MFI (PE wax - paraffinic oil content is 4.5 %wt)

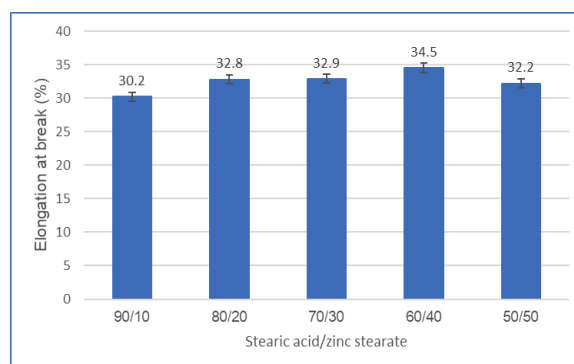


Fig. 5. Effect of stearic acid/zinc stearate ratio on compound tensile strength (PE wax - paraffinic oil content is 4.5 %wt)

Obviously, the processing ability of compounds expressed through MFI values increases with stearic acid content. On the contrary, mechanical properties improved with zinc stearate content. Therefore, the stearic acid/zinc stearate ratio should be chosen according to the requirement of the end product. Note, at a 50/50 ratio all considered properties showed a decreasing trend, especially (particularly) MFI value.

Fig. 6, 7 and 8 show the effect of the PE wax-paraffin oil ratio on the properties of the compound.

Unsimilar to the case of stearic acid/zinc stearate ratio, both MFI and mechanical properties of the compound increase with paraffinic oil content. However, in both cases, the change of additive ratio causes a remarkable change of MFI (max/min values ratio is about 1.5 times) but has almost no effect on tensile properties - the change of tensile strength and elongation at break is only about 15% in considered ratio range.

3.4. Mechanical Properties of Compounds

The mechanical properties of compounds depend remarkably on PE blend and compatibilizer used. Therefore the effect of these factors on mechanical properties was considered.

3.4.1. Effect of PE type

Blend of HDPE/LDPE with various ratios was studied, at their total content of 72.7 %wt in the compound. The results are presented in Fig. 9, 10, 11, 12 and 13.

From these figures, we can observe that the HDPE/LDPE ratio strongly affects both the processing and mechanical properties of the compound. The higher HDPE content the higher MFI values and mechanical properties. The exception is impact resistance: this property improves with LDPE content. This phenomenon is due to the property relation of two types of PE. HDPE has higher mechanical properties while lower viscosity, so compounds with higher HDPE content have higher both mechanical properties and MFI in comparison with ones that have higher LDPE content. Analogically, DSC patterns of the compound showed a rise in melting temperature with HDPE content (Fig. 14)

The rise of impact resistance with LDPE content is related to a higher branch degree of LDPE in comparison with HDPE: the higher the branching degree of molecules, the higher the material's ability to disperse impact energy that leads to improvement of impact resistance [12].

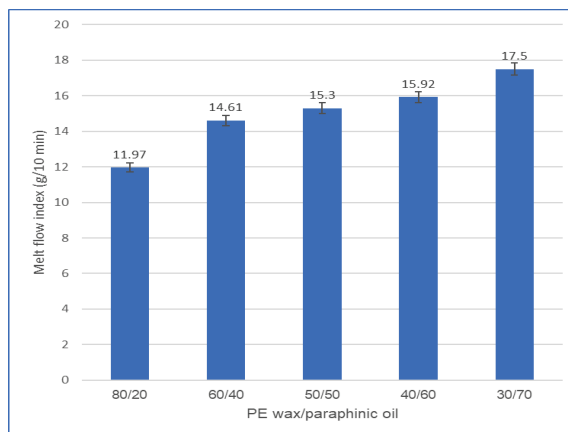


Fig. 6. Effect of PE wax/paraffinic oil ratio on compound MFI (Stearic acid/zinc stearate = 60/40 at total content 2 %wt)

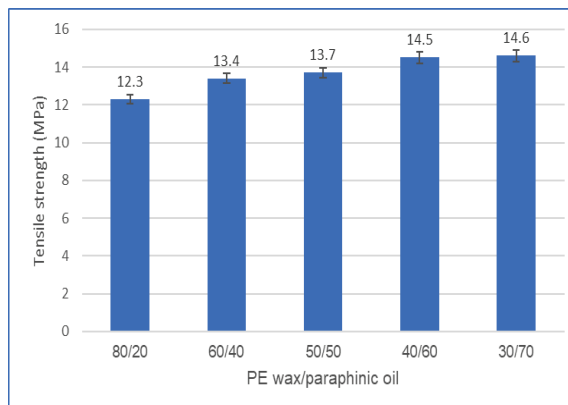


Fig. 7. Effect of PE wax/paraffinic oil ratio on compound tensile strength (Stearic acid/zinc stearate = 60/40 at total content 2 %wt)

