Experiment 11: PVC - Influence of plasticizer content and testing temperature.

Aim: (a) To make "plastisol" compositions (suspension of fine spherical particle of PVC in a liquid like di-octyl phthalate, DOP), in which the PVC/DOP ratio is varied.

(b) To measure the shear-stress-shear rate relation of these plastisol compositions, and thus the viscosity-shear rate relations, using the Bohlin coaxial cylinder viscometer and to determine viscosity as a function of volume fraction of PVC.

(c) To estimate the temperature T_{gel} at which, upon heating, the fluid plastisol turns to a crumbly paste, and the higher temperature T_m at which the opaque crumbly paste becomes transparent.

(d) To form 2" diameter rings of the plastisol compositions by heating in aluminum molds in a heated platen press, at a temperature about T_m.   To test the quenched rings for their elastic response and compare it to that of laboratory vinyl tubing.

(e) To measure the stress-strain-time-temperature response of the rings before, as a function of plasticizer content.

Materials and Apparatus:

 DOP -- Dioctyl phthalate or di-2-ethyl hexyl phthalate
 PVC powder (paste grade resin)
 ZCS - Zinc Cadmium Stearate, the heat stabilizer
 Methanol
 Al weighing dishes
 Glass scintillation vials (20 ml capacity)
 stirring rod
 plastic vials (>10 ml)
 glass containers (disposable)
 Papers and cotton swabs
 Al foil
 Bucket
 Mortar and pestle
 Forceps
 Thermistor probe
 Al molds
 High temp. gloves/pliers

Ring stand

Weighing machine

Vacuum desiccator or vacuum oven + vacuum pump

Bohlin viscometer

Sand bath (dry sand in a stainless steel beaker on a hot plate)

hand held force gauge

Brief Background:

PVC is a vinyl polymer that can be produced with different stereoregularity. The syndiotactic PVC can be particularly crystalline with a very high melting point and hence impossible to process. Thus, stereoregularity of the PVC produced is important. PVC is usually synthesized by either emulsion polymerization (to produce "paste grade" PVC -- very fine particles) or by suspension polymerization (to produce "dry blending" PVC --- larger size particles). The paste grade PVC is particularly useful for "plastisols" which are dispersions of glassy PVC in plasticizing liquids like DOP. The rheological behavior of these plastisols is of particular interest to the PVC processing industry. When the plastisols are heated above the T_g of PVC, the PVC particles become rubbery -------> the diffusion coefficient of DOP into the polymer increases ------> the PVC absorbs the suspending solvent ------> We have a PVC paste with DOP inside it. This paste can then be molded into products at temperatures above the melting temperature of PVC . The resulting polymer product is viscoelastic and hence shows the characteristic property of hysteresis. The more the DOP, the lower the Tg of the resulting PVC.

The properties of a polymer are strongly affected by whether the polymer is isotactic, syndiotactic, or atactic. See Rabek, Section 1.2.4 for more information about tacticity of polymers. For more information about the synthesis of PVC plastisols, refer to the handout from Rempp & Merrill (pp 267-272).

<u>PVC is a semicrystalline polymer</u>:

PVC is a semicrystalline polymer i.e., it has crystalline and amorphous regions within it. Among the other polymers we have studied so far, Nylon was also a semicrystalline polymer. On the other hand, PMMA (plexiglass) and (atactic) polystyrene are not semicrystalline (these have no crystals; they are completely amorphous). Note that only polymers that have crystals can show a melting point (T_m is the temperature at which the crystals melt) whereas all polymers show a glass transition temperature (T_g is the temperature above which segments of the polymer chain exhibit motion). The T_g is always lower than T_m. For example, for PVC, $T_g \sim 100$ C while $T_m \sim 170$ C.

PVC usually shows fringe-micellar crystals as opposed to Nylon, which shows chain folded crystals. Thus you end up with crystals that are "tie points" for the interconnected amorphous regions. When these amorphous regions are plasticized with DOP, their glass transition is lowered to a value below room temperature. This makes the amorphous regions flexible at room temperature. Applied stress results in a tough rubbery mechanical behavior. Heating above the melting point of the crystals results in flow of the entire matrix. See the handout from Rabek, Experimental Methods in Polymer Science, pp443-450 for a description of the two types of crystal morphologies.

The viscoelastic behavior of polymers is strongly dependent upon temperature, especially around the important transition temperatures, Tg and Tm. As a result, there are five "regions" of viscoelastic behavior that are common to most polymers. The behavior in these regions and the locations of the transitions can also be affected by plasticizers. This important behavior is described in more detail in the handout from Sperling, *Introduction to Physical Polymer Science* (1992), pp309-319.

Precautions:

1)   Use vinyl or nitrile rubber gloves

Procedure:

Parts A through C should be completed in Day One; Day Two will involve Part D.

A. Plastisol preparation:

1.   Make three identical master batches (of the following composition), one after the other, using the same mortar and pestle (note ZCS is a heat stabilizer). Each batch will be used for a different part of the experiment (Parts B-D).

Master batch composition	wt%	Master batch preparation
ZCS 1 g	3%	1) First weigh out ZCS in Al dish,
DOP 13 ml (12.7 g) (ρ=0.90732)	38%	2) then, add DOP to it, stir, mix, transfer to mortar.
PVC 20 g (14.4 net ml) (density of PVC = 1.39 g/ml)	59%	3) Then add PVC slowly while mixing.

2.   Grind the initial PVC-DOP-ZCS mixture in mortar until fluid. No powdery PVC should remain. Divide each of the three master batches into four equal portions. Transfer approximately 8.25 g (but note the exact amount transferred) of each master batch into glass scintillation vials (20 ml capacity).

