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Mixing Polymers under Rheo-Fluidification Conditions

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Summary: Shear-thinning is known to decrease the viscosity of polymer melts and is commonly used in processing. It is due to the influence of strain rate on viscosity. Rheo-Fluidification conditions are realized when shear-thinning and strain softening combine to further reduce melt viscosity (to simplify, we have called this "disentanglement"). The combination of extrusion flow (pressure flow) and drag flow, produced by the cross-lateral shearing of the melt (in a Couette type of configuration) is not new, has been described, for instance, by Cogswell[1] and results in the vectorial increase of the strain rate, hence producing more shear-thinning and further decrease of viscosity. The addition of a low frequency vibration component (0.25 to 80 Hz) to the lateral shear rate induced by the rotation of the inner shaft introduces the possibility to control the amount of non-linearity triggered by the amplitude of the oscillating shear rate, producing strain softening and new states for the melt, in particular new meta-stable oriented states that modify the rheology of pellets manufactured from such "Rheo-fluidified" melts.[2–4] Under these specific processing conditions, the viscosity reduction of the melt obtained by combining strain softening and shear-thinning can be preserved in the pellets granulated at the exit of the line. These "treated" pellets display a lower viscosity when they are reheated in a melt flow indexer or in a dynamic rheometer after being compressed into disks. The Rheo-Fluidizer can either treat a melt "statically" (as a batch) or continuously (in conjunction with an extruder feeding melt into it). The on-line reduction and control of the melt viscosity during extrusion allows the Rheo-fluidizer to be used to mix, disperse and blend polymer mixtures and additives. The purpose of this paper is to report results obtained with the Rheo-Fluidizer, used continuously to blend two immiscible polymers, polycarbonate and polymethylmethacrylate (PC, PMMA) in proportions that have been challenging other continuous feed dispersing devices such as a twin-screw. In other words, the homogeneous PC/PMMA mixtures described in this paper were not processed successfully by other classical processing methods. We show that the use of a Rheo-fluidification treatment during melt extrusion of polymer blends/alloys yields a battery of novel characteristics, often large improvements, for the pellets and the products created by such a process.

Keywords: blends; disentanglement; polycarbonate; rheology

Experimental Part

The two-station Rheo-fluidizer used in this work is presented in details in other publications.[3,4] It allows reducing the viscosity of a plastic melt by "disentanglement", i.e. by modification of the network of interactions by the combination of shear, extensional flow and vibration. The melt is fed by an extruder, goes through the gap in a first Rheo-Fluidification station, station 1, where it is cross-laterally sheared, elongated and vibrated, then goes into the gap of a second Rheo-Fluidification station, station 2, where it is also sheared, elongated and vibrated but with a different set of

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parameters for the shear rate, frequency of vibration, strain amplitude and temperature, and finally the treated melt exits through a gear pump to a strand die/cooling bath to produce solid pellets. The pellets are used to injection mold ASTM samples which are characterized mechanically in tension, flexion and for their impact strength.

PMMA used for the blend was provided by Arkema and contained 5% of ethyl acrylate comonomer (grade V920). It is a general purpose injection molding resin with Mw = 80,205 and a melt flow index (MFI) of 10.6 (under 230 °C/3.8 Kg). Polycarbonate was a Makrolon provided by Bayer (grade 3208) with MFI = 4.3 under flow conditions of 300 °C/1.2 Kg. It is a highly viscous resin mostly for extrusion. Under the same MFI conditions as PMMA (230 °C/3.8 Kg), the virgin PC has a MFI of 0.8. The ratio of viscosity between the two polymers to blend is 13, which represents quite a challenge for the homogeneity and the quality of the blends. Blends of PMMA/PC of % 80-20 and 50-50 by weight were produced without compatibilizer, coupling agent, or processing aid.

