

Polypropylene Copolymers and Blends for HVDC Cable Insulation: Initial Characterization and Pilot-scale Production

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Abstract- This paper introduces a preliminary characterization of polypropylene-based copolymers as well as a possible ternary blend as a candidate to be used for HVDC cable insulation in the framework of the European project NEWGEN (New GENERation of HVDC insulating materials, cables and systems). The effect of production process scale-up (from mini-scale to pilot-scale cast-processing) is also investigated for the promising PP ternary blend which is essentially composed of homophasic PP random copolymer (RACO), heterophasic PP copolymer (HECO), and propylene-based elastomer (PBE). The preliminary dielectric characterization introduces a promising RACO/HECO/PBE blend with a similar and comparable performance of mini-scale and up-scaled specimens. Mechanical characterization show that incorporating HECO and PBE in the ternary blend reduces the stiffness metrics of RACO towards suitable values for HVDC cable applications.

I. INTRODUCTION

The development of High Voltage Direct-current (HVDC) cable insulation is gaining more attention due to its effect on the reliability of the entire cable system [1]. Cross-linked Polyethylene (XLPE) has become the dominant extruded HVDC cable insulation because of its good electrical, mechanical, and thermal properties. However, many drawbacks of the XLPE, including the space charge accumulation, the limited thermal properties, and the complex and long production processes, have pushed towards developing new thermoplastic insulating materials that are able to withstand higher temperatures and electric fields. Polypropylene is considered a good candidate for future HVDC cables insulation because of its excellent electrical and thermal properties as well as recyclability [2]. However, thermomechanical properties of plain PP homopolymer are not suitable for extruded HVDC cables application. Thus, in the framework of the European project NEWGEN (NEW GENERation of HVDC insulating materials, cables, and systems) [3, 4], the authors have found in prior works [5,6] a promising PP ternary blend based on PP

random copolymer. This paper comes to further investigate the properties of the three components of the latter PP ternary blend, also highlighting the effect of the production process scale-up (from mini-scale to pilot-scale) on its electrical and mechanical characteristics.

II. MATERIAL CHARACTERIZATION AND COMPOUNDING

A. Material Characterization

In this paper, three base polymers and a ternary blend thereof are investigated: (i) a homophasic PP random copolymer (RACO) with ethylene content of <5 wt-%, (ii) a heterophasic PP copolymer (HECO) essentially comprising of PP homopolymer matrix with dispersed ethylene-propylene rubber (EPR) phase, and (iii) a propylene-based elastomer (PBE) with 16 wt-% ethylene content. An antioxidant (AO) comprising of a synergetic 1:1 blend of a hindered phenolic antioxidant (Irganox® 1010) and a phosphite processing antioxidant (Irgafos® 168) was added to the blends to prevent thermo-oxidative degradation.

TABLE I
PP BLENDS COMPOSITION

Material Code	Polymer component weight ratio			PP blend	
	RACO	HECO	PBE	Polymer [wt-%]	AO [wt-%]
RACO	1	-	-	99.7	0.3
HECO	-	1	-	99.7	0.3
PBE	-	-	1	99.7	0.3
RACO/HECO/PBE	0.55	0.2	0.25	99.7	0.3

B. Material Compounding

Mini-scale samples: the materials were melt-blended by using a mini-scale twin-screw extruder (temperature 230 °C, screw speed 100 rpm, 4 min mixing time) after which the molten compound was mini-injection moulded into 25×25×3 mm³ specimens. Finally, the mini-injection moulded specimens were hot-pressed to obtain flat specimens. For PEA, the thickness is

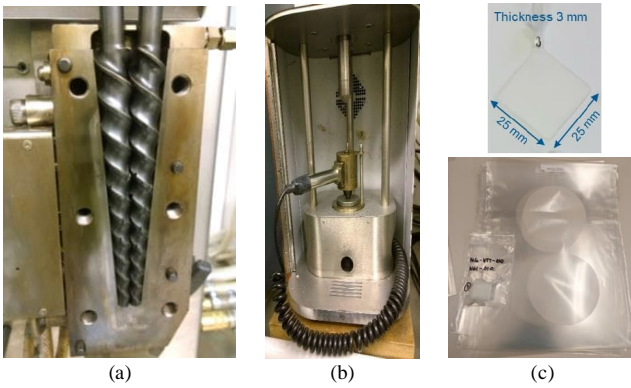


Fig. 1 Mini-scale compounding and manufacturing of flat specimens for characterization: (a) mini-scale twin-screw extruder, (b) injection moulding, (c) injection moulded specimen before hot-pressing (small specimens) and final hot-pressed flat specimens (large specimens).

approximately 0.25 mm, while it is approximately 0.1 mm for the other measurements, as shown in Fig. 1.

