The Rheology and Adhesion of Magnetic Monocomponent Toners

Derek E. Wilson and J. Patrick N. Haxell
Coates Electrographics, Bath, England

Abstract

Many previous rheological studies of molten toners have been confined to non-magnetic systems comprising polymer blends with relatively small amounts of pigmentary colourants. A series of more heavily pigmented, monocomponent magnetic toners were measured in oscillation, creep and flow modes and it was found that no one single rheological parameter could be assigned to account for the fuse-fix-release properties. Rather, all these techniques relate to different aspects of the toner fixing process.

Introduction

Photocopier and laser toners comprise intimate blends of thermoplastic acrylic or polyester polymers and pigments plus charge control agents and almost invariably radiant heat or hot rollers are used to melt and fix the plastic toner powders to the printed sheet.

There is a considerable body of literature dealing with the fusing and fixing of two-component powder electrophotographic toners. In a much cited paper, Lee[1] described the main stages of fixing as

a. coalescence by sintering,
b. the subsequent spreading of the molten drop
c. penetration into the paper fibres.

The primary factor controlling the radiant fusing of these toners was shown to be the melt viscosity which itself was a strong function of the temperature.

Since then, a number of further studies have examined the rheological factors involved in Hot-Roll fusing. In a seminal report, Forgo[2] et al refer to the complex relationships between the polymer's molecular architecture and the final toner's viscoelastic behaviour and its influence on the toners fusing performance. Forgo described the use of 6.4 Hz oscillation in an attempt to account for carbon black pigmented toner fusing windows and found a strong relationship between 'tan delta' (the ratio of viscous/elastic response) and the width of the fusing window. A typical 2 component toner contains 4-10%wt of carbon black (corresponding to a pigment volume concentration (pvc) of the order of 2.5-6.5 %).

Magnetic, monocomponent toners are widely used in laser printers and are frequently hot-rolled fixed. They differ from the previously mentioned systems in that they contain significant quantities of sub-micron electrically resistive magnetic oxides (30-45 wt%, 10-17.5% pvc) melt blended into a thermoplastic polymer vehicle. Frequently, the polymeric vehicle is itself a complex blend of molecular weights, distributions and cross-linking to achieve a satisfactory balance of fusing properties and it normally contains an incompatible, low melting polyolefin that forms an additional release layer against the hot fuser roller.

Whilst the literature is replete with rheological descriptions of the behaviour of pure, molten polymers e.g., Ferry[3], (and apart from the patent literature), very little exists on the technically challenging subject of these pigment filled, incompatible wax containing magnetic toners.

It is the object of this short note to describe the use of a controlled stress rheometer in the development of such toners and to show that different rheological test protocols are necessary to characterize different aspects of the fusing process.

Experimental

Trial toners were prepared by melt-blending and dispersing selected acrylic copolymers with sub-micron iron oxide and a low-melt viscosity anti-offset agent and minor quantities of charge-control agents. The polymers were picked to represent a range of visco-elastic properties typically used in the toner industry and varied from low melt viscosity, low molecular weight (e.g., polymer E) to highly viscous, highly visco-elastic and crosslinked (e.g., polymer D).

After cooling, the solidified masses were converted to toner by air grinding, classification and finally were dry blended with small quantities of external amorphous silica flow additives.

Table 1. General Toner Polymer Properties

Polymer	Molecular Weight	Polydispersity	Gell Content	Tan Δ
A	High	Narrow	Nil	5.6
B	Medium	Narrow	Nil	11.4
C	Medium	Narrow	–50%	1.0
D	Medium	Narrow	~70%	0.3
E	Low	Wide	Nil	19.0
F	Medium	Bimodal	Low	8.4
G	Medium	Wide	< 5%	1.7

The toners were functionally print tested in a laser printer and the fusing assessed using both an adhesive tape pull-off and a crease test. The fuser was set to run at 165-175°C with a hard PTFE roller on the printside and a softer, silicone rubber roller on the reverse. The 6mm nip

Table 2. Experimental Toner Formulations

Material	Toner 1	Toner 2	Toner 3	Toner 4	Toner 5	Toner 6	Toner 7
magnetic oxide	35	35	35	45	45	45	45
Poly A	12		16				27
Poly B	21.5	33.5	21	27	21		
Poly C	21.5	21.5					
Poly D			21.4		6		
Poly E						15	
Poly F						15	
Poly G				16	16	15	16

* All these toners contained 5% anti-offset agent within the polymeric matrix.

width corresponded to a fuser contact time of 0.06 sec at a pressure of approximately 30000 N/m^2.

