Rheological Properties of Polyvinyl Chloride - Thermoplastic Polyurethane Blends

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The qualitative and quantitative information concerning the dependence between the kinematic viscosity and the activation energy of the viscous flow by the polyvinyl chloride – thermoplastic polyurethane blends composition were obtained. The results reveal that the blend composition and the melt temperature are the most important parameters that control the PVC – TPU blends melt processing. A high injection speed increases both the tensile strength and the breaking elongation. The shorter time for the mould loading increases the tensile strength and decreases the breaking elongation. The measurement of the rheological properties based on the MFI methods is a good instrument for the estimation of the rheological properties of the polymeric blends in practical conditions

Keywords: polyvinyl chloride -thermoplastic polyurethane blends, rheological properties, kinematic viscosity, melt viscous flow, activation energy of the viscous flow

Despite of the ecologists critics related to the safety, and the agresivity upon the environment, the polyvinyl chloride (PVC) is still successfully used, as a consequence of the huge profitability, in constructions, electrotechnics, cable and footwear industry, i.e., in applications with medium and / or long life, such as: pipes, windows, automotive parts, electric cable, footwear, etc.

Not all the PVC properties fulfill the requirements of the abovementioned application. The properties as density, flexibility, abrasion, crack resistance, fatigue behaviour, sliding index on certain surfaces, the value of the melt processing temperature, the service life in dynamic conditions, make from the PVC physical modification an important method for improving and diversifying the PVC properties and its usage as compounds [1] .

The PVC – thermoplastic polyurethane (TPU) compounds can be compared with plastified PVC, with the difference that these blends have improved mechanical properties and a significant extraction and migration resistance that means better mechanical resistances, in the dynamic conditions, over long periods (table 1) [2].

Bearing in mind the known polymeric blends with practical importance (fig.1 [3]), the PVC – TPU compounds can be obtained by following methods [2, 4]: physical modification, grafting the PVC with polyurethane and performing the inter-penetrating networkings.

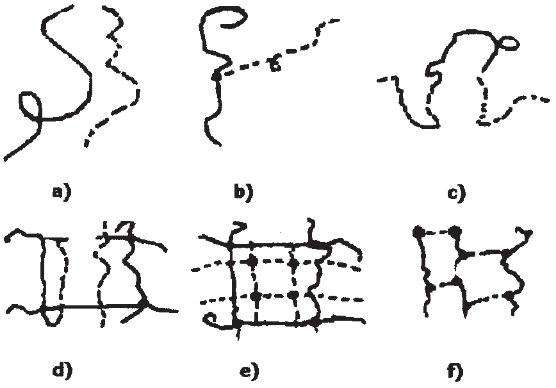

Fig.1 Schematic diagram of the possible 2 polymers combinations: a-polymeric blend; b-grafted copolymer; c- block copolymer; d- semi interpenetrating networking; e- interpenetrating networking; f- cross-linked copolymers (solide line : polymer I; dotted line : polymer II)

Due to the possibilities of the industrial level manufacture control, for performing the PVC – TPU blends, the physical modification method was preferred .

The studies of polymeric materials melt processing into finished product, needs the knowing of the relationship between the process variables and the melt flow properties. The estimation of the rheology into solid state

Table 1
PROPERTIES OF PVC -TPU BLENDS OBTAINED BASED ON PHYSICAL MODIFICATION METHOD SET BESIDES OF PLASTIFIED PVC [2]

No.crt	Property	Plastified PVC	PVC – TPU blends
1	Tensile strength, psi (kg/cm^2)	1100 (77)	3400 (239)
2	Breaking elongation, %	330	450
3	Hardness, ^{0} Sh	61	63
4	Extraction in mineral oil, % gr. (50 ^{0}C)	24	9.5

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based on the mechanical properties are also significant for a good designing of a polymeric material for a chosen application. The understanding of the polymeric materials viscoelastic behaviour makes possible the optimization of the relationship between the material characteristics and the finished product properties, the designing of the processing equipment and subsequently the selection of the optimum melt processing conditions.