Pilot-scale samples: VTT Technical Research Centre of Finland built a new clean compounding environment that has been used in NEWGEN for pilot-scale processing of HVDC cable insulation materials, and later, for up-scaling the production of best performing insulation compounds to produce mini-cables and HVDC cable prototypes. The compounding equipment comprised of a Leistritz ZSE18 MAXX twin-screw extruder (48D) equipped with precision gravimetric feeders, a melt pump and a screen changer. The extruder nozzle, cooling and pelletizing sections were placed inside a mobile soft-wall clean room with ULPA air filtering (ISO 6 class clean room). All raw material handling (pre-treatment, weighing, dry mixing) was performed in the same room, inside a fume cupboard. Fig. 2 shows photographs of the clean compounding environment. For pilot-scale compounding and cast film extrusion, the twin screw extrusion line was equipped with a melt pump, a screen changer, a 120 mm wide flat film die and a tempered chill roll unit. Compounding and cast film extrusion was performed for the PP blend RACO/ HECO/PBE at 220–230 °C (throughput 2.5 kg/h, specific energy input ~0.20–0.22 kWh/kg, 84 Mesh filter, chill roll temperature 70–85 °C). Two different film thicknesses were produced, with the target thicknesses of 100 μm and 200 μm .

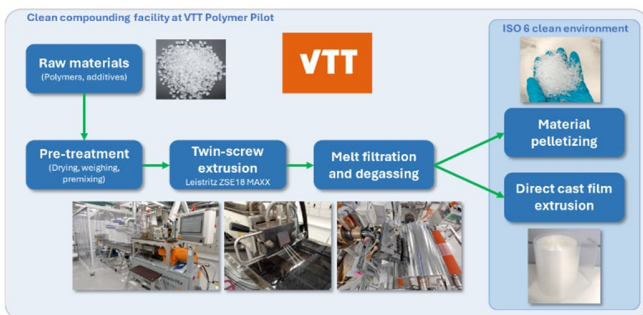


Fig. 2 Flow chart of the clean compounding facility at VTT Technical Research Centre of Finland.

III. MECHANICAL AND DIELECTRIC CHARACTERIZATION OF SPECIMENS

The initial dielectric characterization was carried out (as applicable) at a high temperature $T=90^{\circ}\text{C}$, and an average electric field of 30 kV/mm representing the maximum operation stress target of the future HVDC cables. The mechanical characterization aims at the verification of whether the tested materials satisfy the tensile, flexural and thermomechanical properties for HVDC cable applications according to CIGRÉ TB 852 [7].

A. Morphology and Mechanical Properties

Cross-sectional sample morphologies were imaged at VTT using JEOL JSM 6360-LV scanning electron microscope (SEM). The polymer samples were fractured in liquid nitrogen and sputter-coated with a thin layer of Au before imaging. Differential scanning calorimetry tests were made at VTT using a TA Instruments MDSC2920 (temperature range $-50\dots+230^{\circ}\text{C}$, dynamic heating rate of $10^{\circ}\text{C}/\text{min}$, constant Nitrogen gas purge of 33 ml/min, samples encapsulated in aluminum pans). Tensile and flexural testing of the PP compounds were made at VTT by Instron 4505 universal testing machine in accordance with ISO 527 and ISO 178 standards, respectively (the tensile and flexural data for the individual RACO, HECO and PBE polymer components were taken from the technical data sheets). Tensile tests were performed on dog-bone-shaped hot-pressed film specimens and injection moulded specimens. Flexural modulus was measured from injection moulded specimens.