In addition, the fusing latitudes were examined between 120-220°C in an off-line fuser rig.

The rheological properties were assessed on a Carrimed CSL 500 controlled stress rheometer with a 4 cm parallel plate geometry at temperatures between 100-220°C. Heating was supplied by a PRT controlled RF heating coil around the plates.

Samples were prepared for the rheometer by loading predensified (gentle sintering) pellets between the 2mm plate gap.

There was concern that the low melt viscosity polyolefin would lubricate the plates and cause erroneous results. Use of vertical TiO_2 painted stripes were used as visual "streamlines". No slippage could be detected.[4] Use of a high temperature serrated plate gave results near identical to the plane plates, which again confirmed the lack of slippage.

The rheometer was used in three different modes:

a. A 150°C isothermal stress sweep to examine the toners' responses to increasing stresses and strain rates.

b. 0.01 and 10 Hz, low amplitude (0.005 strains) temperature sweeps (100-220°C). These tests probed the toners "rest state" structures without breaking the microstructural features that these complex, heterogeneous materials almost certainly contain.

c. A series of creep tests were made at 150°C. In addition to the steady state viscosity, the creep tests gave data on the contributions from the viscoelastic elements and therefore the data was resolved into the so-called Voigt units in which the materials were considered to be combinations of springs and dashpots, each with their characteristic relaxation times and viscosities.

Results and Discussion

a) Low Frequency Oscillation Applied to Toner Adhesion Strength

Three toners (1,2,3) were evaluated at both .01 and 10 Hz in low amplitude oscillation temperature sweeps and assessed for fixing on a range of papers. Figure 1 shows the very marked differences in the dynamic viscosity at 0.1 Hz whereas at 10 Hz, the properties were near identical. At 0.01 Hz, the longer relaxations characteristic of toner flow are emphasized and the values obtained tend toward the zero shear rate values that characterize a polymer's viscosity and molecular weight.

The dynamic viscosity η′ was plotted against the tape adhesion results (see Fig. 2). Assuming that the fixing strength is proportional to the toner penetration depth into the paper fibers[1], the following relation should hold;

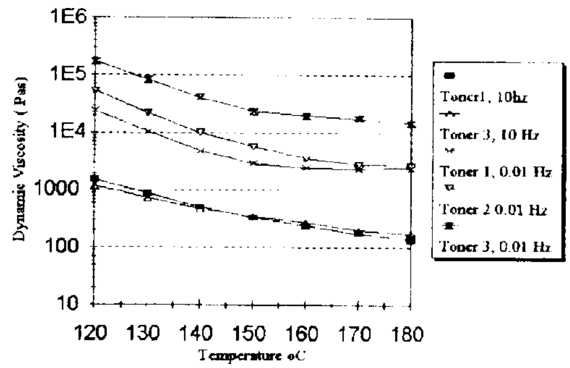

Figure 1. Oscillation-temperature sweep at 0.01 and 10 Hz.

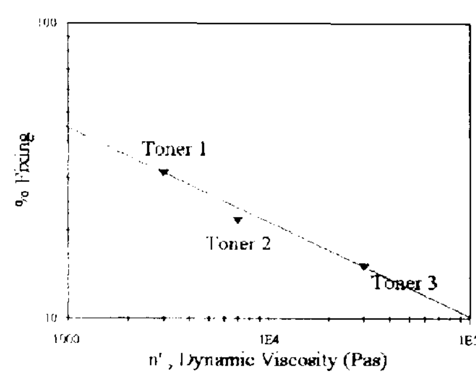

Figure 2. Fixing vs dynamic viscosity at 0.01 Hz. at 150°C

$$Z = (\gamma wt/A\eta)^{0.5}$$

where

Z = penetration depth
Y = surface tension
w = capillary width
t = time
A = pore shape factor
η = viscosity

which suggests that $Z = K(\eta)^{-0.5}$

Table 3. Relation between the flow, creep and oscillation properties of some mono-component toners.