The mechanically blended polymers were prepared in two steps: 1st: tumble a certain % by weight of pellets of each resin to homogenize their bulky mix, dry overnight (17 hours) at 80 °C in a vacuum oven, then 2nd: feed the mix into a hopper attached to an extruder feeding the Rheo-Fluidizer processor. The reduction of the melt viscosity induced by "disentanglement" in the two-station Rheo-fluidification processor enables processing the blends at much lower temperature than usual. The usual processing temperature for PMMA and PC is 230 °C and 285–300 °C respectively. Using the first station to reduce the viscosity of the blends it was possible to lower the processing temperature in the second treatment station to 190 °C. Processing under such a low temperature provided the homogeneous melt and pellets characterized in this paper, even for the 50–50% by weight mix. Strands coming out of the exit die were water cooled and pelletized on-line. We tested the pellets produced by this on-line mixer working under disentangling conditions and compared their properties with those of the original pellets. We performed MFI, Dynamic Frequency tests, DSC, TMA, SEC, TEM and mechanical tests (Tensile, Flexural properties, Izod Impact resistance-notched and un-notched).

The melt flow rate measurements were performed following the ASTM method D1238. A Laboratory Melt Indexer model LMI 4000 by Dynisco was used. The procedure used to test the MFI of the materials had to be refined to prevent moisture pick up at every step. The samples were dried in unsealed bags in a vacuum oven at 80 °C overnight. The vacuum was broken using N_2. Then the bags were taken out of the vacuum oven and immediately sealed. As for the MFI test itself, the bottom of the barrel of the MFI machine was blocked, then the barrel was filled with N_2 using a glass pipette. Feeding of the material into the barrel (about 5 g) was also performed under N_2. After 3 min of preheating at 230 °C, 3.8 Kg was loaded on the piston to extrude the material through the die. Melt flow rate measurements were performed twice on each sample.

Molecular weight measurements were performed using a Waters 150CV+ automated GPC apparatus. A 2% w/v sample was dissolved in THF @ 55 °C for five hours, shaking all the way. After cooling, a 0.2% w/v solution was prepared from the 2% solution and injected @ 30 °C (column and pump are also set @ 30 °C) at a flow rate of 1 mL/min. RI was the measured parameter for the molecular weight distribution. The columns were phenogel pore size 105, 104, 500 Å. Reference samples were included in each carrousel (carrying 16 samples at a time). They were prepared by dissolving the two polymers in THF in the same PC/PMMA proportion as for the processed blends. Their molecular weight was compared with the processed blends to determine the amount of degradation.

Thermal mechanical analysis (TMA) was used to compare the softening temperature of the PC/PMMA blends with one of the virgin PC and PMMA. The tests were performed under N_2 using a TMA-80 from Mettler with a flat probe and a 0.1N force. The samples were heated up to 300 °C at a heating rate of 20 °C/min then cooled back to room temperature at 10 °C/min.

Dog bones and flexural bars were injection molded on a 150 ton Van Dorn machine for the blends and also for the virgin PC and virgin PMMA. For each, tensile tests were performed following ASTM D639 at a crosshead speed of 5 mm/min. The reported values are the average properties measured on five different tensile tests.

The flexural properties of the PC/PMMA blends and virgin resins were determined using a three-point loading system. The tests were performed following procedure A of ASTM D790 with a straining rate of 0.01. The reported values are the average properties measured on five different flexural tests.

Impact bars were also injection molded on a 150 ton Van Dorn machine for the blends and also for the virgin PC and virgin PMMA. Izod impact tests were performed at room temperature on notched and un-notched samples following ASTM D256. Five tests were done for each blend and virgin resins.