B. Thermally Stimulated Depolarization Current TSDC

For thermally stimulated depolarization current (TSDC) and DC conductivity measurements, circular gold electrodes with diameter of 22 mm and thickness of 100 nm were deposited on both sides of samples using a custom-built e-beam evaporator (Instrumentti Mattila, pressure $<1\times 10^{-6}$ mbar, deposition rate of 0.18 nm/s) inside an ISO 6 class clean room facility at the Tampere University (TAU). The evaporated samples were short-circuited and stored in a vacuum oven at $+50^{\circ}\text{C}$ for at least 24 hours prior to electrical measurements.

TSDC was used to identify the charge relaxation processes as a function of temperature. For TSDC measurements, a DC source (Keithley 2290E-5) and an electrometer (Keithley 6517B) were utilized. A shielded sample cell equipped with a PT100 temperature sensor was used for all the measurements at TAU. Temperature control (accuracy of $\pm 0.1^{\circ}\text{C}$) was realized using the Novocool system.

The TSDC measurement procedure includes: (i) polarization at DC field $E_p=15$ kV/mm for 40 min under isothermal conditions at $T_p=90^{\circ}\text{C}$, (ii) rapid cooling to $T_0=-50^{\circ}\text{C}$; hold isothermally for 5 min, (iii) removal of the poling voltage and short-circuiting of the sample through the electrometer; hold isothermally for 3 min, (iv) linear heating at $\beta=3.0^{\circ}\text{C}/\text{min}$ up to $T_{max}=140^{\circ}\text{C}$ while recording the depolarization current.

C. DC Conductivity

The conduction current measurement system consisted of a high voltage DC source (Keithley 2290E-5 5kV), a 100 k Ω

current limiting resistor in series with the sample (in case of breakdown), a shielded sample cell equipped with a PT100 temperature sensor (Novocontrol BDS1200 HV sample cell) and an electrometer (Keithley 6517B). The measurements were performed at temperatures of 70 °C and 90 °C under electric field of 35 kV/mm at TAU. The polarization phase was 24 h and the depolarization phase was 6 h.

D. Space Charge

Space charge measurement aims at finding the charge carriers behavior, dynamics, and stability inside the PP blend flat specimens. The PEA method measures space charge density distribution inside the thickness of the specimen over time. Three hours of polarization (volt-on) and one hour of depolarization (volt-off) periods are chosen as a compromise between time restriction of each measurement and the time enough to obtain a quasi-stable space charge pattern. Specimens with 0.25 mm thickness are tested at 25°C (dissimilar to the initial characterization plan to be carried out at 70°C) because HECO and PBE specimens showed a significant mechanical deformation between the PEA cell electrodes at high temperature. Then, the raw acquired data is post-processed to obtain the deconvoluted pattern.

E. DC Breakdown Strength

Breakdown strength measurement of insulating materials can be used to determine its applicability in HV power cable insulation [8]. The flat sample is placed between two electrodes (diameter of 25 mm, edge rounding of 3 mm) immersed in mineral oil (Shell Diala S4 ZX-1) in a setup designed according to IEC60243 [9]. The test cell is kept at room temperature ($T \approx 20$ °C) during the test. The applied ramp voltage has two slopes; during the first slope, the ramp rate is 1 kV/s until approximately 70% of the expected breakdown voltage, while during the second slope the ramp rate becomes 0.25 kV/s until the breakdown. Five to ten samples of each material were tested at TAU. After the breakdown, the thickness of a sample is measured near the breakdown hole. Then, the results are subjected to statistical processing and fit to two-parameter Weibull distribution.

IV. RESULTS AND DISCUSSION

A. Morphology and Mechanical Properties

Fig. 3 presents SEM cross-sectional morphology of plain RACO, HECO and PBE, along with the RACO/HECO/PBE ternary blends processed in mini- and pilot-scale. Plain RACO exhibits a fine granular morphology whereas HECO shows a coarser morphology with a more distinct elastomer phase being visible, see Fig. 3 (a-b). PBE morphology, Fig. 3 (c), is largely featureless due to its structural disorder. For the ternary blends, Fig. 3 (d-e), relatively smooth blend morphologies are observed with some distinctive isolated elastomer domains (EPR) being visible especially in mini-scale sample (Fig. 3d). However, for the pilot-scale extruded cast film (see Fig. 3e), the interphase between elastomer- and PP-rich domains is dissimilar to the mini-scale morphology. This aspect is related to differences in processing such as mixing efficiency and screw profile in mini- vs. pilot-scale twin-screw extrusion (i.e. the degree of