The PVC - TPU compounds were performed for an application which regards PVC base materials, with extraction resistance, low density and good mechanical properties in dynamic state, at negative temperatures [5]. Considering the melt and solid state of the PVC – TPU blends with the aim of getting qualitative and quantitative informations about the melt processing and for the selection of the best injection molding conditions that ensure desired mechanical properties, a rheological study was performed.

A study of the melt rheological properties of the PVC – TPU blends and the influence of the injection conditions on some mechanical properties of the blends will be presented.

Experimental part

The PVC - TPU blends with : (100 – 0) parts PVC and (0 – 100) parts TPU were studied. After compounding within a Brabender plastograph, each blend was rolled on into sheets in classical working conditions. The physico-mechanic characterization was made using samples stamped from plates pressed sheets. The known possibilities for studing the polymeric melt rheology are presented in figure 2 [6-14]. However, each techniques has its limitations and advantages and the selection of the appropriate method to be used is depending on many factors, not only on the intended applications of the obtained data.

Because it can be easyly applied in industrial conditions, the melt flowing rheological study was performed by the melt flow index (MFI) method [15 - 17].

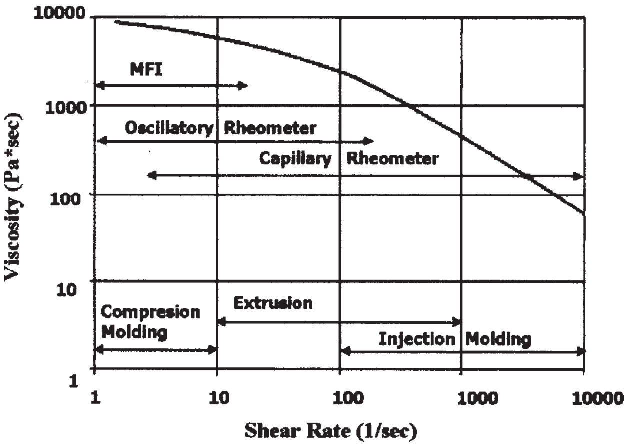


Fig.2 Known possibilities for studing the polymeric melt rheology

The variation of the melt kinematic viscosity and of the activation energy of the viscous flow, with the blend composition and the MFI measurement conditions, was determined. Based on these two melt rheological properties it can be estimatimated, the blend behaviour at the melt processing into finished product, in practical conditions. The melt kinematic viscosity and the activation energy of the viscous flow were calculated based on the formulae 1 and 2 [15,16].

The MFI was determined at different temperatures (185, 195, 205^{0}C) and plastometer loadings (2.18; 3.80 and 5.00 Kg). From it the activation energy of the viscous flow – E_a and the kinematic viscosity - υ were calculated.

$$E_a = R\,(T_i/T_j)/(T_j - T_i)\ln(MFI_{Ti,G})/(MFI_{Tj,G})\ \text{[kJ/mol]} \quad (1)$$

$$\upsilon = 5 \text{ x } 10^4 \text{ x}(G_{i,j}/MFI_{Tj,G}) \quad \text{[stokes]} \quad (2)$$

where:

$G_{i,j}$ represents the plastometer loading (kg);

T_{i-j} are the operating plastometer temperatures (^{0}K), $MFI_{Ti,G}$ and $MFI_{Tj,G}$ represent the MFI at $T_{i,G}$ respectively at $T_{j,G}$,

R is the gas constant (kJ/mol·K).

The study of the injection molding was made on an Engel injection device, by scanning the entire range of following melt processing parameters: temperature, speed, injection, loading and cooling time, mould temperature. (table 2). The temperature is measured in 3 points nozzle, area 2 and area 3.