Results

Table 1 compares the MFI of the PC/PMMA blends with the MFI or the virgin PC and PMMA. Results indicate that the 20/80 PC/PMMA blend has almost the same melt flow index (MFI = 9.9) as the Virgin PMMA (MFI = 10.6). The blend has very little degradation (2%), as measured by GPC. This is shown in Figure 1. The calculated MFI for the blend, based on a logarithmic compounding law, shows a 45% MFI improvement for the blend, which we attribute to the disentanglement capability of the Rheo-Fluidification processor.[5] The same improvement is also perceived for the 50/50 blend. The 50/50 PC/PMMA mix has a melt flow of 4.4 (vs 2.9, the theoretical calculated MFI value of the mix). The GPC analysis shows 4% degradation for that mix, under our present processing conditions, which yields 34% disentanglement, after reduction of the MFI improvement by the viscosity reduction due to degradation.

The higher MFI obtained (measured) for the processed blends compared to the calculated value for the reference (solution blends) is due, we suggest, to partial recoverable disentanglement [4] occurring while the melt is processed under shear-thinning and strain softening conditions in the Rheo-Fluidizer. To verify that this is the case, one needs to perform "re-entanglement" experiments and determine the extent of recovery. The amount of unrecovered viscosity may be a sign that, along with a modification of the entanglement network, the process also produced a modification of the chain topology, in particular long chain branching (LCB), see the note in ref. 5. We did not perform recovery experiments.

DSC analysis was performed on the PC/PMMA blends and also on the virgin PC

Table 1.

The samples identified as "MIX20-b2-S" etc. correspond to different sets of processing parameters in the Rheo-Fluidification stations.

Sample ID	MFI 230 °C/3.8 Kg	% Degradation	% Disentanglement
Virgin Plexiglas V920	10.6	—	—
80% Plexiglas + 20% PC 3208			
MIX20-b2-S	8.1	1.3	23
MIX20-b3-S	9.9	1.2	51
MIX20-b3-G	9.3	2.4	35
50% Plexiglas + 50% PC 3208			
MIX50-b3-W	4.5	2.1	56
Virgin PC 3208 lot 100	0.8	—	—

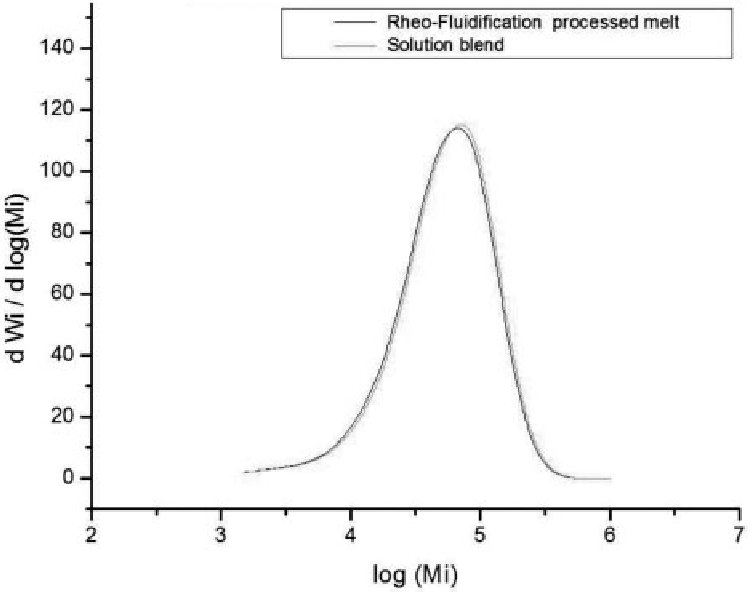

Figure 1.
Comparison of the molecular weight distribution for the solution blend and the 50/50 processed blend.

and virgin PMMA to determine the presence of one or two phases and for comparison purposes.