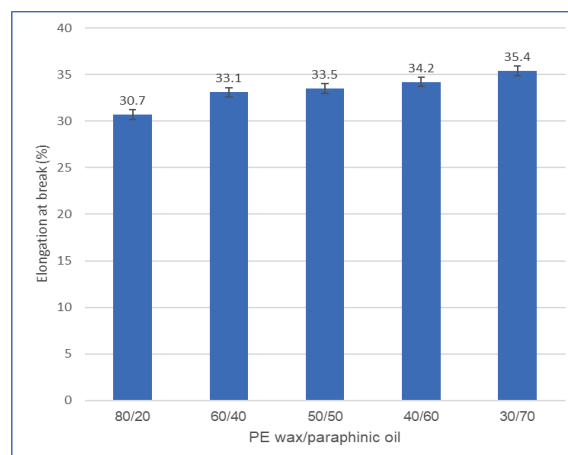


Fig. 8. Effect of PE wax/paraffinic oil ratio on compound tensile elongation (Stearic acid/zinc stearate = 60/40 at total content 2 %wt)

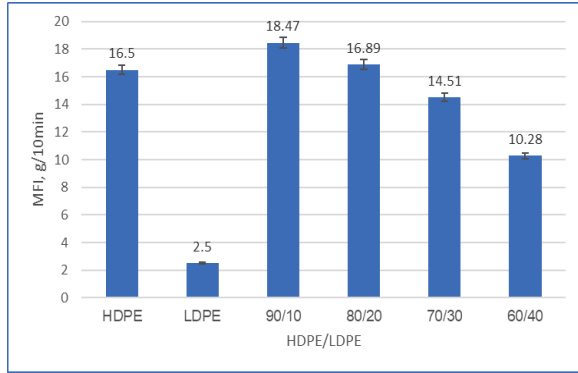


Fig. 9. Effect of HDPE/LDPE ratio on compound MFI

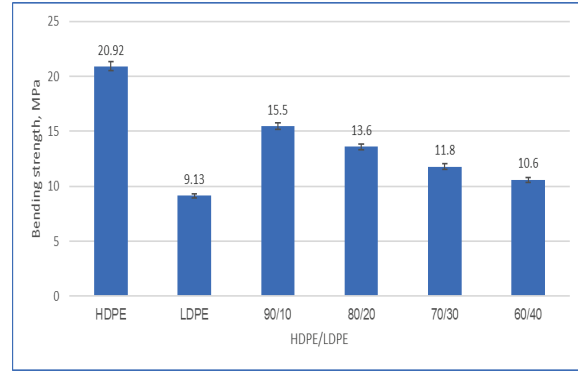


Fig. 12. Effect of HDPE/LDPE ratio on compound bending strength

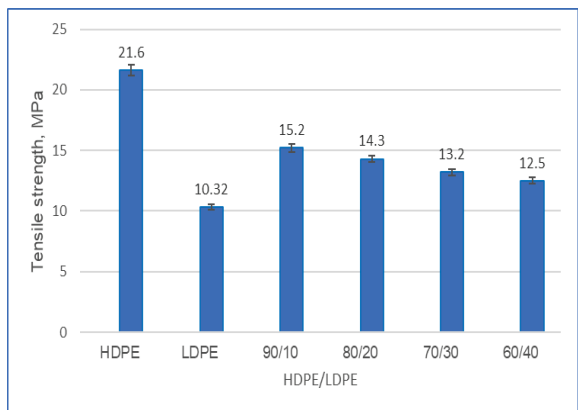


Fig. 10. Effect of HDPE/LDPE ratio on compound tensile strength

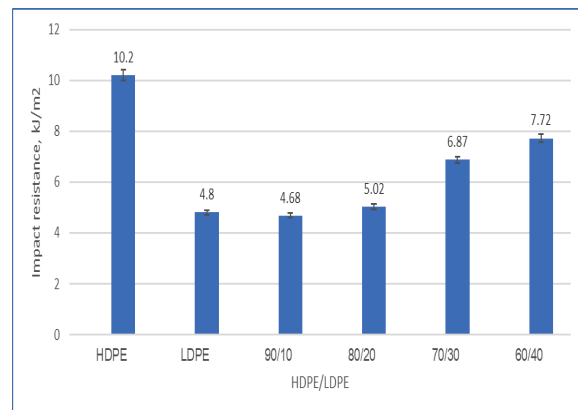


Fig. 13. Effect of HDPE/LDPE ratio on compound impact resistance

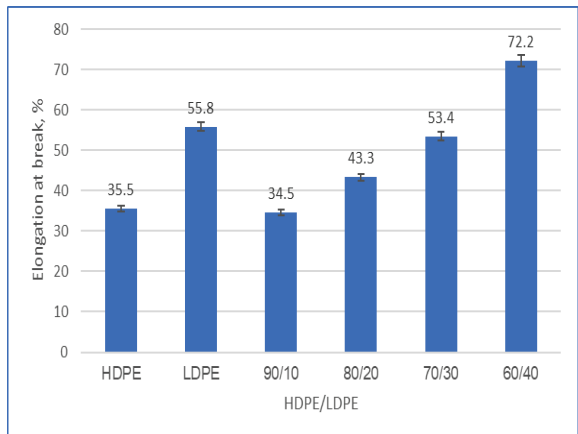


Fig. 11. Effect of HDPE/LDPE ratio on compound elongation at break

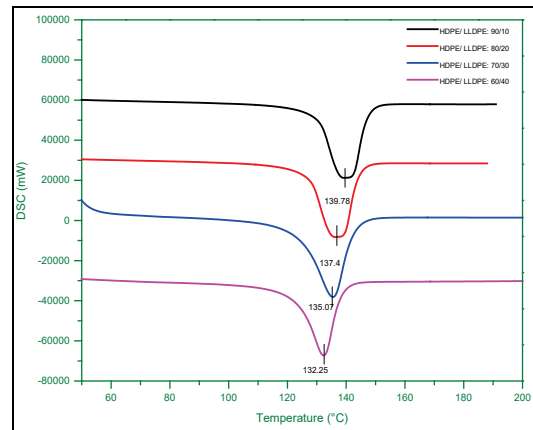


Fig. 14. DSC patterns of compound with various HDPE/LDPE ratio

3.4.2. Effect of compatibilizer PE-g-MA

Compatibilizer PE-g-MA may enhance interaction between HDPE and LDPE in the blend and between silica and PE as well. So the PE-g-MA content has a certain influence on compound properties (Fig. 15 - 18)

Results from Fig. 15 - 18 show PE-g-MA as compatibilizer has improved the mechanical properties

of compounds. However PE-g-MA seems to have softened material - the properties such as blending strength and elongation at break increase remarkably, while tensile strength and impact resistance undergo less change. Also, when PE-g-MA content is too high, 1.2-1.4% tensile properties have almost no change while bending and impact resistance suffer a slight decrease.

