Study on molding of various articles of PVC soles with Methocells

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Abstract:
Various articles of PVC namely Surfer (size 8); Angola (size 8); Stiff (size 8); Angola (size 8); Stiff 9size 8) and Celery (size 8) were studied for their lustiness, softness, compatibility, weight, sole length, hardness Shore A, cup depth, sole thickness, heal thickness and cell structures. Methocell of cellulosic nature was employed for improving these quality parameters for regular production at the shop floor. The methocell was used in the dosages of 0.150 Kg of overall batch size of 58 Kg. The results were quite interesting when the soles were evaluated in the quality control laboratory. Methocell F 50 specifically imparted the best quality to the soles. Since it was of cellulosic nature hence the soles were quite flexible and most competent at the European and Foreign wearing conditions. The 20 station machine operation with this formulation was found to give satisfactory yield of the soles. These articles are basically cheap in their selling price and hence manufactured in large volume.

Keywords: PVC soles, Methocell, articles, microcellular network.

1. Introduction

Carlos A. Diaz, Laurent M. Matuana (2009) have studied and examined the effect of Poly [vinyl chloride] (PVC) formulation on the cell morphology and density of rigid PVC foamed with supercritical CO_2 in a continuous extrusion process. Cell morphology and the density of foamed samples were controlled by blending two acrylic-based processing aids (all-acrylic foam modifier K-400 and acrylic-based impact modifier KM-334), using a mixture design. The effect of blend ratios on the fusion and die swell behaviors of PVC was investigated by means of a torque rheometer and on a single-screw extrusion capillary rheometer, respectively. Fusion was promoted as the relative amount of the all-acrylic foam modifier increased in the blends. Similarly, the elastic constant of PVC, derived from the linear relationship between the die swell and apparent shear stress, increased upon increasing the relative amount of the all-acrylic foam modifier in the blends, thus suggesting an increase in the melt elasticity of PVC. Microcellular rigid PVC foams with densities of approximately 0.15 g/cm^3 and a tenfold volume expansion were produced. An optimum ratio of impact modifier to all-acrylic foam modifier of 1:3 was found to maximize the foam expansion. Using impact modifier alone or all-acrylic foam modifier alone yielded expansions considerably lower than that achieved with the 1:3 blends. The experimental results indicated that fusion is not the only criterion to control the cell morphology and density achieved in microcellular rigid PVC foams. The melt must have a viscosity low enough to allow bubble formation and growth, as well as elasticity high enough to prevent cell coalescence [1, 2]

Jean-Louis G (2004) have studied the die swell behavior of PVC melts is a manifestation of melt elasticity and is of considerable commercial as well as fundamental importance. This behavior is a critical issue in extrusion blow molding application where die swell (i.e. parison thickness) needs to be controlled. Advantageously, the addition of high molecular weight acrylic processing aids to PVC provides better die swell control, thus, improving dramatically the process ability of PVC. Hence, knowledge of molecular weight variables of such acrylic processing aids is important from both the commercial and rheological point of view. Various acrylic processing aids were prepared by polymerization designed to provide systematic variation of molecular parameters. Molecular weight distribution of the polymers was characterized by GPC, and their die swell behavior in a typical PVC blow molding formulation was determined at 200°C over various ranges of residence times using different L/D capillary dies. The results are presented showing effects of specific molecular variables. [3, 4]

PVC is one of the major plastics in use today, yet it continues to be an enigma to anyone not fully familiar with the parameters of proper handling and processing. Fears of degradation and HCl evolution, the whining of Greenpeace and other environmentalists with their anti-chlorine agenda, and the phthalate plasticizer issue all combine to fuel the unease of those considering use of PVC in their products. Perhaps the following little "course" on PVC will help ease some of these concerns.