Figure 2a displays the 2nd heating Heat Flow trace for the 20/80 PC/PMMA blend, revealing two glass transitions, the first at 103.9 °C and the second at 141.2 °C, which correspond to the glass transitions of the PMMA (105.7 °C for the Virgin) and PC phases (151.7 °C for the Virgin), respectively. Notice, however, that the Tg of the PC-rich phase is almost invisible, very weak, and notably depreciated (by ~10 °C), which might be a sign of good alloying of PC and PMMA segments in that phase. The presence of two phases certainly explains the ivory white appearance of the blend. Figure 2b is a stained TEM micrograph clearly showing the two phases. The PC phase is the dark region. One sees that

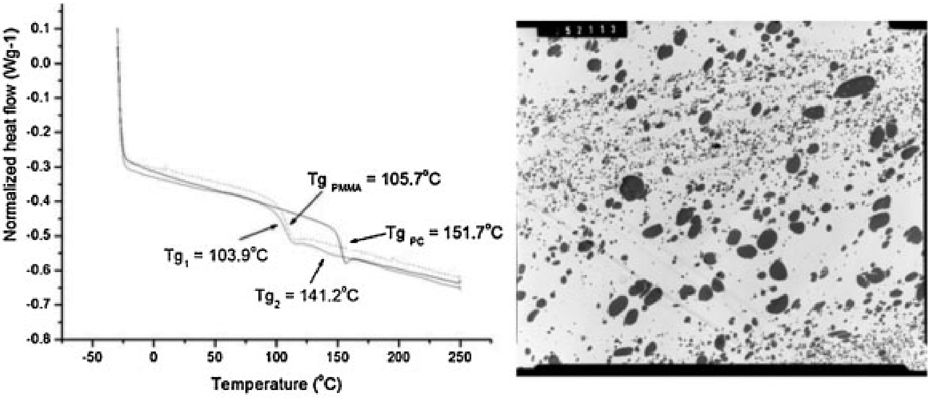

Figure 2.
a) DSC trace for the 20% PC blend. b) stained TEM micrograph of the processed blend. The PC phase is in black.

there are two sizes of PC droplets, a very small one corresponding to very well dispersed PC nodules and droplets roughly 30 times bigger in cross-section that are found in a sea of PMMA with no smaller nodules around. The large droplets look like coalesced agglomerates of small nodules, explaining the absence of any of them in between. This peculiar behavior might be the source of unexpected mechanical features, as will be shown later.

Figure 3a and 3b, for the 50/50 PC/PMMA blend, are comparable to those of Figure 2: one can also see both glass transitions with the glass transition associated with the PC being more marked this time. The first glass transition (associated with the PMMA phase) is at 108.5 °C and the second glass transition (associated with the PC phase) is at 143.7 °C. Noticeably, even at this rather high concentration of these immiscible polymers, the melt is completely homogeneous, and could be treated like any regular single phase molten polymer. This is due to the high degree of alloying of the phases resulting in an increase of Tg for the PMMA phase and a reduction of Tg for the PC phase. The stained TEM micrograph in Figure 3b attests to the extreme homogeneity of the size of the nodules and to their regular localization in the structure. Notice that the PMMA phase (white region) surrounds all droplets of PC and that the size of the droplets is evenly monodispersed.

The virgin PMMA resin has a hardness D-shore of 85; the virgin PC has 79, the MIX 20/80 has 89.5 and the MIX50/50 has 84.5. These values indicate that the PMMA phase imposes its hardness in the 50/50 blend. The increase of hardness for the 20/80 PC/PMMA blend is quite intriguing and unexplained at this time. Is it perhaps due to the presence of the small nodules of PC phase shown in Figure 2b, which would act as hard filler. Note that the hardness of a similar injection molding grade of PP is 58, much softer.