	Toner 4	Toner 5	Toner 6	Toner 7
Critical Yield (Pa)	100	700	300	200
Zero Shear η (Pas)	850,000	3,330,000	8,500,000	110,000
Upper Shear η (Pas)	8,500	9,000	12,000	12,000
Relaxation times of Voigt units (seconds)	None	242 20 (primary)	269 23 (primary)	473
	viscous only	viscous and 2 elements	viscous and 3 elements	viscous and 1 slow element
Newtonian Creep Viscosity (Pas)	11,010	902,400	1,368,000	28800
Tan Δ (10 Hz)	1.05	0.86	0.81	0.81
Tan Δ (0.01 Hz)	0.75	0.56	0.33	1.1
Fusing Window (°C)	30	50	40	40
Offset (duplex)	worst	best	second best	third best

In Figure 2 the general form implies the slope of the graph is nearer –0.3 rather than the theoretical –0.5. This suggests that the toner penetration and flow into the paper pores was affected by the presence of the magnetic pigment as previous work reported by Satoh[5] et al. on carbon black/polyester toners showed an excellent agreement with the theory.

b) The Relationship Between Creep, Flow and Oscillation Data

Toners 4, 5, 6, and 7 were run in controlled stress sweep and creep modes at 150°C to compare against their fixing and release properties. In addition, oscillation temperature sweeps were made to observe if the relation noted by Forgo et al. and Ekong[6] that the fuse-fix window of twocomponent toners is dominated by the tan delta value also applied to these monocomponent magnetic toners.

It was believed that the presence of the dense, larger particle size magnetic oxide at a higher pigment volume concentration could affect the results and therefore follow a different relationship to the more lightly pigmented two component toners.

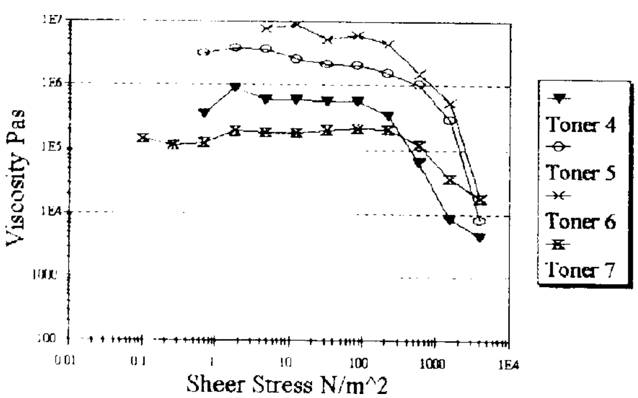

Figure 3. Flow Rheology at 150°C

From the flow results, Fig. 3, the toners were in two groups. Toners 4 and 7 containing lower quantities of the visco-elastic polymers exhibited lower critical yield stresses where the viscosity dropped to an upper Newtonian region. This upper viscosity of around 10000 Pas appeared to plateau at a higher level than toners 5 and 6.

Analysis of the creep curves revealed the viscoelastic elements within these four toners. See Table 2, Toners 5 and 6 clearly contain visco-elastic elements with short retardation times originating from their content of polymers D and E, but polymer A in toner 7 is probably responsible for its long, slow relaxation time, its very high fusing temperature and its narrow fixing window. Toner 4, with its very low stress yield point and low content of viscoelastic polymer, appeared to behave as a purely viscous fluid, devoid of elastic behaviour and it too exhibited a very narrow fixing window.

There appears to be no clear correlation between the Tan Δ values and the fuse-fix behaviour. There does seem to be a link between the greater elastic responses of Toners 5 and 6 as indicated by the nature of their Voigt units and the (flow) critical yield stresses, and their greater fusing windows.

However, it should be noted that the practical behaviour of these toners was only partly reflected in the low amplitude oscillation data results and it is believed that the origin of this deviation is due to the difference between the oscillation test method protocol, in which the oscillation is normally conducted in the linear viscoelastic region (LVR) and the "real -life" situation in the printers user roller system where the toner is deformed well beyond its elastic limit and the LVR. In contrast, both the creep and the flow tests tend to "stretch" the internal structures of the monocomponent toners beyond their elastic limits therefore perhaps model the behaviour in a more realistic manner.

It is not obvious from these results that Tan Δ or the Newtonian viscosity or any other parameter is responsible in isolation for the control of the fixing and fusing process. Rather, it is the combination of the results that have to be considered and interpreted.

Conclusion

In this report, an attempt has been made to show the correlation between the theological properties of polymers, and toners measured in different protocols and the toners practical fusing performance. The importance of using an appropriate test regime to simulate the actual fusing condition was demonstrated and it was shown that creep, oscillation and flow measurements all can contribute to the characterization of the fixing of a monocomponent, magnetic toner,

Acknowledgment

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