PVC resin is a product of the polymerization of vinyl chloride monomer or VCM (CH_2=CHCl), in a "head-to-tail" manner via free radical catalysts. The resultant (ideal) PVC is a hydrocarbon chain (like polyethylene) but with a chlorine atom on every other carbon. (~CH_2-CHCl-CH_2-CHCl-CH_2-CHCl-CH_2~) Being an imperfect world, there is some chain branching during polymerizations, which are weak points subject to degradation. [3, 4]

In Suspension polymerization, VCM droplets (containing free radical catalyst) are agitated with suspending agents in water for a given time and temperature to achieve the desired molecular weight (or “K value”). This is the most common production method, and furnishes “popcorn-like”, irregularly shaped resin grains that can absorb liquid plasticizers and additives to form dry blend powder compounds. Most flexible and rigid PVC calendering, molding, and extrusion (from powder or pellets) is done with Suspension PVC (S-PVC). [4, 5]

Emulsion polymerization consists of emulsifying very small VCM droplets in water, with a water soluble free radical catalyst. Depending on the type of “soap” or emulsifying agent, agitation, and temperature, Emulsion PVC of varying molecular weight is produced. These resin particles are much smaller than Suspension PVC, and are smooth surfaced, non-absorbent to plasticizers at ambient temperatures. Emulsion PVC resins (E-PVC), also called “Dispersion resins” and “Paste resins, are used to make Plastisols and Organosols for molding, dipping and coating applications. [6, 7]

Bulk (or Mass) polymerization entails just the VCM monomer, containing catalyst, in a two-stage reactor. The first stage reactor, with reflux condenser, agitates the VCM monomer to about a 10% conversion to polymer. This slurry is then transferred to a horizontal reactor with a ribbon blending type low RPM agitator, where polymerization is finished as a dry powder. This PVC (M-PVC) is similar in particle size and shape to S-PVC, and is used in the same (mostly rigid) processes as S-PVC. The main difference between M-PVC and S-PVC of the same molecular weight or K-Value is the higher bulk density of M-PVC. After all the above reactions are complete, the PVC resin is “steam-stripped” and dried in order to remove any residual VCM monomer--down to a fraction of a PPM. [6, 7]

PVC has a unique degradation sequence. Unlike most other polymers that exhibit mainly oxidative degradation with peroxide formation and chain scission, protected by antioxidants, PVC (while ALSO undergoing oxidative degradation) has a nasty habit of releasing HCl under heat and shear of processing an “unzippering effect” that rapidly progresses to catastrophic charred blackening if left unchecked. The art and science of stabilization a whole industry sector has developed very effective protective stabilizer additives to retard this type of degradation. This HCl elimination is most likely to start at a “weak link” site typically chlorine on a carbon at a branching site in the chain. [8]

2. Materials and methods

PVC resin, DOP, DBP, R9, Stearic acid, Ivamol, and CPW were purchased from the leading manufacturers. Methocell F50 was imported from Dow Chemical’s USA. All the raw materials were tested for their qualities before taking to the shop floor.

2.1Pre-treatment of the formulation

All the raw materials were charged in the agitating reactor with the temperature control. PVC resin was charged first and heated at 90 ^{o}C and then DOP/DBP was charged. Thereafter all the raw materials were charged. It was heated and agitated for 45 minutes. Subsequently the Methocell F50 was charged. The temperature was not allowed to exceed beyond 100±5 ^{o}C. It was then discharged and poured in the rectangular container and was hold for until the temperature of the blend comes to an ambient temperature.

2.2Molding of the soles

The batch size of 58 Kg of pre-cooled blend was charged into the hopper of 20 station machine with the automatic control of mold weight of soles. Molding and de molding of the soles were continued until the batch size gets processed.

2.3Quality control

The produced soles were then tested for the tensile modulus, abrasion and Bennewort test.

3. Results

Table 1 shows the data of Surfer article of size 8. The regular soles weight 226 g, sole length 289 mm, hardness Shore A 42, cup depth 4.03 and 4.32 mm, sole thickness 10.21 mm and heal thickness 30.89 mm. The soles with Methocell gave weight 222 g, sole length 288 mm, hardness Shore A 35, cup depth 4.15 and 4.32 mm, sole thickness 10.45 mm, and heal thickness 31.9 mm. Whereas the recycle batch with Methocell gave weight 245 g, sole length 287 mm, hardness Shore A 37, cup depth 4.20 and 4.42 mm, sole thickness 9.98 mm and heal thickness was 29.2 mm. [9. 10]

Table 2 shows the Angola article has the weight of the soles 188 and 177 g, sole length 276 and 275 mm, hardness Shore A 42 and 41, cup depth 3.29-4.04 mm and 3.38-4.04, sole thickness 9.69 and 9.67 mm, heal thickness 29.69 and 28.65 mm. These results were of left and right soles.