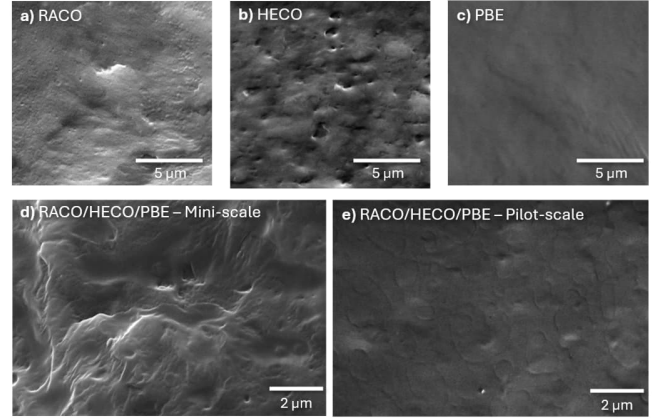


Fig. 3 SEM cross-sectional morphology of a) RACO, b) HECO, c) PBE, and RACO/HECO/PBE ternary blends in d) mini-scale (hot-pressed film) and e) pilot-scale (extruded cast film).

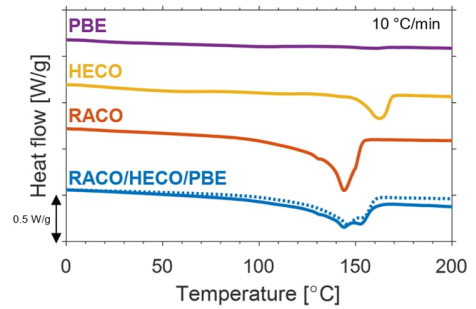


Fig. 4 DSC second heating endotherms of the PP copolymers and blend. Solid lines: Mini-scale, Dotted line: Pilot-scale.

dispersive and distributive mixing); further optimization of the processing and morphology is currently under investigation.

DSC melting endotherms of the PP components and a RACO/HECO/PBE blend are presented in Fig. 4, and the calculated crystalline melting peak temperatures (T_m) and melting enthalpies (ΔH_f) are enlisted in Table 2. RACO, being a random propylene-ethylene copolymer, shows a lower melting point (~ 144 °C) in comparison to HECO for which the higher melting point (~ 162 °C) is associated with the PP homopolymer phase. However, the melting enthalpy (*c.f.* degree of crystallinity) of RACO is found to be higher than that of HECO (see Table 2). On the other hand, PBE exhibits only minor crystalline melting due to its structural irregularity arising from the high ethylene content. For the RACO/HECO/PBE blend, the main crystalline melting peak occurs at 144 °C and the melting enthalpy is found to be an intermediate between the constituent PP components.

Tensile and flexural properties of the materials, including tensile modulus (E_{tens}), stress at break (σ_{break}), elongation at break (ϵ_{break}) and flexural modulus (E_{flex}), are presented in Table 2. The tensile properties of the RACO/HECO/PBE blends are in-line with the expected values presented in CIGRE TB 852 for HVDC cable insulation (minimum tensile stress and elongation at break of 8.5 MPa and 350%, respectively). Moreover, The RACO/HECO/PBE blends exhibit flexural moduli in the range of ~ 280 – 300 MPa which is suitable for HVDC cables (target 300 ± 100 MPa). In contrast, plain RACO is seen to be too stiff while HECO and PBE or too soft.

TABLE II
SUMMARY OF TENSILE, FLEXURAL, AND DSC RESULTS

Material Code	Scale	Tensile			Flexural	DSC	
		E_{tens} [MPa]	σ_{break} [MPa]	ϵ_{break} [%]	E_{flex} [MPa]	T_m [°C]	ΔH_f [J/g]
RACO	Mini	N/A	28	600	850	144.1	63.1
HECO	Mini	N/A	12	500	85	162.4	21.6
PBE	Mini	N/A	7.6	800	14	99.4/ 160.2	9.15
RACO/HECO/PBE	Mini	369	18.8	575	304	144.0	43.3
	Pilot	330	19.3	1099	281	145.9	46.6

B. Space Charge

Fig. 5 shows the space charge evolution inside the specimens during the polarization and depolarization periods. RACO, in Fig. 5(a) accumulates a low amount of positive charges in the bulk and negative charges near the cathode up to $\approx \pm 1$ (C/m³). While HECO and PBE show in Fig. 5(b-c) a significant amount of homocharges (greater than ± 5 C/m³) with the dominance of positive charges in the bulk. Similarly to RACO, the PP blend (RACO 55%, HECO 20%, PBE 25%), in Fig. 5(d), tends to have low charge accumulation in the entire thickness of the specimen with a clear dominance of the positive charges up to $\approx 1-2$ (C/m³).

