Development of a Gel-Counting Technique for Quantifying Cleanliness of Film-Grade Resins

YI-BIN HUANG[1,*] and THOMAS E. WESSEL[2]

[1]Designed Thermoplastics Research (Bldg. 438), and [2]Engineering Thermoplastics Technical Service and Development, The Dow Chemical Company, Midland, Michigan 48667

SYNOPSIS

A novel gel-counting technique was developed to precisely quantify the cleanliness of film-grade resins. The technique involves cross-polarization on stretched film and counting gels at various magnifications. By combining the gel-count data and the resolution power of the microscope at these magnifications, one can obtain detailed gel size distribution in the resins. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Resin cleanliness is a critical quality parameter to control for a polymeric material to be used in high-performance film applications. In an effort to pursue the potential of syndiotactic polystyrene (SPS) in such applications, a study was carried out to quantify the cleanliness in SPS resin. SPS is a new semi-crystalline polymer currently under development by The Dow Chemical Company (Dow).[1]

For quantifying cleanliness in film-grade resins, typically, a film sample is prepared and then the number of gels is counted. Here, gel is defined to be any visible discontinuity in polymer films. A gel may be composed of one or more oxidized, high molecular weight, unmelted, nonsolvated, or crosslinked materials of the same composition as the matrix that, for a variety of reasons, has not blended with the matrix.[2] In addition to the resin-based gels, external contaminants such as particles of dirt that are enclosed in polymer are also considered to be gels in this study.

Gel counting is an important task in the plastic industry for qualifying film-grade resins to be used in certain applications; however, no reference on gel-counting techniques can be found in regular journals by searching from Chemical Abstracts (1967 to present) and Rubber and Plastics Abstracts (1970 to present). Among ASTM standards, there is only one test method prepared for gel count of plastic film, as shown below.

The ASTM gel-counting technique involves putting a film on top of an overhead projector and counting the number of visible discontinuities from the image on the projection screen.[3] However, the gels counted this way are typically larger than 100 μm. Smaller gels cannot be seen and counted. One way to include smaller gels is described below. If a film sample is prepared by stretching, then colorful cross patterns can be seen around each gel under crossed polarization as the gels become stress concentrators during film stretching. Therefore, gel counting can be performed simply by sandwiching a stretched film sample between crossed polarizer sheets and counting the stress concentrators recognized by the naked eye. With the aid of the colorful cross patterns around the gels, one can count gels as small as 10 μm. To count even smaller gels, one can use a cross-polarized microscope on the stretched film to help recognize smaller stress concentrators than those discernable by the naked eye. Typically, in the industry, a single magnification is chosen based on the minimum gel size that is critical to cause a problem in either processing or application of the film. The chosen magnification varies from application to application as well as from material to material.

However, to gain more complete information about the cleanliness of film-grade resin, such as the gel size distribution, the above technique needs to

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 57, 1227–1232 (1995)
 CCC 0021-8995/95/101227-06

be modified. The principle for the modification is described in the following section.

CONCEPT OF COUNTING GELS AT VARIOUS MAGNIFICATIONS

When one finds a big gel by looking at a stretched film under crossed polarization, one can always find many smaller gels around the big one. Similarly, if one focuses on a smaller gel, then again, many even smaller gels can be found nearby. This type of self-similarity or self-scaling relationship exists in many other physical systems and is captured in the concept of "fractal dimension."[4] Mathematically, such type of gel size distribution can be expressed as:

$$N \sim d^{-\tau_1} \tag{1}$$

where N is the number of gels per unit volume, d is the gel size (for example, equivalent diameter of gel), and $-\tau_1$ is an exponent with $\tau_1 > 0$. The negative sign in $-\tau_1$ is used to emphasize the inverse proportionality relationship between N and d. Graphically, such a distribution is illustrated in Figure 1(a).

