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Melt Relaxation Studies of Polymeric Structures in Gel-type Toner Resins

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Abstract

Many toners use resins which are crosslinked to some degree. These resins are used in toners due to the fusing latitude they impart to the toner. These partially crosslinked or “gel” type resins are relaxed in the melt mixing step used to prepare the toner, thus their properties are different from the “as manufactured material”. We have studied the relaxation of the polymeric structure in a gel resin using a Haake batch mixer to simulate the melt mixing step. Resin samples were compared using a Shimadzu CFT-500C flow tester and a Rheometrics RMS Rheometer. Our data show that the properties of the resulting polymer are a function of the shear experienced by the polymer during the melt mixing step. The temperature at which the melt mixing step is performed appears to be the dominant variable influencing the shearing of the polymer.

Introduction

The polymers used as binders in toners have evolved to meet changing needs. The original resins used were materials developed for other purposes i.e. paint binders (Paraloid B-66™) which were pressed into service in toners due to their availability. These materials were able to attach the toner to the paper but offered little else. As the industry grew, specialized polymers were designed which were aimed at improving toner performance by tailoring the polymer properties to meet specific needs. One such need was to offer better performance by increasing the fusing latitude of the toner. Partially crosslinked polymers were quickly developed which had good fixing and improved hot offset. US patent 3,938,992 assigned to Kodak detailed the use of crosslinked polymers.

These partially crosslinked polymers can be distinguished from “fully” crosslinked polymers, such as those used in ion exchange resins, by the large portion of soluble material they contain. Amberlite XAD-4™ is a product of Rohm and Haas Co. which is a “fully” crosslinked resin. Solvent extraction of XAD-4 yields very little or no soluble polymer. Performing the same test on Acrybase 1405 from Polytribo Inc. yields 75% soluble material. Further depending on the conditions of the extraction (temperature/solvent) more or less soluble material is extracted.

Melt blending is another area where the difference between the partially crosslinked polymers used for toners differ from “fully” crosslinked polymers is melt processing. Few “fully” crosslinked resins would be considered for melt processing. The ability to melt process the partially crosslinked resins used in toners is unique. This paper was hopes to explore these properties.

Experimental

The polymer chosen for this study was a commercial resin - Acrybase 1405 which is a styrene / n-butyl acrylate copolymer produced by Polytribo Inc.

The polymer samples were melt kneaded using a Haake System 90 drive unit and a Rheomix 600 batch mixing attachment. The Rheomix 600 employs two counter rotating rotors turning at a 3:2 ratio. The Rheomix 600 was equipped with roller type blades for high shear mixing.

The polymer samples were analyzed for melt index using a Tinius Olsen Extrusion Plastometer operated at 150°C using a 2160 gram test load.

Polymer flow properties were determined using a Shimadzu CFT-500C Flow Tester. The flow tests were run using 20 kilograms of applied force. The test samples were held at 80°C for 5 minutes then the temperature was increased at 0.5°C per minute until the polymer was completely extruded.

Parallel plate rheology was determined using a Rheometrics RMS 800. Samples were melt formed in place between 25 mm plates. Temperature (125 to 150°C) and frequency (0.1 to 100 radians/second) sweeps were then run at 10% strain in the dynamic mode. This data is pending.

Polymer molecular weights were determined using a Waters liquid chromatograph equipped with a refractive index detector. Tetrahydrofuran was the mobile phase and the instrument was calibrated with polystyrene standards.

The amount of insoluble material in a polymer sample was determined using a cold extraction technique. A sample of polymer was mixed with filter aide and toluene, and then shaken for 3 hours. The slurry was then filtered and the cake was dried to determine the amount of polymer retained.

Experimental Design

The experimental program was designed as a statistical experiment using a software package (Design Expert) from Design-Ease Inc. Three factors were chosen for the design: rotor rpm, temperature, and time. Next a range was set for each factor.

Table 1 Design Variables and Ranges

Variable	Low	High
Rotor RPM	70	150
Temperature	150°C	200°C
Time	3 minutes	11 minutes

The software was then used to generate a series of random experiments in which all possible combinations of the factors were tested. Each combination was run in duplicate to gain a measure of the variability. The software then was used to determine which factors produced statistically significant changes in the response chosen. The values of the responses were compared with the inherent error or noise in the system. If the value of the response was greater than the error then it was chosen as a significant point.

Plots of the design values on half normal probability paper illustrates the significance of the results relative to random error. The results of the experimental design indicated that several of the responses tested do indeed show values that were smaller than the noise level. Since these responses produced values for the measured property that could not be distinguished from the noise they were dropped from further analysis. The responses that were eliminated from further consideration were: % toluene insoluble and the Shimadzu viscosity, Eta* (145°C melt viscosity). The remaining responses were analyzed further.