C. Thermally Stimulated Depolarization Current TSDC

Charge relaxation properties (i.e. thermally stimulated detrapping) of the studied materials are shown in Fig. 6 where TSDC spectra are presented. In principle, the TSDC peaks at higher temperatures are associated with detrapping of space charge accumulated during the polarization stage while the lower temperature peaks (below 0 °C in Fig. 6) can be mainly associated with molecular relaxations of the PP blends (i.e. glass transition).

In the whole temperature range considered, RACO has very low TSDC current while HECO has high TSDC peaks at +60 °C and +95 °C indicating high trap density. PBE has a broad

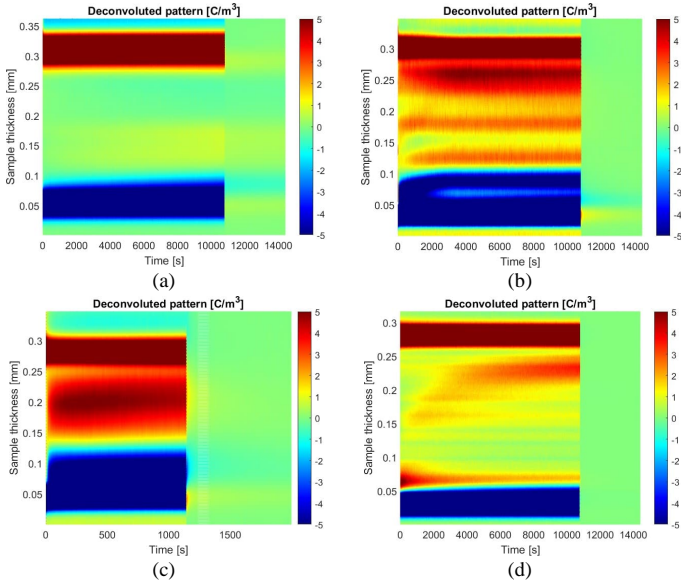


Fig. 5 Space charge (color bar in C/m³) evolution inside the specimen (y-axis) over time (x-axis) at electric field $E=30$ kV/mm and temperature of 25 °C, for: a) RACO, b) HECO, c) PBE, d) RACO/HECO/PBE – mini-scale.

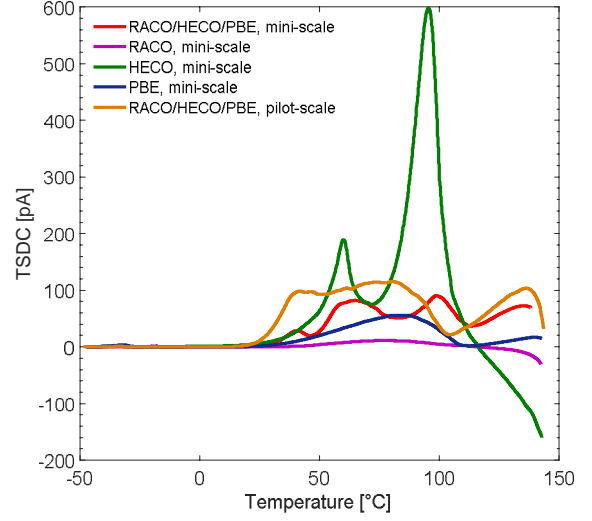


Fig. 6 TSDC current in (pA) with polarization at $E=15$ kV/mm and $T=90$ °C for all the studied materials.

peak in the range of +30 ...+85 °C and a lower peak at +135 °C. For the mini-scale ternary RACO/HECO/PBE blend, TSDC peaks can be seen at similar temperatures as for the constituent PP materials. Interestingly, the corresponding pilot-scale blend film exhibits relatively similar TSDC features with the mini-scale film, with however some differences being observable for the peak locations. These differences can be associated with e.g. morphological differences between the mini- and pilot-scale compounds.