3.   For each batch, add additional DOP to each of the scintillation vials according to the table below to get compositions α through δ of four different volume fractions of PVC. The amounts shown below are for the case where 8.25 g of master batch are used. If the amount of plastisol used by you is different, then calculate the corresponding amount of DOP to be added to get the same volumetric fractions of PVC given below.

<div align="center">Table: Recipes</div>

Plastisol composition	Master batch	Add. DOP	Volume fraction PVC
α	8.25 g	none	ϕ_α = 0.51
β	8.25 g	1.1 ml	ϕ_α = 0.44
γ	8.25 g	2.2 ml	ϕ_α = 0.39
δ	8.25 g	3.3 ml	ϕ_α = 0.35

4.   The DOP added to the scintillation vials should be mixed in well by stirring rod.

5.   Thus we should have three sets of vials. Each set of four vials shall consist of four different plastisol compositions, α - δ. The first set of vials should be placed under vacuum in a vacuum desiccator or vacuum oven (not heated) to remove entrained air for part D. The other two sets will be used for part B and C and do not need to be placed under vacuum.

B. Bohlin viscometer: Shear stress-shear rate vs. composition

1.   We have about 8 ml of sample for each composition. Place this in a "sawed-off" plastic vial, the capacity of which is about 10 ml. Then lower the Bohlin viscometer into the vial. Place a weighing dish under the vial to collect the overflow. The bottom of the cylinders should be just clear of the bottom of the vial to fill the gap between the cylinders.

2.   Start with pure DOP as the control, because we will be seeking to find the relative viscosity (viscosity paste/viscosity DOP) as a function of the volume fraction PVC. Record the (room) temperature at which you carry out these experiments. Then run the same experiment for compositions α-δ. After each run, i.e., DOP, α-δ , pour out the paste as much as possible into a common metal or glass discard container, wipe out the cylinders with paper and/or cotton swabs, then introduce the next sample. You may find that a few ml of methanol will aid in cleaning up the cylinders. Be sure to dump methanol rinses in a methanol waste bottle, NOT the container used for undiluted plastisol.

C. Temperature response of plastisol:

1.   This will not be an exact experiment. You will have a sand bath, i.e., dry sand in a stainless steel beaker on a hot plate. The temperature of the sand bath should be about 180-200 C. (Be careful. Hot!)

2.   Hold your vial (containing α–δ) with forceps, and immerse it halfway in the hot sand. Use the probe of your thermistor to mix and stir the sample. Record the temperature at which it turns to a crumbly, non-fluid gel, still opaque.

3.   Continue heating until the contents become transparent. This will happen at the wall first, so position the thermistor next to the wall.

4.   After these measurements are made, the vials are discarded in glass trash.

D. Forming rings for tensile property evaluations ("Fluxing")– To be done on Day 2

1.   You will use the aluminum molds previously used for making rubber rings by evaporation of latex. Each team has one mold. Pour your plastisol which has been under

vacuum into the circular slot. Avoid trapping air bubbles. Avoid overfilling. Place aluminum foil on top.

2.   Place in Carver press, with platens at 350 F. Close press. Develop slight gauge pressure. After 30 seconds to 60 seconds, open press (lower the bottom platen). Remove the hot mold (Careful! Hot!) with pliers. Under no conditions should you grab the mold by hand. Drop the mold into a bucket of cold water. When cool, remove, pull off foil, pry out fused ring.

E. Tensile property evaluation

1.   Experiments at room temperature: At room temperature (record it), pull each of your rings ($\alpha-\delta$) until the maximum force (2.5 lb) is reached on your hand-held meter. Read the strain $\Delta L/L_o$ produced by that force as accurately as possible. Maintain that strain $\Delta L/L_o$, whatever it is, and record the force as a function of time for 15 minutes.

2.   Experiments in the cold: Place your ring ($\alpha-\delta$) in ice water for 2 minutes. Then, keeping it cold with a wet towel, or under ice cubes, pull it to a maximum tensile force of 2.5 lb. Record the strain (to the best of your ability).

3.   Experiments at around 60C:

        a) Measure temperature and record. Set up ring in stand, with hand held tensile force gauge connected to PVC-DOP ring by a wire around 6" long. Connect lower end of ring stand clamp. Raise upper ring stand clamp, or trim connecting wire until gauge shows 2.5 lbs force. Record strain.

        b) Slowly pour the hot water over the DOP-PVC ring and record the force gauge load with time, every 5 seconds, until you run out of hot water. If this were an "ideal" rubber, the force would go up. Does it?

4.   If you have the time, determine the % of strain recovery on release for the PVC as a function of strain. Is there any permanent (unrecovered) deformation?

Observations and Calculations:

1.   Tabulate the torque and RPM (tested at various RPMs) for each of the recipes (Part B of the experiment).

2.   Record visual observations at different temperatures for part C.

3.   Part E: For each of the recipes,

        a) Record elongation at 2.5 lbs force for 0 C, room temperature and 60 C.

        b) Record relaxation of stress with time at room temperature.

        c) Record changes in stress at fixed strain as temperature is changed.

4.   The raw data for part B should be processed as you did in experiment 2.

5.   The raw data for part E should be processed as into plots of stress and elastic modulus vs temperature, to show the viscoelastic (glassy or rubbery) behavior of the plastisol.,

Discussion:

1.   Do you see differences in the mechanical behavior of the plastisols with differing amounts of plasticizer?   Describe these differences, and why you see them.

2.   Do these materials follow the expectations of ideal rubber elasticity, including the thermoelastic behavior? Why or why not?   Explain what you expect to see in these materials, and how they differ from the crosslinked natural rubber bands in terms of mechanical behavior.