The analysis of the remaining responses showed that there were no multiple factor interactions observed for any parameters in the design.

Results

There were two responses (melt index, and Shimadzu $T_{1/2}$) that showed a dependency on all three design factors. Molecular weight distribution is related to temperature and rpm. The Shimadzu T_{fb} is related to temperature alone. These relations are tabulated in Table 2 below.

Table 2 Correlation of Variables and Responses

Response	RPM	Temperature	Time
Melt Index	yes	yes	yes
% Insoluble	no	no	no
MWD	yes	yes	no
T_{fb}	no	yes	no
$T_{1/2}$	yes	yes	yes
Viscosity	no	no	no

Since this is a three factor design, the results for any response could be plotted three dimensionally on the faces of a cube to give a visual presentation of the data (see Figures 1-4). The following tables present the data as the average value for each face of these cubic plots.

The melt index response is related to all three factors as stated above. One way to highlight the relationships is to compare the averages of the opposite faces of the cubes as seen in Tables 3-6. Temperature exhibits the largest spread in averages indicating that it is a major factor.

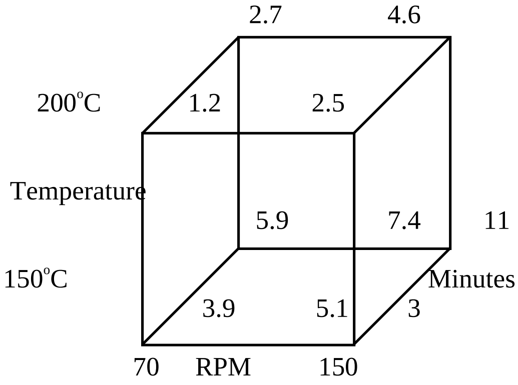

Figure 1. Melt Index as a Function of Design Variables

Table 3 Melt Index as a Function of Design Variables

Variable	Low	High
Rotor RPM	3.4	4.9
Temperature	5.6	2.8
Time	3.2	5.1

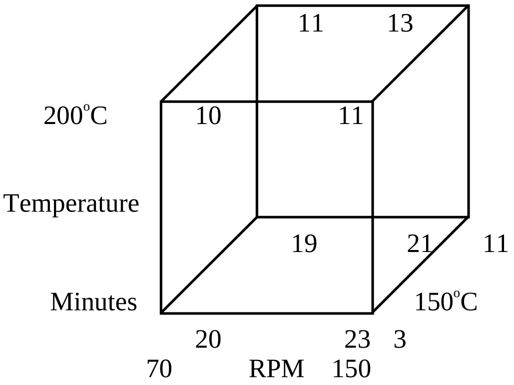

Figure 2. Molecular Weight Distribution as a Function of Design Variables

Table 4 Molecular Weight Distribution as a Function of Design Variables

Variable	Low	High
Rotor RPM	14.5	17.0
Temperature	20.9	10.9
Time	15.8	15.8

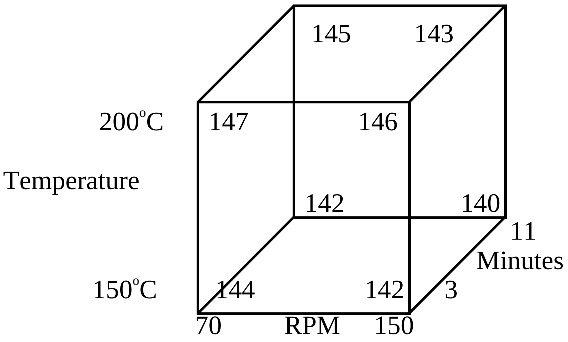

Figure 3. Shimadzu $T_{1/2}$ as a Function of Design Variables

Examining the responses determined for the molecular weight distribution, one sees two important factors : temperature and RPM. Temperature is again the primary variable.

As stated earlier Shimadzu $T_{1/2}$ is dependent on all three design factors. In this case temperature still appears to be the major factor but the difference in effect is smaller than seen in the two examples above.

Table 5 Shimadzu $T_{1/2}$ as a Function of Design Variables

Variable	Low	High
Rotor RPM	14.5	17.0
Temperature	20.9	10.9
Time	15.8	15.8

The final response is Shimadzu $T_{fb.}$ The significant factor related to this response is temperature by the software. This is somewhat questionable since the point representing the temperature is still along the line derived from the normal errors (see slide).