By looking at a film at a higher magnification, one can discern smaller gels, mathematically,

$$d \sim M^{-\tau_2} \tag{2}$$

where M is the magnification, and $-\tau_2$ is another exponent with $\tau_2 > 0$. Again, a negative sign is used to emphasize the inverse proportionality relationship between d and M. Figure 1(b) depicts such a relationship. Substituting eq. (2) into eq. (1), one obtains

$$N \sim M^{\tau_2 \cdot \tau_1} \tag{3}$$

Because both τ_1 and τ_2 are positive, the exponent $\tau_2 \cdot \tau_1$ is positive. Therefore, the gel count N is expected to be positively associated with the magnification M [as depicted in Fig. 1(c)]. In other words, one would obtain a higher gel count by looking at a film under a higher magnification.

By counting gels at a single magnification, one cannot obtain information about the gel size distribution, as one would only get a snapshot at a certain scale but not the whole picture. Even a state-of-the-art image analyzer that can measure gel size directly cannot properly obtain the complete gel size distribution at a single magnification. No matter what magnification is used, based on the type of gel size distribution shown in Figure 1(a), most of the measuring time would be spent on the small gels and, thus, it is impossible to measure statistically enough

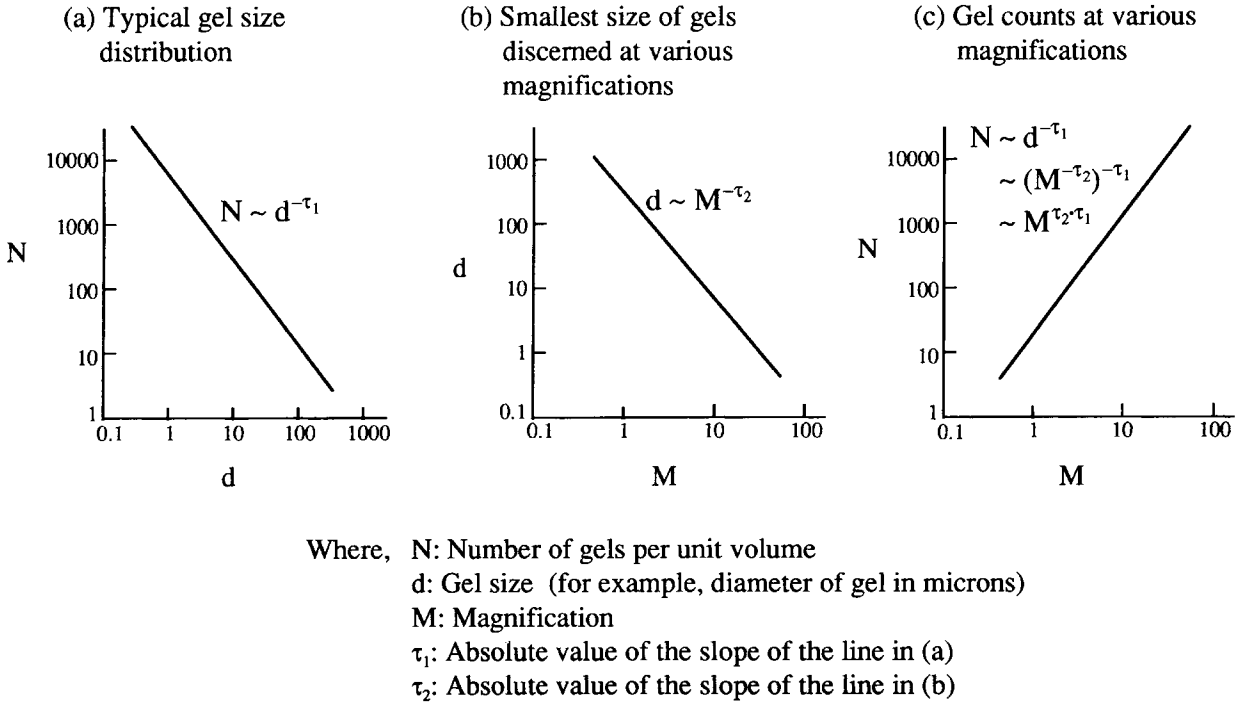


Figure 1 Principle of obtaining gel size distribution from gel counts measured at various magnifications.

big gels in a reasonable amount of time. Yet, in terms of gel volume, big gels dominate and, thus, should not be ignored.