Results and discussions

The melt rheology properties

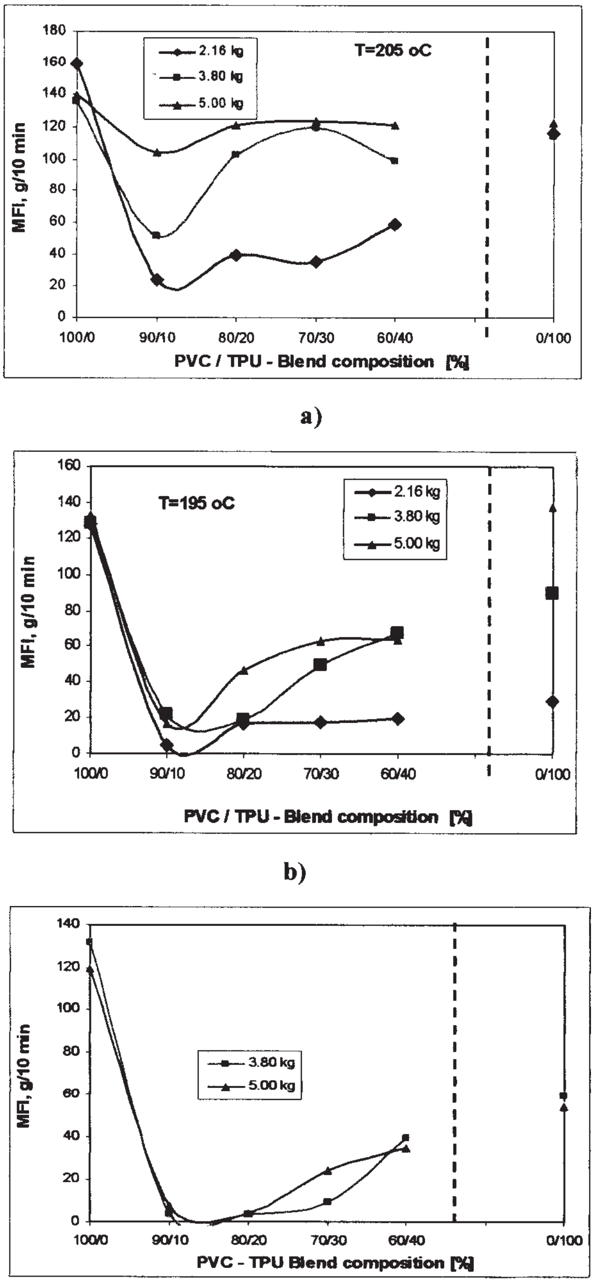
The MFI changes very much depending on the blend composition and of the measurement temperature (fig.3). The highest variations were recorded for the 80 – 90 parts PVC / 20 – 10 parts TPU blends compositions (fig.3 a, b, c). These variations are less obvious for the high temperatures (205^{0}C - fig.2 a) and more visible for the low temperatures (185^{0}C - fig. 3b, c). A high MFI value is the equivalent of an increased melt fluidity and a low MFI is the reverse [7]. This could mean that the fluidity of the blends with these compositions, at the 185 ^{0}C, is too small for a good melt flow. This is the reason for which these blends need, for a good melt flow, a higher activation energy.

Another parameter which controls the MFI values is the plastometer loading. Bigger the used weight for the plastometer loading, higher the MFI values. These results mean that if the PVC – TPU blends are melt processed in the equipment which ensures higher shear forces, then the developed specific melt fluidity is higher.

If the temperature is 205 ^{0}C and the plastometer loading is 3. 80 kg or 5.00 kg, then the MFI values almost do not depend on the blend TPU quantity (fig.3a). Practically, at 205 ^{0}C, for a high plastometer loading (mosly 5.00 kg), all

Table 2
STUDIED INJECTION CONDITIONS

Injection parameters\ Sample code		A	B	C	D	E
Temperature, ^{0}C	**Nozzle**	168	172	168	168	168
	Area 2	160	164	160	160	160
	Area 3	155	159	155	155	155
Time, s	**Injection**	20	5	5	5	5
	Loading	5	10	10	10	5
	Cooling	10	10	10	10	10
Injection speed, m / s		1	1	5	10	5
Pressure: N/m^2		140	140	140	140	140
Mold temperature, °C		68	68	68	68	25



a)

b)

c)

Fig.3. MFI variation of PVC / TPU blends with the composition and the MFI measurement conditions.
a) T = 205 °C, M = 2.16 kg, 3.80 kg, 5.00 kg;
b) T = 195 °C, M = 2.16 kg, 3.80 kg, 5.00 kg;
c) T = 185 °C, M = 2.16 kg, 3.80 kg, 5.00 kg;

the studied mixtures have the highest fluidity. At 195 °C, the bigger the plastometer loading, the higher is MFI, especially if the blends contain more TPU. It can be noticed that at 195°C the blends fluidity increases less, if the loading is 2.16 kg and much more, if this is 3.80 or 5.00 kg (fig.2b). At 185 °C, the MFI value does not depend on the plastometer's loading (fig.3 c). It was noticed that at T = 185 °C and 2.16 kg, MFI could not be determined either for PVC, or for all the studied blends. At this temperature there are big differences, between the PVC MFI (that is higher than 100 g/10 min.) and those of the PVC – TPU blends (placed within the 3 – 40 g/10 min range).