The TMA characterization technique provides the variation of (% L/Lo) with temperature during a ramp up at 10 °C/min under the influence of an imposed small force acting on the sample, where L is the actual length of the sample at temperature T and Lo is its initial length. The sample is either a pellet in the case of the virgin resins or a sliced sample from the strand produced by the rheo-fluidizer. The strand can be sliced perpendicular to its pulling direction from the strand die (the TMA sample is called cs for "cross-section") or it can be sliced longitudinally. Figure 4 shows results

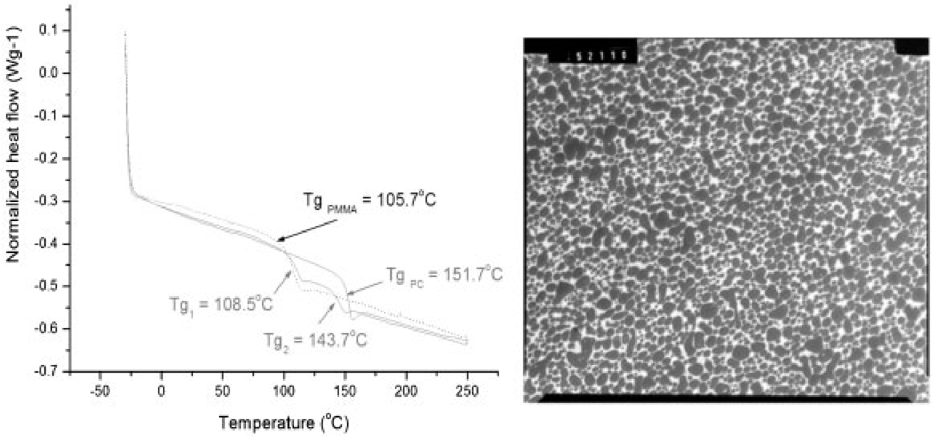

Figure 3.
a) DSC traces (2^{nd} heating) for the virgin resins and the 50/50 PC/PMMA processed blend. b) TEM micrograph of the 50/50 blend. PC is the phase dark.

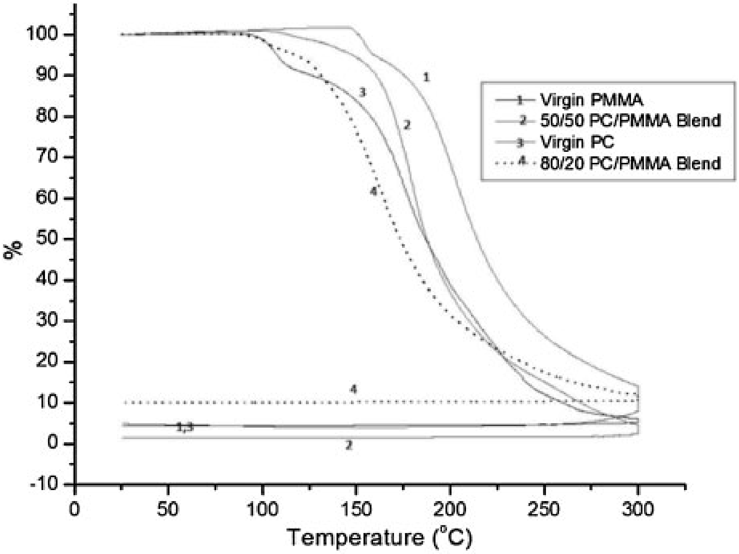

Figure 4.
(%L/Lo) vs. Temperature for the virgin resins and for the processed 20/80 and 50/50 blends.

for cs samples obtained with the 20/80 and 50/50 PC/PMMA blends and compares them with the virgin resins. The softening temperature of the sample can be determined from the TMA graph; it is located at the 1st inflection of the curve before the steep drop off. The Virgin PMMA and PC have a softening temperature of 100.0 °C and 150.4 °C respectively. The 20/80 blend has a softening temperature raised to 110 °C and the 50/50 blend clocks at 125 °C.

The softening temperature of the 20/80 and 50/50 PC/PMMA blends falls right in between the virgin values, following a mixing law, as if the blends were actually alloys. The behavior of the 20/80 blend at higher temperature, from 230 °C to 300 °C, is remarkably different from the virgin resin or even the 50/50 blend: in this temperature region the rate of the contraction of the sample due to the force acting on it is decreased, the dotted curve in Figure 4 crosses the other curves and produces a slack of 10% on cooling. This behavior is typical of the recovery of a strained entanglement network [4]. The presence of the small nodules in Figure 2b may be responsible for this high temperature retained orientation.