Table 3 shows the Stiff article with Methocell F50; the weight 183 g, sole length 300 mm, hardness Shore A 38, cup depth 4.36-4.60 mm, sole thickness 6.02 mm and heal thickness 33.3 mm. the same article with K100 shown the weight 202 g, sole length 295 mm, hardness Shore A 45 mm, cup depth 4.03-4.30 mm, sole thickness 5.82 mm and heal thickness 30.91 mm.

Table 4 as the repeat batch to conform the results has shown the same data as that shown in table 2. Table 5 shows that the Stiff article sole weight 194 (L) and 193 (R), sole length 291 and 288 for L and R, hardness Shore A 44 and 43 (L&R), cup depth 4.06 (L) and 4.12-4.91 (R), sole thickness 4.81 and 5.97 (L&R) and heal thickness of 31.6 and 32.16 respectively.

Table 6 has the interesting comparison of Angola and Celery article, the sole weight 203 and 201, sole length 294 and 294, hardness Shore A 48 and 48, cup depth 3.57-3.83, 3.32-3.39 mm, sole thickness 9.56 and 8.87 mm, heal thickness 27.6 and 27.89 mm. Celery article data were with the lower values. [9, 10]

4. Discussion

Methocell F50 has the good control of the qualities on the soles whereas the K100 did not. This may be due to their different functional structure and thus having the different synergies with the PVC resin. As it is seen clearly from the table interpretation that the cell structures were not uniform in the regular article but were much better with F50 but in cases of recycle batch the cell structures were uniform and smaller. In some cases the air traps were also observed specially with Angola article. Since for each article the molds also change and hence may be observed. In the left article of the Angola the cell structures were uniform and only were non-uniform at the heal areas where pinholes were observed. Methocell very well exhibited the reduction in the sole weights and this could add to the feasibility of the economy. The variations in the left and right articles were doing observed but very marginally. Figures 1, 2, 3 and 4 shows the cellular network in the articles molded and they clearly differs in their network cross linkages. The Methocell processed articles were seen with the uniform cellular network that had shown the quality parameters conforming the international standards as per Bata and STARA norms. [11, 12]

In figure 4 the molded article of the sole has shown the improved lustiness than that was processed with the regular formulation. K100 processed articles were not found to be compatible with the F50 and found with the yellow tans on the soles that was found to interfere with the coloring of the soles.

Conclusions

Methocell F 50 has proven to improve the quality, lustiness, compatibility, and uniform cellular structures, with low abrasion. The formula mold output was found to have withstanding with the European and Foreign weather conditions where the normal complaints of cracking the soles come from. This has certainly improved the process ability and the ease of production with the injection molding. K100 on the contrary gave the unacceptable results and also increased the sole length than the required size. Our invention hence concludes the successful use of Methocell F 50 for future PVC sole molding.

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Table 1 Article: Surfer; size: 8

Sr. No.	Inspection Description	Method	Regular	Fresh (Film Former Added)	Fresh (Film Former Added) + Waste
1	Weight (gm)	Weighing Balance	226	222	245
2	Sole Length (mm)	Scale	289	288	287
3	Hardness (Shore A)	Durameter	42	35	37
4	Cup Depth (mm)	Vernier	4.03 4.32	4.15 4.32	4.20 4.42
5	Sole Thickness (mm)	Vernier	10.21	10.45	9.98
6	Heel Thickness	Vernier	30.89	31.9	29.2
7	Cell Structure	Visual	Cells Structure was not uniform, big and small, both are present	Not Uniform Cells Structure but less than Regular one.	Uniform (small) cells Structure.