The dependence of the kinematic viscosities by the blend compositions are presented in figure 4. The kinematic viscosity of the PVC / TPU blends depends on their composition and on the measurement temperature and less on the plastometer 's loading. At 205 °C, the kinematic viscosity of the blend with low TPU content (30 – 10 parts of TPU at 70 – 90 parts of PVC) is almost twice higher than that of the blends with higher TPU content (40 – 50 parts of TPU at 60 – 50 parts of PVC) (fig.4a). If in the first case the kinematic viscosity is 45000 – 50000 stokes, in the second situation the kinematic viscosity is 10000 – 30000 stokes.

The difference between the kinematic viscosity of compounds with low TPU content, and those with high TPU percentage increased if the processing temperature, has average (195 ° C fig.4b) or reduced values (185°C - fig.4c).

At 195 °C, the kinematic viscosity of the blends with the low TPU content is 3 times higher than that of the blends with higher TPU content (150000 stokes related to 50000 stokes). At 185°C, the kinematic viscosity of the compounds with low TPU content is almost 5 times higher than that of the blends with a high TPU content (350000 – 550000 stokes for the blends with low TPU content and 80000 – 100000 stokes for the blend with high TPU percentage).

Based on the above-mentioned results, it can be stated that, along the blend composition, the melt temperature has a great influence upon the kinematic viscosity of the PVC – TPU compounds. At a variation with only 10 °C of the melt processing temperature, the kinematic viscosity of the PVC – TPU blends with low TPU content is very much changed. The kinematic viscosity of these blends increases from simple to triple, at a temperature decrese from 205 °C to 195 °C and 10 times, if the temperature decreases from 205°C to 185 °C. This great increasing of the kinematic viscosity at a temperature decrease with 20 °C, can make impossible, the melt processing of the low TPU content compounds.

The situation is almost the same for the blends with high TPU content. At 195 °C, the kinematic viscosity of the blends increases 2 – 4 times as compared with the values recorded at 205 °C. If the temperature decreases at 185 °C, then the kinematic viscosity of the blends with high TPU content is upto 8 times higher than the values recorded at 205 °C.

The blends with low MFI have very high melt viscosity, especially at low temperatures. Depending on the temperature value, the kinematic viscosity of the PVC – TPU blends can be very high, until such values that make impossible the melt processing into finished product.

The dependence of the activation energy of the viscous flow, upon the blend composition and the MFI measurement conditions is presented in the figure 5. The analysis of these dependences leads to the interesting conclusions.

First of all, it can be noticed that the activation energy of the viscous flow has higher values for the blends with less TPU percentage (fig.5).

It was also noticed the increase of the activation energy of the viscous flow at the temperature decrease. If at 205 °C the necessary energy for the melt flow of the low TPU content blends is within the range of 100000 – 250000 kJ / mol·K, for lower temperatures (185 – 195°C), this necessary increases at 150000 – 350000 kJ/mol·K. (fig.5-a,b,c).

The necessary flow energy for the melt of the higher TPU content blends is smaller than that needed for blends with less TPU ratio. This energy is by 50000 – 150000 kJ/ mol·K at 205 °C, 50000 -200000 kJ/ mol·K at 195 °C and, about 100000 – 300000 kJ/ mol·K at 185 °C (fig.5).