Table 2 summarizes the tensile properties found for the PC/PMMA blends and both PMMA and PC virgin resins. The 20/80 PC/PMMA blend has tensile properties similar to Virgin PMMA, perhaps a little improved, with a tensile strength at break of 83.8 MPa (vs 82.9 MPa) and an elongation at break of 3.8% (vs 3.4%).

Figure 5 shows the typical tensile properties of the 50/50 PC/PMMA blend compared to the Virgin PC and PMMA. The 50/50 PC/PMMA blend has a much higher tensile strength at yield than Virgin PC, a higher secant modulus, and shows ductility, unlike the fragile behavior of Virgin PMMA, yet it has a lower tensile strength at break (55.1 MPa) compared to both virgins PC and PMMA (71.7 and 82.9 MPa respectively). The elongation at break of the 50/50 PC/PMMA blend (77.2%) is intermediary to both Virgin PMMA (3.4%) and to Virgin PC (110.4%).

The flexural properties for the PC/PMMA blends are summarized in Table 3. The 20/80 PC/PMMA blend has a flexural modulus (2.42 GPA) slightly

Table 2.
Comparison of the average tensile properties determined by five tensile tests performed on each material.

Sample ID	Tensile strength at yield (MPa)	Elongation at yield (%)	Tensile strength at break (MPa)	Elongation at break (%)
Plexigas-Specification	—	—	70.0	5.0
100% PMMA	—	—	82.9 ± 6.5	3.4±1.2
(80/20) PMMA/PC				
MIX20-b2-T	—	—	79.5 ± 2.5	3.8 ± 1.1
MIX20-b3-R	—	—	83.4 ± 1.7	5.1 ± 3.3
MIX20-b3-F	—	—	70.4 ± 9.8	2.1 ± 0.9
(50/50) PMMA/PC				
MIX50-b2-F	77.2 ± 1.4	3.5 ± 1.2	57.1 ± 1.3	17.9 ± 4.3
MIX50-b3-S, T, W	76.3 ± 1.6	3.3±1.6	55.5 ± 0.6	41.5 ± 3.5
100% PC	60.9	4.8	80.3	125.6
PC-Specification	63.0	6.0	—	Min 50

higher than Virgin PMMA (2.38 MPa) and higher than Virgin PC (1.73 GPa). The flexural strength at 5% strain of the 20/80 PC/PMMA blend (105.5 MPa) is the same as the Virgin PMMA and higher than Virgin PC (79.4 MPa). The 50/50 PC/PMMA blend has flexural properties intermediary to Virgin PC and Virgin PMMA, with a flexural modulus of 2.04 MPa and a flexural strength at 5% strain of 90.5 MPa.

Figure 6 compares the flexural properties of both blends to the virgin resins. The flexural properties of the 20/80 PC/PMMA blend is very similar to Virgin PMMA and that the 50/50 PC/PMMA blend has intermediary properties to both Virgin resins, as expected.

The impact resistance of the PMMA/PC mixes was determined following method ASTM D256. Table 4 and 5 show the Izod impact resistance determined on notched and unnotched samples, respectively for the processed blends and the virgin resins (injection molded samples).