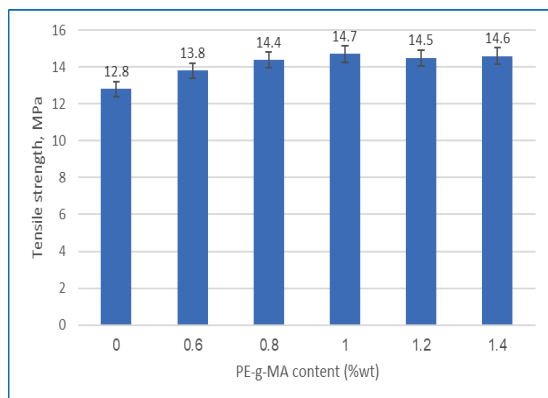


Fig. 15. Effect of PE-g-MA content on compound tensile strength

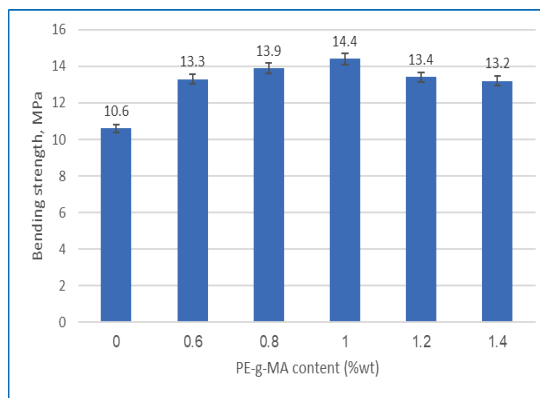


Fig. 17. Effect of PE-g-MA content on compound bending strength

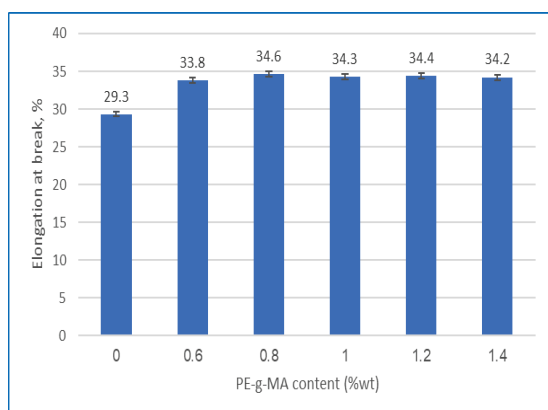


Fig. 16. Effect of PE-g-MA content on compound elongation at break

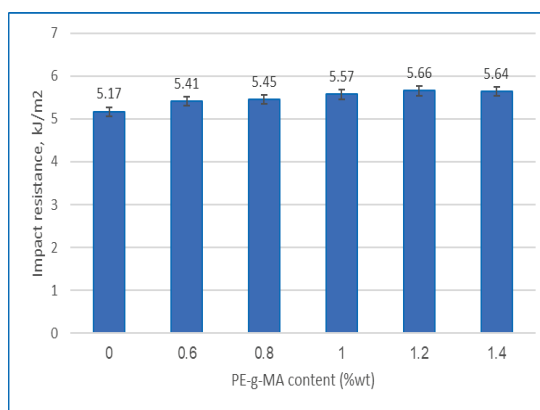


Fig. 18. Effect of PE-g-MA content on compound impact resistance

4. Conclusion

Wasted silica - silica TA and silica TT modified with TESPT were compounded with HDPE/LDPE blends. Compounds with silica loading of 20 %wt have MFI greater than 13 g/10min, quite suitable for injection technique.

By regulation of the processing aid additive ratio, the compound MFI may be adjusted correspondingly. However, the additive ratio has less influence on the mechanical properties of the compound.

HDPE/LDPE ratio has a strong effect on both the mechanical and technological properties of inflectional compounds. HDPE contributes tensile and bending properties, MFI, and melting temperature while LDPE improves the impact resistance of material.

Maximum processing temperatures of 190-200 °C and screw speed of 50-100 rpm are suitable for compound preparation. This processing condition provides good homogenization and steady compound properties.

Acknowledgments

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References

- [1] Strong A. Brent, *Plastics: Materials and Processing*, Pearson Prentice Hall, 2006.
- [2] J.A. Brydson, *Plastics Materials*, 7th ed., Butterworth-Heinemann, 1999.
- [3] John Murphy, *Additives for Plastics Handbook*, 2nd ed., Elsevier Science and Technology Books, 2001.
- [4] S.Chandrasekhar, K.G. Satyanarayana, P.N. Pramada, P. Raghavan, T.N.Gupta, Review processing, properties and application of reactive silica from rice husk - an overview, *J. of Materials Science*, 38, 3159-3168 (2003).
<https://doi.org/10.1023/A:1025157114800>