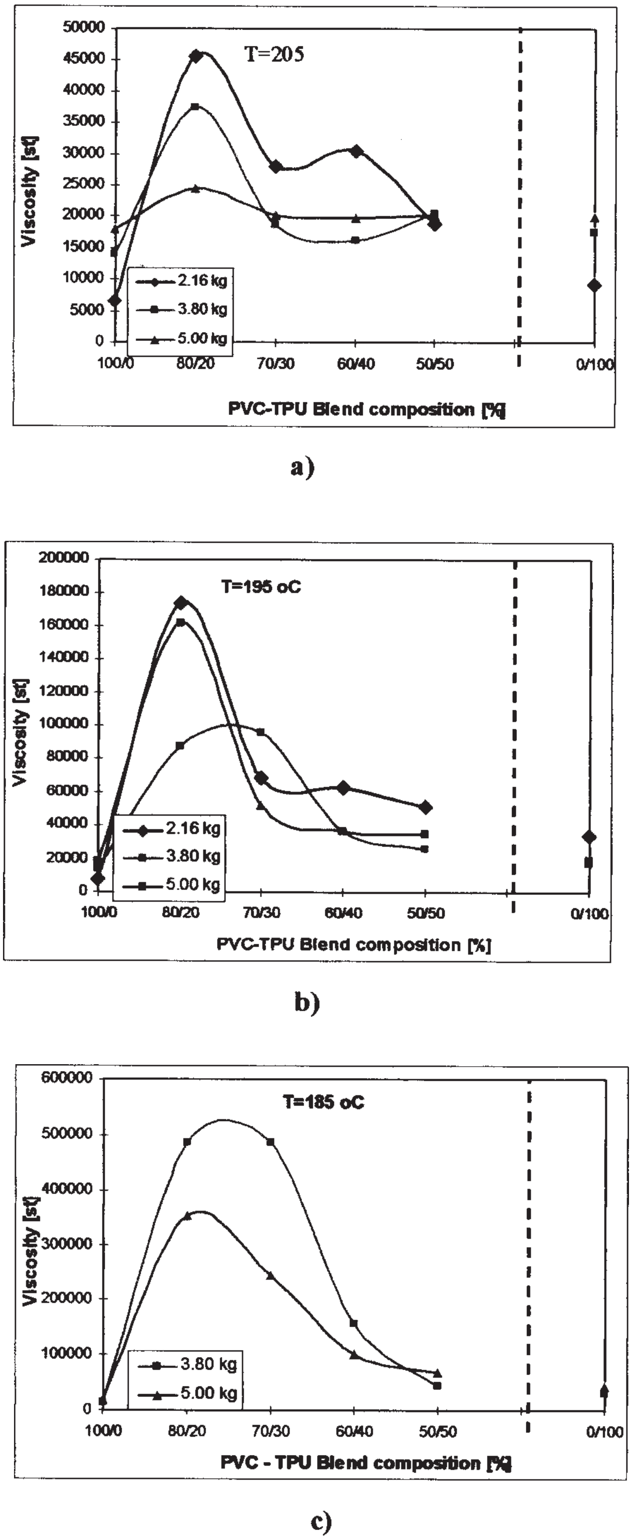


Fig.4 Dependence of kinematic viscosity of the PVC / TPU blends, on the composition, the temperature and the plastometer’s loading: a) T = 205 ^{0}C at 2.16; 3.80 and 5.00 kg; b) T = 195^{0}C at 2.16 ; 3.80 and 5.00 kg ; c) T = 185^{0}C at 2.16 ; 3.80 and 5.00 kg;