In this study, pictures were taken from the stretched SPS films at various magnifications, and then gels were counted from these pictures. Next, the smallest size of gels discerned at each magnification used was determined. The actual gel size distribution was then reconstructed from these two sets of data.

EXPERIMENTAL

Materials

The SPS resin used in this study was produced in Dow's SPS pilot plant. The weight-average molecular weight of the resin was 216 kg/mol.

Processing

Part of the resin passed through a melt filtration step. The filter used is a leaf-disk-type filter composed of sintered metal fibers as the filter elements. The nominal pore size of the filter is 10 μm. Both the unfiltered pellets (those that bypassed the melt filtration step) and the filtered pellets were then separately extruded into 60 μm thick webs using an extruder. Finally, the webs were biaxially stretched to 6 μm thick films using a batch film stretcher. No heat setting was applied after the film stretching so that the stress developed around the gels during stretching could be preserved for easy identification of gels during gel counting.

Gel Counting

Pictures were taken from the SPS film samples at six magnifications (0.4×, 1×, 2.9×, 10×, 32×, and 70×) under cross-polarized light using an MP-4 copy stand (for 0.4× and 1×) and a Wild M-400 Photomarkoskop microscope (for 2.9–70×). The actual magnifications determined from calibration pictures were: 0.405–0.416×, 0.957–1.010×, 3.0×, 10×, 32×, and 76×. Then, gels were counted from each picture by identifying the cross patterns. The area of measurement on the picture was converted to the actual area on the SPS film based on the magnification used to take that picture. The volume of measurement was calculated by multiplying the above area by the film thickness (6 μm). The gel-count data were then expressed as the number of gels per unit volume of the resin.

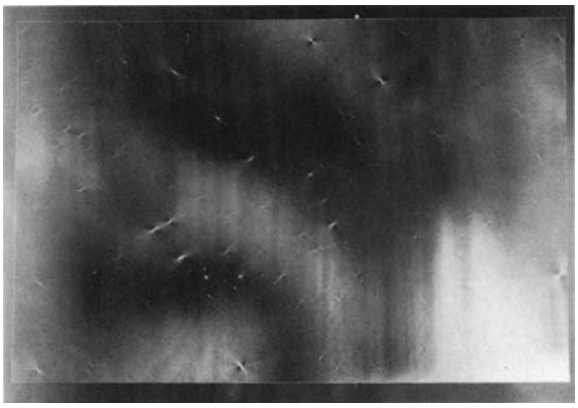
RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the pictures of two SPS film samples taken at 0.4× magnification under cross-polarized light. One can see many more gels, by identifying cross patterns, from the film made of unfiltered SPS resin [in Fig. 2(a)] than from that made of filtered SPS resin [in Fig. 2(b)]. This indicates that the filtration did a good job in removing the gels that are big enough to be seen at this low magnification.

Figures 3(a) and 3(b) show two pictures of a SPS film sample taken at different magnifications. From the same area of the film, that is, the area enclosed by the rectangle in Figure 3(a) and the whole area in Figure 3(b), one can see many more gels at 10× magnification [Fig. 3(b)] than at 3× magnification [Fig. 3(a)]. This provides direct evidence to support the statement that one can discern smaller gels at a higher magnification.

Figure 4 shows the gel-count data measured at the six magnifications mentioned above. Multiple

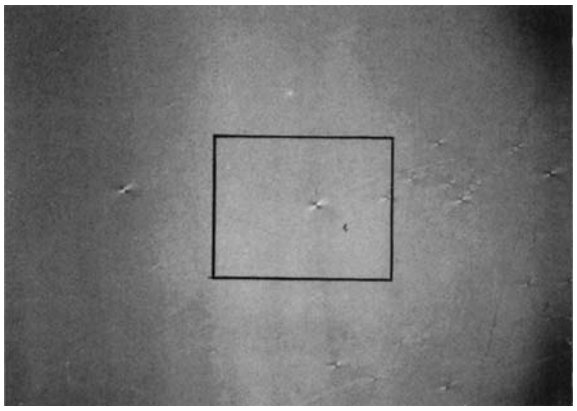
(a) Film made of unfiltered SPS



(b) Film made of filtered SPS

Figure 2 Typical pictures taken from SPS film under cross-polarized light (at 0.4× magnification).