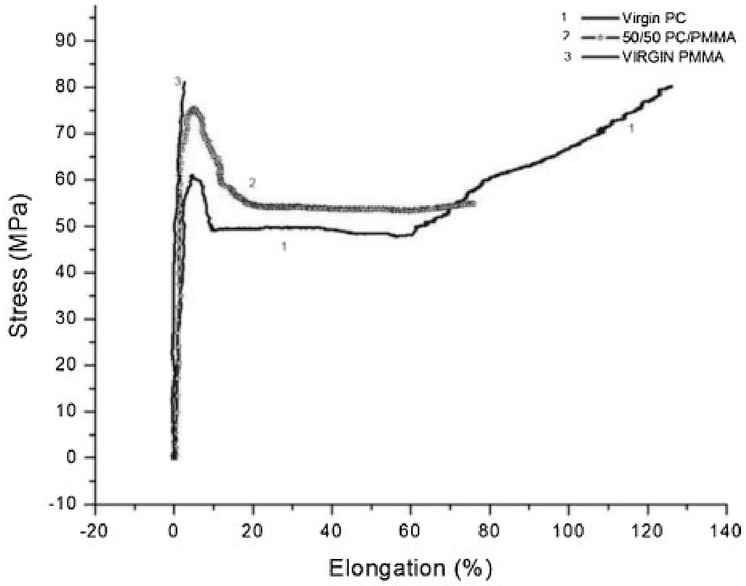

Figure 5.
Stress strain curves (tensile) comparing injection molded samples of the virgin PC and PMMA and the 50/50 blend.

Table 3.
Average flexural properties determined by three flexural tests.

Sample ID	Flexural modulus scan at 1% strain (GPa)	Flexural strength at 5% deformation (MPa)
Plexigas-Specification	3.15	104.9
100% PMMA	2.38 ± 0.11	105.5
(80/20) PMMA/PC		
MIX20-b2-T	2.28 ± 0.04	99.4 ± 1.4
MIX20-b3-R	2.42 ± 0.01	106.1 ± 1.5
MIX20-b3-F	2.38 ± 0.03	104.9 ± 3.9
(50/50) PMMA/PC		
MIX50-b2-F	2.12 ± 0.04	96.0 ± 0.3
MIX50-b3-S, T, W	2.04 ± 0.02	90.5 ± 0.16
100% PC	1.73 ± 0.07	79.4 ± 2.1
PC-Specification	2.3	86.0

Results indicate that the 20/80 PC/PMMA mix has a slightly but clearly higher impact resistance (both on notched and un-notched sample) compared to the Virgin PMMA. The 50/50 PC/PMMA blend has about twice the impact resistance of PMMA on notched samples and about three times the impact resistance of Virgin PMMA on un-notched sample. Considering that the melt strength for such a blend is improved, that tensile and flexural properties are much improved, it can be concluded that Rheo-Fluidification processing of PC/PMMA blends, at least up to 50-50 wt%, present useful enhancement characteristics which can benefit users.

Conclusion

A Twin screw extruder failed to produce an homogeneous blend at a 20 to 50% by weight concentration level for immiscible PC and PMMA. The challenge was to operate under Rheo-Fluidification (disentanglement) processing conditions to see if this technique opened new horizons in blending immiscible polymers. Mixing PC

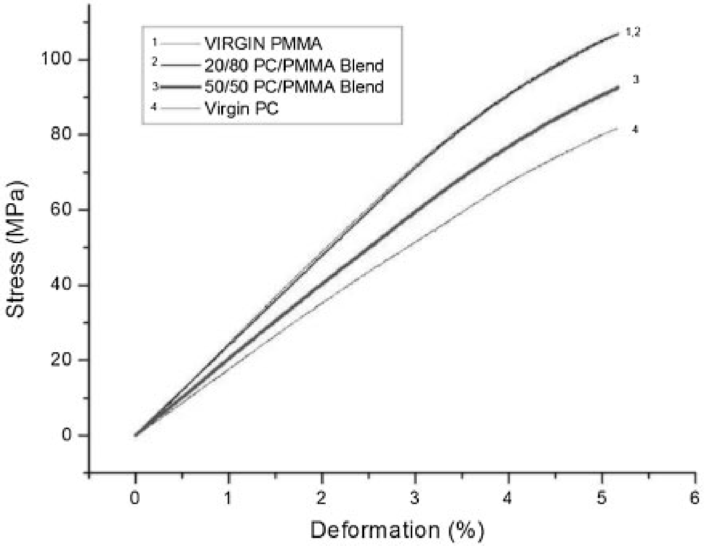

Figure 6.
Stress–strain curves for flexural deformation of the virgin and processed blends.