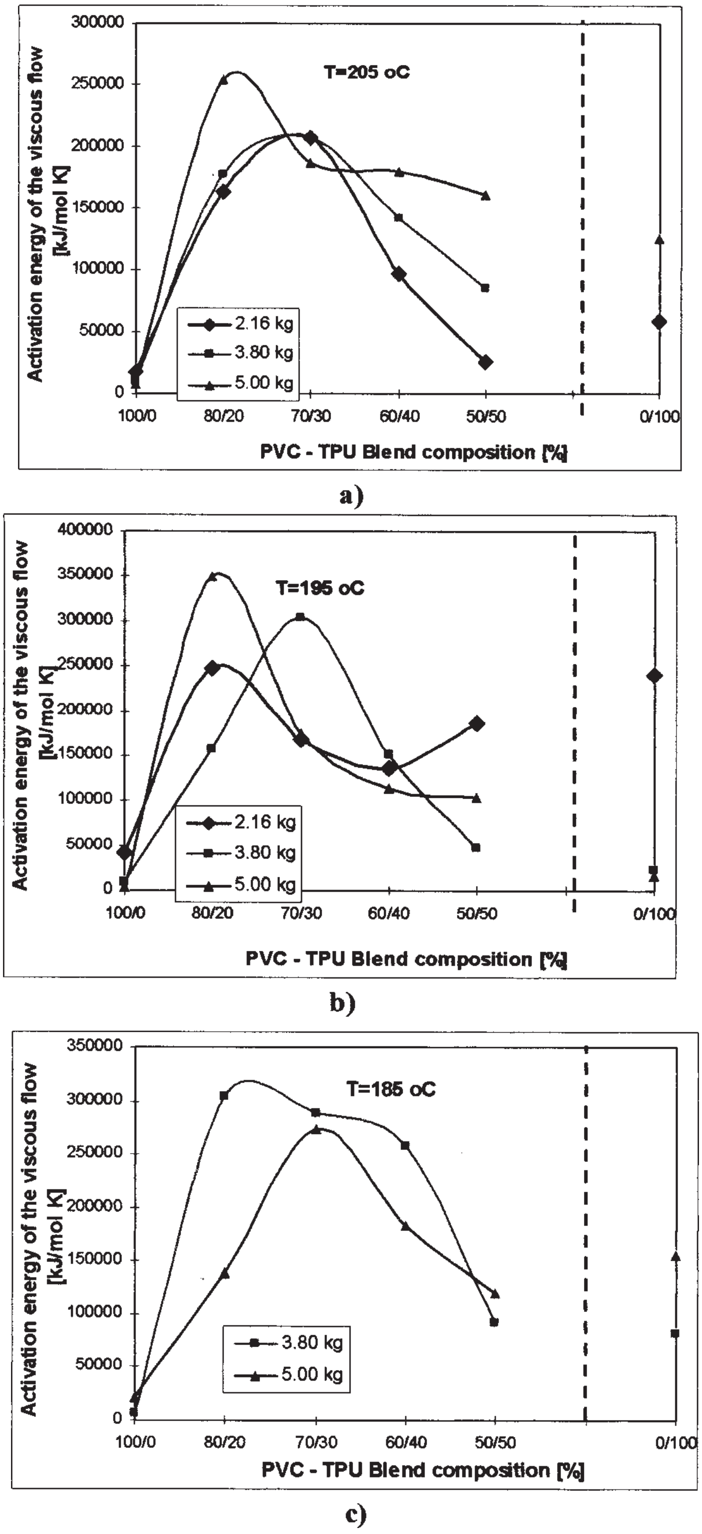
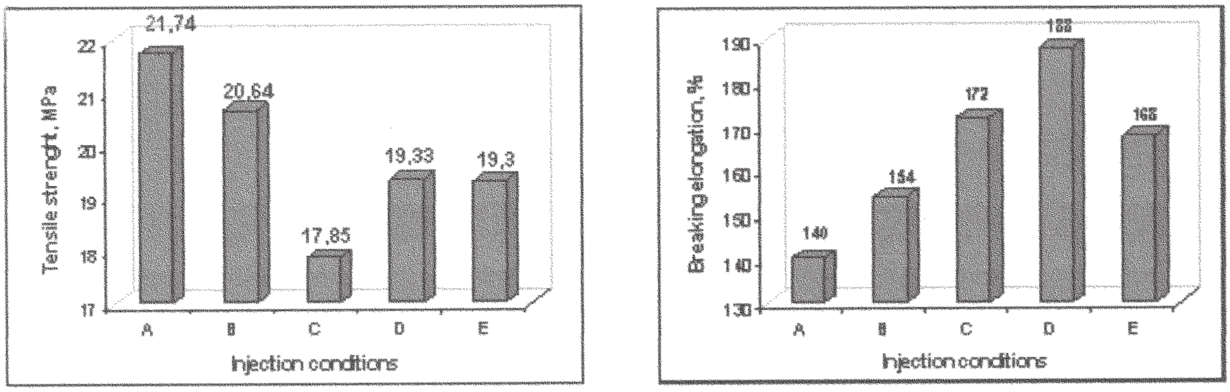