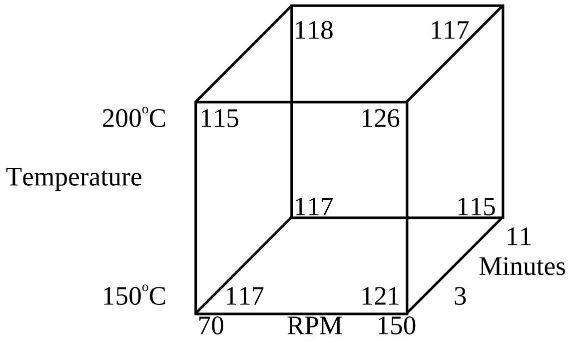

Figure 4 - Shimadzu T_{fb} as a Function of Design Variables

Table 6 Shimadzu T_{fb} as a Function of Design Variables

Variable	Low	High
Rotor RPM	14.5	17.0
Temperature	20.9	10.9
Time	15.8	15.8

Discussion

The experimental analysis of the data clearly shows that temperature is the major factor in the melt relaxation of the partially crosslinked polymer studied. The rotor RPM and time are also factors but of lower impact.

The effects of these factors can be explained after one understands the structure of the polymer. As stated earlier, Acrybase 1405 is a partially crosslinked resin. By cold extraction in toluene 75% of the sample is soluble material. The remaining insoluble portion we call “gel”. Using hot toluene in a soxhlet extraction, we can extract <85% of the polymer as soluble material. Thus, a large portion of this “gel” is not apparently from covalent crosslinks otherwise the soxhlet results would be similar to those of the cold extraction. My picture of polymers represented by Acrybase 1405 is a mixture of some crosslinked polymer along with some branched polymer dispersed in a large amount of linear polymer.

The chromatograms from the GPC analysis (see slide) illustrate the change occurring due to melt blending. In the chromatograph of the unprocessed polymer one peak is observed which contains a high molecular weight shoulder. This would represent the linear and branched portions which were extracted by the THF. After melt processing, a third peak appears at very high molecular weight, which represents the fragments of the crosslinked polymer. The fragments are pieces of the “gel” which have undergone scission of covalent bonds from the melt blending. The mechanism of bond breaking reactions has been described in the literature[1,2] and our results appear to be in agreement. The breakage of bonds below the polymer ceiling temperature can occur by chemical reaction i.e. radical induced scission by oxygen, or by mechanical reaction. The conditions for mechanical breakage have been described by Bueche[1] to favor breakage of chains longer than some critical length which is a function of the shear in the system. Chains smaller than this length remain unbroken. Overlaying the chromatograph (see slide) of the un-melted polymer with one of the melt processed samples clearly shows no change in the low molecular weight portion which suggests that 1405 melt processing is breaking the longest chains as indicated in Bueche’s paper[1].

Temperature exhibits such as strong influence on the melt processing of these polymers due to the relationship between melt viscosity and the shear rate. Low temperatures increase the melt viscosity which increases the shear rate. As the shear rate increases the molecular weight of the largest molecules becomes greater then the critical length and the chains break. High temperatures reduces the shear rate and less chains are broken mechanically. Of course very high temperatures will lead to depolymerization of the chains as well.

The rotor RPM influences the chain scission, since it also contributes to the shear in the system. Higher rotor RPM lead to higher shear rates. Along these same lines one would predict that using different rollers, such as the sigma blades, in place of the roller blades would result in less change in the measured responses, since the sigma blades impart lower shear to the polymer when mixing.

For a system at a high enough shear rate to be above the critical value of the system, increased time of processing increases the probability that all chains above the critical length will be broken. Basically increased time allows the system to come to a steady state.

Conclusion

We have studied the melt processing of a partially crosslinked polymer in a batch mixer. We see that the temperature, rotor speed and time of mixing all influence the responses measured. These observations seem to agree with the theoretical calculations of Beuche[1] who described the mechanical chain breaking of entangled polymers as dependent on the shear rate in the system and a critical molecular weight.

References

1. F. Bueche, *Journal Of Applied Polymer Science*, vol. IV, **10**. pp101-106, (1960).
2. J. A. Odell, A. Keller, and A. J. Muller, *Colliod & Polymer Science*, vol 270, **10**, pp307-324, (1992).
3. Paraloid and Amberlite are registered trademarks of the Rohm and Haas Co., Philadelphia, PA 19040.

Acknowledgments

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Biography

Ed Wilkowski received his B.S. in Chemistry from Saint Joseph’s University in Philadelphia in 1974 and has done graduate work at Lehigh University in Bethlehem, PA. Mr. Wilkowski joined Rohm and Haas Co. in 1974 and for the past 12 years has devoted his energies to polymer development for toners at Polytribo, Inc , a joint venture between Rohm and Haas Co. and Fujikura Kasei. Polytribo is a supplier of polymers and pigment dispersions for the non-impact printing industry.

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