- [5] Devendra Shrestha, Tulsi Nayaju, M.R. Kandel, Raja Ram Pradhananga, Chan Hee Park, Cheol Sang Kim, Rice husk-derived mesoporous biogenic silica nanoparticles for gravity chromatography, *Heliyon*, V. 9, Iss. 4, April 2023, e15142,
<https://doi.org/10.1016/j.heliyon.2023.e15142>.
- [6] D.M. Gomez Mejia, D.F. Hincapie - Rojas, F.N. Jimenez - Garcia, César Augusto Alvarez Vargas, Effect of the addition of silica obtained from rice husk on physicochemical and mechanical properties of fiber cement, *Heliyon*, V. 9, Iss. 2, February 2023, e13567
<https://doi.org/10.1016/j.heliyon.2023.e13567>

- [7] Haider, J. B., Haque, M. I., Hoque, M., Hossen, M. M., Mottakin, M., Khaleque, M. A., ... & Zargar, M., Efficient extraction of silica from openly burned rice husk ash as adsorbent for dye removal, *Journal of Cleaner Production*, (2022) 380, 135121 <https://doi.org/10.1016/j.jclepro.2022.135121>.
- [8] Kydyr Askaruly, Alina V. Korobeinyk, Seitkhan Azat, Mukhtar Yeleuov, Azamat Taurbekov, Kainaubek Toshtay, Zhandos Tauanov, Xintai Su, The electrochemical behavior of silica and activated carbon materials derived from the rice husk waste for li-ion cells, *Diamond and Related Materials*, V. 133, March 2023, 109759, <https://doi.org/10.1016/j.diamond.2023.109759>
- [9] W. Zurowski, J. Zepchlo, A. Krzyzak, E. Gevorgyan, M. Rucki, Effect of the quartz on the performance of the two layers glass fiber reinforced polymer composite with emulsion binder, *Composite Structures*, V. 298, 2022. <https://doi.org/10.1016/j.compstruct.2022.116024>
- [10] Van Hai Le, Chi Nhan Ha Thuc, Huy Ha Thuc, Synthesis of silica rice husk by sol-gel method, *Nanoscale Research Letters*, V. 8, 2013.
- [11] Bui Chuong, Dang Viet Hung, Nguyen Thuong Giang, Using TESPT modified silica as a reinforcement filler for blend of NR/BR. Part 1. Preparation and characterization of TESPT modified silica, *Vietnam J. Chem.*, 2007, 45(5A), 67-71 (Vietnamese).
- [12] A.K. Van der Vegt, *From Polymers to Plastics*, DUP Blue Print, 2002.