Fig. 5. The dependence of the activation energy of the viscous flow for the PVC / TPU blends upon the composition, temperature and plastometer loading
a) T = 205 ^{0}C at 2.16; 3.80 and 5.00 kg
b) T = 195 ^{0}C at 2.16; 3.80 and 5.00 kg
c) T = 185 ^{0}C at 2.16; 3.80 and 5.00 kg

If at 205^{0}C, the activation energy for the viscous flow, does not record significant variations with the plastometer loading, it cannot be said the same about the behavior at lower temperatures (195 and 185^{0}C).

The conclusions of this paper have a special practical importance. If the melt processing conditions are not adequately chosen, then the PVC – TPU blends cannot be melt processed, because of the extremely high kinematic viscosity and of the too much higher energy required for the viscous flow of the melts.

The performed works proved that the PVC – TPU blends that have a low MFI, are very viscous and needs higher activation energy for the melts flow. The blends with high MFI are not viscous and do not need high energies for the melt flow.



a) b)

Fig. 6. Dependence upon the injection conditions of the tensile strength (a) and of the braking elongation (b) of the 60/40 PVC – TPU blend

The dependence of the mechanical properties on the injection molding conditions

The injection molding of the 60 PVC / 40 TPU blend was performed in the conditions presented in table 2. The dependence of the injected blends properties upon the injection conditions are shown in fig.6. The tensile strength is higher if the injection time is longer and the injection speed has lower values (conditions A from table 2). The sample injected in 20 s with a speed by 1 m/s has 21.74 MPa tensile strength and if the sample was injected in 5 s and with 5 m/s injection speed (C conditions) it has a 17.85 MPa tensile strength (fig.6a).

The longer injection times and lower injection speeds lead to small values for break elongation (conditions A from table 2). The injection under these conditions leads to a breaking elongation of 140%, as comparing with the injection molded at short time (5 s) and average injection speeds (5 m/s), which leads at a breaking elongation of 172 % (fig.6 b).

If it is wanted an application with a great tensile strength, then the melt processing must be made at long injection times and relatively low injection speeds. High breaking elongations are achieved if the injection is made at short injection time and relatively low speeds.

A higher injection speed increases both the tensile strength and the breaking elongation (D and C conditions). The shorter loading time of the mould increases the breaking resistance from 17.85 MPa (C condition) to 19.33 MPa (E condition) and easily decreases the breaking elongation from 172% (condition C) to 168% (condition E).

The studied blends are temperature sensitive. The increase with 10 ^{0}C of the injection temperatures, determines the blend colors changing. Too high speed changes also the blends colors. It was recorded an optimum injection speed at which, the blends do not have a modified colour and the breaking elongation has the desired values.

Conclusions

It was achived a rheological study in the melt and solid state of the PVC – TPU blends with the aim of getting qualitative and quantitative information about the melt processing and for best selection of the injection molding conditions that ensure desired mechanical properties.

Along with the blends composition, the temperature has a high influence upon the kinematic viscosity and on the activation energy of the viscous flow of the the PVC – TPU blends.

The PVC – TPU blends that have a low MFI and the high kinematic viscosity need, for melt flow, the highest activation energy. The blends with the highest MFI values are not viscous and do not require high energies for the melt flowing. Depending on the temperature value, the kinematic viscosity of the PVC – TPU blends can have extremely high values, that can make impossible the melt processing.

If the melt processing conditions are not apropiate, then, because of the extremely high kinematic viscosity and of the too much higher energy required for the melt viscous flow, the PVC – TPU blends cannot be melt processed.

For higher tensile strength obtaining, there are preferred longer injection times and lower injection speeds. Higher breaking elongations are achived if the injection time is short and the injection speed has medium value. A high injection speed increases both the tensile strength and the breaking elongation. The shorter time for the mould loading increases the tensile strength and decreases easily the breaking elongation.

The measurement of the rheological properties based on the MFI methods is a good instrument for the estimation of the rheological properties of the polymeric blends in practical conditions

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