(a) 3x magnification



(b) 10x magnification

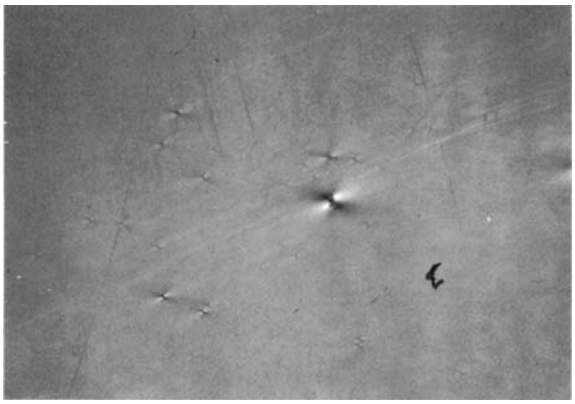


Figure 3 Two pictures taken from an SPS film sample at different magnifications.

measurements were made, from different areas, at each magnification to show the degree of data scattering. The data from both the filtered and the unfiltered samples are shown in the same figure for easy extraction of the melt filtration effect.

Focusing on the data from the unfiltered sample only, one can see a very similar picture to that shown in Figure 1(c), indicating the appropriateness of using the approach of counting gels at various magnifications for our samples. The slight curvature formed by the data points from the unfiltered sample in Figure 4, as opposed to the absolute linearity in Figure 1(c), reflects the minute difference between the real and the ideal systems. The data from the filtered sample deviate from the ideal linearity even more. In fact, the curve connecting the data points from the unfiltered samples could be divided into two lines intersecting around magnification = 3×, which must be related to the melt filtration operation that separated the filtered and unfiltered samples. At magnifications below 3×, one can clearly see the effect of melt filtration on gel reduction. However,

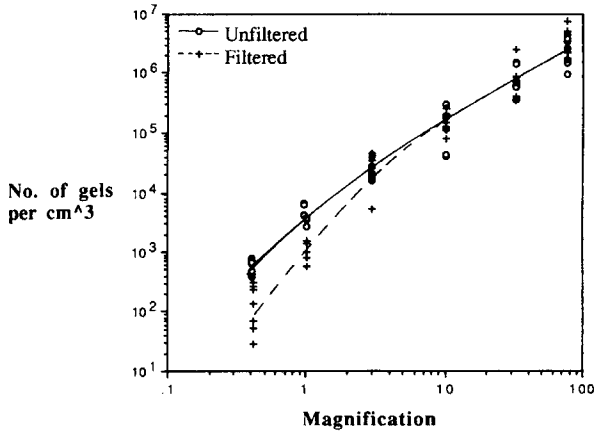


Figure 4 Effect of filtration on gel counts measured at various magnifications.

at 10× or higher magnifications, there is no difference in gel counts between the filtered and the unfiltered samples.

To determine the resolution as a function of the magnification, the smallest gel at each magnification was identified from the pictures, and its size was measured directly from the corresponding film sample using a bright-field transmitted light microscope (Nikon Optiphot-2). The data are shown in Figure 5, which shows a relationship consistent with that depicted in Figure 1(b).

To reconstruct gel size information from Figures 4 and 5, we did the following data analysis with the calculation shown in Table I. D_{min} is the minimum size of the gels seen at a particular magnification and was read directly from the line in Figure 5. D_{max} is the maximum size of the gels that were seen at a particular magnification but not seen at the next