D. DC Conductivity

DC polarization/conduction current measurements were performed for the mini- and pilot-scale ternary blends at 70 °C and 90 °C. The results are shown in Fig. 7 where the conductivities at the end of the polarization period are at similar levels for both mini- and pilot-scale specimens. At 70 °C, the conductivity at the end of the polarization period is 3.8×10^{-15}

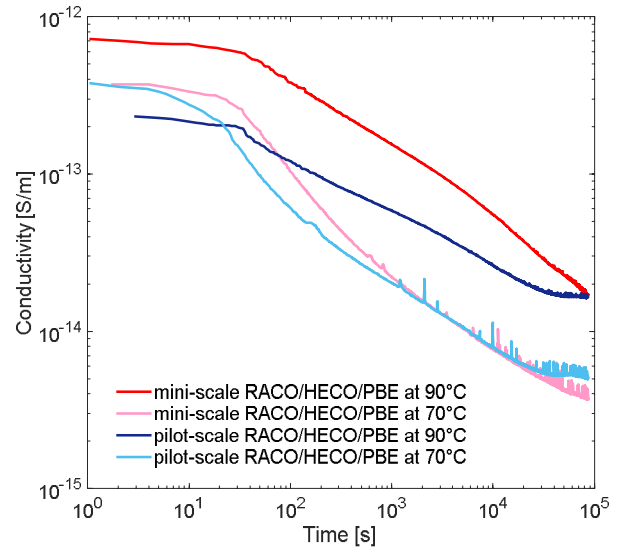


Fig. 7 DC conductivity of the mini- and pilot-scale ternary blends at 70 °C and 90 °C under electric field of 35 kV/mm during 24-hour polarization period.

S/m for the mini-scale blend and 5.0×10^{-15} S/m for the pilot-scale film. At 90 °C, the values are 1.7×10^{-14} S/m for the mini-scale and 1.6×10^{-14} S/m for the pilot-scale.

E. Breakdown Strength

Short-term breakdown strength results of each material and the blends (mini- and pilot-scale) are presented in Table 3. The results of RACO, HECO and PBE are based on five parallel samples while the results of the RACO/HECO/PBE blends are based on 8 to 10 results. In accordance with the results of the blends, the up-scaling process seems to be successful since the BDS values are very similar. However, there is quite high inhomogeneity in the results of the blends (quite low Weibull β). This can be associated with the differences between hot-pressed and extruded cast film morphologies and should be optimized further.

TABLE III
BREAKDOWN STRENGTH OF THE STUDIED MATERIALS.

Material Code	Scale	$E_{50\%}$ [kV/mm]	$E_{63.2\%}$ [kV/mm]	β
RACO	Mini	498	529	7.0
HECO	Mini	218	237	4.8
PBE	Mini	143	154	6.0
RACO/HECO/PBE	Mini	444	469	8.1
	Pilot	518	554	6.5

V. DISCUSSION

Both mechanical and electrical characterization show consistent results of incorporating HECO and PBE with RACO in the introduced ternary blend. DSC, PEA, and TSDC show the minor space charge accumulation in RACO due to its high degree of crystallinity. On the other hand, the incorporation of PBE in the blend reduces the degree of crystallinity and increases the amorphous phase, leading to more space charge accumulation and charge traps (see Fig. 5 and Fig. 6). On the other hand, adding PBE and HECO significantly reduces the stiffness tensile and bending metrics, essentially flexural modulus, from 850 (MPa) in RACO to 300 (MPa) in the ternary blend. The above-mentioned mechanical and dielectric characteristics in both mini-scale and pilot-scale blends represent a significant milestone towards a future move to full-scale production.

VI. CONCLUSION

In this paper, the authors present a preliminary characterization of polypropylene-based copolymers as well as a promising ternary blend for HVDC cable insulation. The ternary blend is up-scaled from mini-scale hot pressed samples to pilot-scale cast-film extrusion. Pilot-scale specimens tend to have similar DC conductivity, higher breakdown strength, and comparable TSDC peaks, compared to mini-scale specimens. The promising ternary blend RACO/HECO/PBE is introduced as a compromise between the excellent dielectric properties of RACO and the elastic mechanical properties of HECO and PBE.

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