Table 2 Article: Angola; size: 8

Sr. No.	Inspection Description	Method	Fresh only W/o. Film Former (RIGHT)	Fresh With Film Former (LEFT)
1	Weight (gm)	Weighing Balance	188	177
2	Sole Length (mm)	Scale	276	275
3	Hardness (Shore A)	Durameter	42	41
4	Cup Depth (mm)	Vernier	3.29 ~ 4.05	3.38 ~ 4.04
5	Sole Thickness (mm)	Vernier	9.69	9.67
6	Heel Thickness	Vernier	29.69	28.65
7	Cell Structure	Visual	Mix Results were observed regarding cell structure, somewhere it seems uniform and somewhere big and cured Air Traps.	Uniform cell structure at all the places except the heel area and small pinholes were observed near the skin.

Table 3 Article: Stiff; size: 8

Sr. No.	Inspection Description	Method	Fresh only W/o. Film Former	Fresh With K 100
1	Weight (gm)	Weighing Balance	183	202
2	Sole Length (mm)	Scale	300	295
3	Hardness (Shore A)	Durameter	38	45
4	Cup Depth (mm)	Vernier	4.36 ~ 4.60	4.03 ~ 4.30
5	Sole Thickness (mm)	Vernier	6.02	5.82
6	Heel Thickness (mm)	Vernier	33.3	30.91
7	Cell Structure	Visual	Cell structure was not uniform, also pinholes were observed throughout the Sole.	Mix results were observed, somewhere uniform cell structure was found and somewhere big and small pinholes were observed. Some burnt compound also found in soles.

Table 4 Article: Angola; size: 8

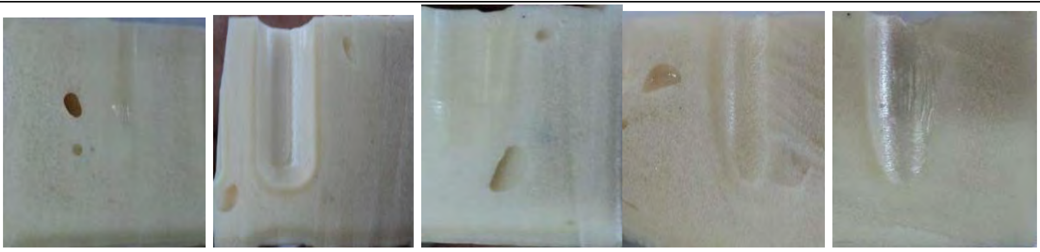
Sr. No.	Inspection Description	Method	Fresh With Film Former (RIGHT)	Fresh With Film Former (LEFT)
1	Weight (gm)	Weighing Balance	187	189
2	Sole Length (mm)	Scale	283	283
3	Hardness (Shore A)	Durameter	46	46
4	Cup Depth (mm)	Vernier	3.45 ~ 3.52	3.07 ~ 4.89
5	Sole Thickness (mm)	Vernier	9.37	8.7
6	Heel Thickness	Vernier	26.91	26.3
7	Cell Structure	Visual	Uniform cell structure was observed except the front sole area where small pinholes were visual; also Chemical clots are found in some places.	

Table 5 Article: Stiff; size: 8

Sr. No.	**Inspection Description**	**Method**	**F/50 Left**	**F/50 Right**
1	Weight (gm)	Weighing Balance	194	193
2	Sole Length (mm)	Scale	291	288
3	Hardness (Shore A)	Durameter	44	43
4	Cup Depth (mm)	Vernier	4.06	4.12 ~ 4.99
5	Sole Thickness (mm)	Vernier	4.81	5.97
6	Heel Thickness	Vernier	31.6	32.16
7	Cell Structure	Visual	Cells Structure almost uniform. But at few places chemical deposition is found and pinholes also found in heel area.	

Table 6 Article: Angola & Celery; size: 8

Inspection Description	**Method**	**F/50 Left**	**F/50 Right**	**F/50 Left**	**F/50 Right**
Weight (gm)	Weighing Balance	203	201	146	144
Sole Length (mm)	Scale	294	294	296	296
Hardness (Shore A)	Durameter	48	48	48	48
Cup Depth (mm)	Vernier	3.57 ~ 3.83	3.32 ~ 3.39	3.33 ~ 3.53	2.22 ~ 2.70
Sole Thickness (mm)	Vernier	9.56	8.87	6.7	6.95
Heel Thickness	Vernier	27.6	27.89	24.92	25.67
Cell Structure	Visual	The cell structure was uniform in most of the places. But big pinholes were found in heel and rising area. At few places Chemical clots also observed.			