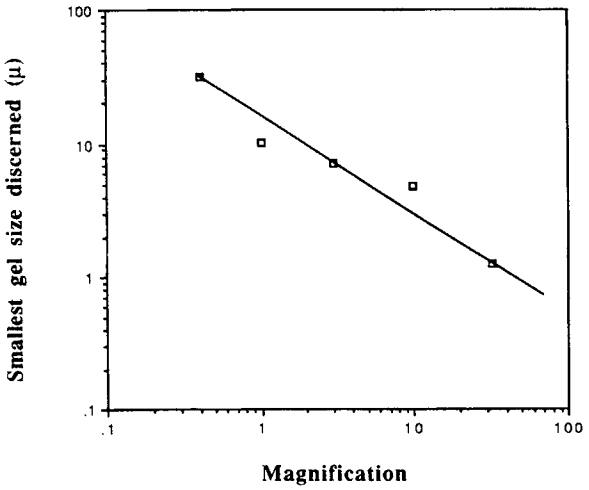


Figure 5 Resolution vs. magnification for gel counting.

lower magnification. For the magnifications from 1 to 76×, the D_{max} of a particular magnification was taken as the D_{min} of the next lower magnification. However, for the 0.4× magnification, the D_{max} was estimated from the measurement of the largest gels in the SPS film samples. Even though there are few gels as big as 200 μm, the majority of the gels were no larger than 100 μm. Thus, 100 μm was taken as the D_{max} of the 0.4× magnification. D_{avg} is the average of D_{min} and D_{max}, representing the average size of the gels that were seen at a particular magnification but not seen at the next lower magnification. N is the number of gels counted at a particular magnification and is read directly from the curves in Figure 4. ΔN, or delta N, represents the number of gels seen at a particular magnification but not seen at the next lower magnification. For the magnifications from 1 to 76×, the ΔN of a particular magnification is calculated as the difference between the N of this magnification and that of the next lower magnification. For the 0.4× magnification, the ΔN is simply the N at that magnification, as there was no lower magnification (than 0.4×) used in this study.

The data of ΔN vs. D_{avg} in Table I are plotted in Figure 6. The data from the unfiltered samples show almost straight line behavior, which is consistent with the hypothetical gel size distribution depicted in Figure 1(a). The data from the filtered samples, however, could form two straight lines. Typically, two straight lines indicate two different mechanisms in generating that particular gel size distribution. In our case, the two different mechanisms would be gel formation and melt filtration. Furthermore, the two straight lines would intersect around gel diameter = 10 μm, which is just the nominal pore size of the filter used.

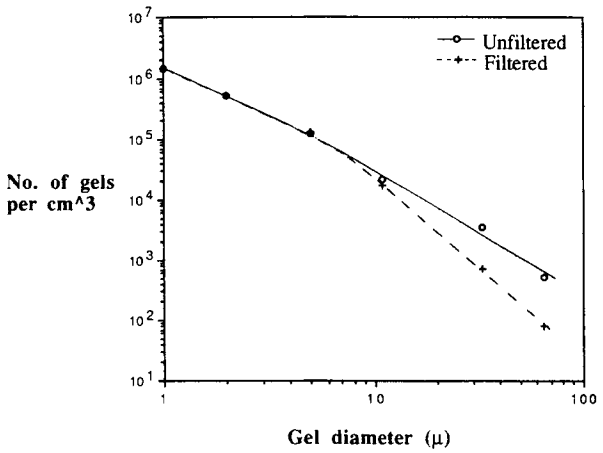


Figure 6 Effect of filtration on gel size distribution.

Assuming that gel volume could be approximated by spherical geometry, we could continue the above