Table 4.
Notched impact resistance.

Sample ID	Impact resistance (ft-lb/in)	Type of break
Plexigas-Specification	0.30	—
100% PMMA	0.29 ± 0.02	Complete
(80/20) PMMA/PC		
MIX20-b2-U	0.28 ± 0.01	Complete
MIX20-b3-P	0.30 ± 0.05	Complete
MIX20-b3-I	0.29 ± 0.01	Complete
(50/50) PMMA/PC		
MIX50-b3-S, T, W	0.53 ± 0.03	Complete
MIX50-b3-U, V	0.53 ± 0.07	Complete
100% PC	16.11 ± 0.46	Partial
PC-Specification	17.0	—

and PMMA in a Rheo-Fluidification Processor, in proportion up to at least 50 wt%, resulted in a new resin with properties combining the best of PC and PMMA, with insignificant level of degradation and 40% improvement of the fluidity. The pellets made from the mix looked white, very similar to a PP or HDPE grade, but with almost twice the hardness and stiffness of PP.

At high concentration, for the 50% blend, the notched impact was double that of PMMA, while the un-notched samples broke at 3 times the impact energy of PMMA. The elastic modulus and tensile yield strength were 27% higher for the 50%-50% blend than for the PC, a benefit attributed to the presence of the stiffer PMMA.

DSC revealed the presence of 2 phases by a double break in the Cp-T curve, especially visible in the case of the 50–50% blend. Stained TEM micrographic analysis confirmed the presence of two phases for the PC/PMMA processed blends. It also revealed for the 20/80 blend an intriguing size difference between two populations of PC nodules, which might be responsible for the higher temperature mechanical stability of the melt for that blend, as shown by TMA (Figure 4), and its greater D-shore hardness. Both the 20% and 50% mix were injection moldable at the same temperature than an Injection Molding PP grade. These results seem to indicate that recycled PMMA and PC could advantageously be mixed in a Rheo-Fluidizer to provide a new grade. The new resins could, perhaps, compete favorably on some of the PP market.

In summary, coupling a Rheo-Fluidification station to an extruder to blend, alloy, disperse polymers or additives in a continuous way, may very well provide new formidable assets to the plastic industry.

Table 5.
Unnotched impact resistance.

Sample ID	Impact resistance (ft-lb/in)	Type of break
Plexigas-Specification		
100% PMMA	3.71 ± 0.35	Complete
(80/20) PMMA/PC		
MIX20-b2-U	5.82±1.18	Complete
MIX20-b3-P	4.77 ± 0.51	Complete
MIX20-b3-I	5.35 ± 0.63	Complete
(50/50) PMMA/PC		
MIX50-b3-S, T, W	13.79 ± 1.47	Complete
MIX50-b3-U, V	9.0 ± 5.9	Complete
100% PC	Cannot break it	—
PC-Specification	17.0	—

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[2] J. P. Ibar, "*Plastics Viscosity Control Method and Apparatus*", US Patent 5,885,496 Mar. 23 (1999). Also PCT WO 00/76735 A1 (2000).

[3] J. P. Ibar, "Method and apparatus to control viscosity of molten plastics prior to a molding operation", US patent 6, 210,030 April 3 (2001).

[4] J. P. Ibar, "The Great Myths of Rheology, Part II: Transient and Steady State Melt Deformation: the Question of Melt Entanglement Stability", *J. Macrom. Sci. Phys.*, **2010**, part B, 49(6), 1148–1258.

[5] Under certain conditions, LCB are formed, a situation which complicates the task to quantify which part of the fluidity increase is due to "disentanglement" (recoverable deformation of the elastic network). "% disentanglement" refers to the increase of MFI after correction for the change of viscosity due to degradation (decrease of Mw).