(A)

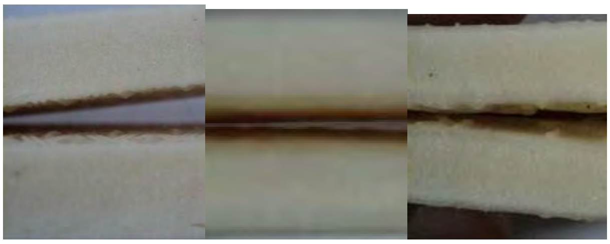
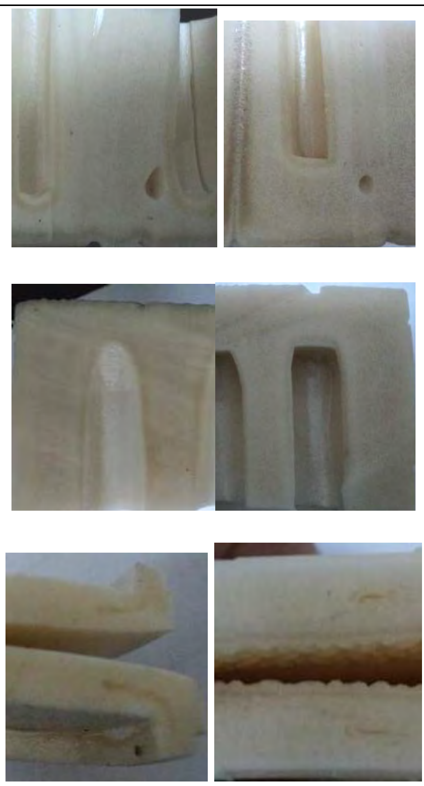
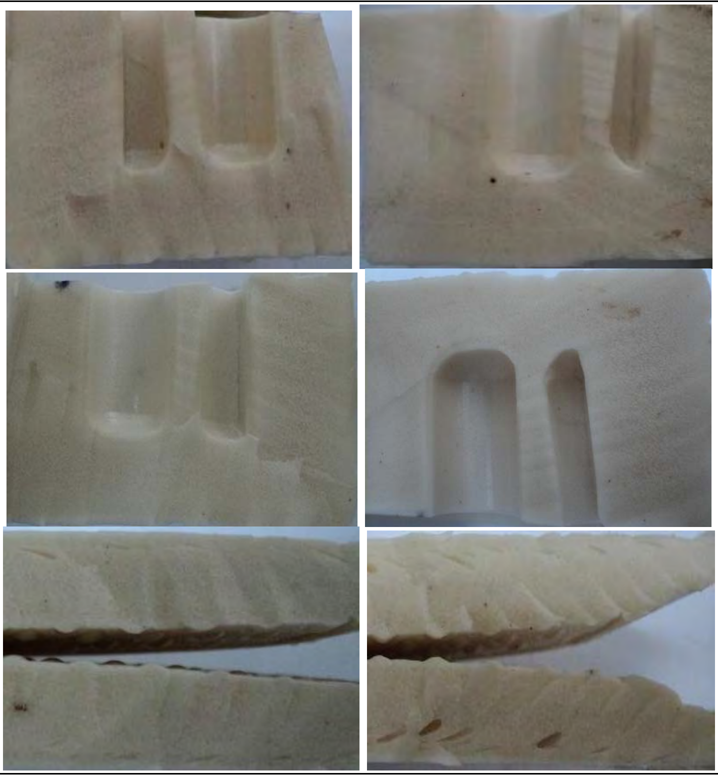

(B)

Figure 1 (A) soles without Methocell (B) soles with Mithocell with uniform network structure



(A) (B)

Figure 2 (A) soles with Methocell K 100 (B) soles with Methocell F 50



(A) (B)

Figure 3 (A) Soles with recycle PVC and (B) Methocell K 100

Figure 4 Internal polymeric network of soles and sole brightness with Methocell F 50