Table I Calculation for Gel Size and Volume Distributions

Magnification	D_{min} (μ)	D_{max} (μ)	D_{avg} (μ)	N	Delta N	Delta V (μ^3)	% V
(A) Unfiltered							
0.4	30	100	65	5.2E + 02	5.20E + 02	7.48E + 07	61%
1	15	30	23	4.0E + 03	3.48E + 03	2.08E + 07	17%
3	7	15	11	2.6E + 04	2.20E + 04	1.53E + 07	13%
10	3	7	5	1.5E + 05	1.24E + 05	8.12E + 06	7%
32	1.3	3	2	6.6E + 05	5.10E + 05	2.65E + 06	2%
76	0.7	1.3	1	2.1E + 06	1.44E + 06	7.54E + 05	1%
							100%
Total Gel Volume: 1.22E + 08 μ^3 Total Gel Volume = 0.012% of Total Resin Volume							
(b) Filtered							
0.4	30	100	65	8.0E + 01	8.00E + 01	1.15E + 07	9%
1	15	30	23	8.0E + 02	7.20E + 02	4.29E + 06	4%
3	7	15	11	1.8E + 04	1.72E + 04	1.20E + 07	10%
10	3	7	5	1.5E + 05	1.32E + 05	8.64E + 06	7%
32	1.3	3	2	6.6E + 05	5.10E + 05	2.65E + 06	2%
76	0.7	1.3	1	2.1E + 06	1.44E + 06	7.54E + 05	1%
							33%
Total Gel Volume: 3.98E + 07 μ^3 Total Gel Volume = 0.004% of total resin volume.							

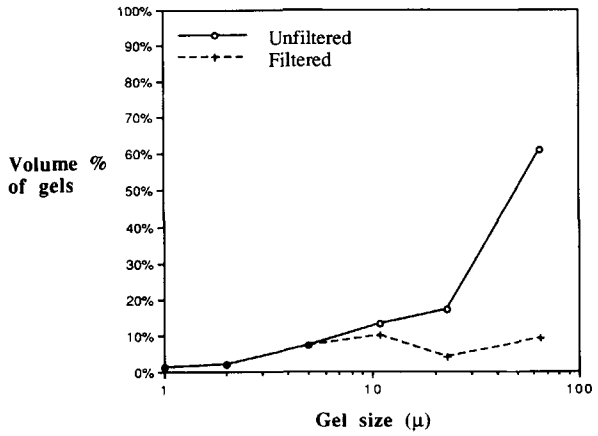


Figure 7 Effect of filtration on gel volume distribution.

data analysis to estimate gel volume information as follows. In Table I, ΔV, or delta V, represents the total volume of gels seen at a particular magnification but not seen at the next lower magnification. ΔV was calculated by multiplying ΔN by the volume of a sphere with D_{avg} as the diameter. Total gel volume is the sum of ΔVs of all six magnifications. $\%V$ is the volume of gels at each magnification divided by the total gel volume of the unfiltered samples. Total resin volume is 1 cm^3, as the gel count data were represented as the number of gels per cm^3. The results, shown in Table I, indicate the total gel volume in the unfiltered resin was on the order of 0.01% of the total resin volume, and the 10 μm filtration removed about 2/3 of the gel volume from the SPS resin used in this study.

The data of ΔV vs. D_{avg} in Table I are plotted in Figure 7. It is obvious from this figure that larger gels dominate in the gel volume distribution of the unfiltered samples. For example, the largest gel category (with D_{avg} = 65 μm) accounts for more than 60% of the total gel volume. And gel volume reduction by melt filtration occurred only for the larger gels. For the gels smaller than 10 μm, the volume did not change.

In conclusion, this gel-counting technique was used successfully to quantify the cleanliness in the SPS resin produced in Dow's SPS pilot plant. In addition, the effect of a melt filtration trial on gel reduction in SPS was also clearly quantified. This technique, of course, is not limited to SPS but can be used for any polymer from which a stretched film can be made.

The authors would like to acknowledge Duane Krueger of Dow's Analytical Sciences Laboratory for taking pictures from the SPS films; Steve Chum, Bill Knight, and Jeff Wooster of Dow's Polyolefins Research for valuable discussion prior to and during this project; and Clive Bosnyak of Dow's Polycarbonate Research for constructive comments on documenting this work.

REFERENCES

1. A. Wood, *Chemicalweek,* **151**(10), 12 (1992).
2. ASTM Standard D883, *Ann. Book ASTM Stand.,* **00.01,** 206 (1993).
3. ASTM Standard D3351, *Ann. Book ASTM Stand.,* **08.02,** 312 (1993).
4. B. B. Mandelbrot, *The Fractal Geometry of Nature,* Freeman, San Francisco, 1982.

Received December 20, 1994
Accepted March 1, 1995