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#### **Publisher's version / Version de l'éditeur:**

<https://doi.org/10.1163/156856194X00177>

*Journal of Adhesion Science and Technology*, 8, 5, pp. 473-484, 1994

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## Swelling and adhesion characteristics of lignin-filled polyurethane sealant

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Revised version received 1 November 1993

**Abstract**—Previously, polyurethane (PU)–lignin polyblend sealants from the point of view of adhesion to various substrates, morphology based on scanning electron microscopy, and miscibility based on differential scanning calorimetry (DSC) and <sup>13</sup>C nuclear magnetic resonance (NMR) were studied. In this study the same polyblends together with PU filled with a few mineral fillers were used. Swelling tests were applied to establish the number average molecular weight between crosslinks of the PU and to assess the degree of interaction between various fillers including different types of lignin and the PU matrix. Lignins were found to restrict less the degree of swelling of PU than that by the Sillitin (siliceous clay)-Titanox TiO<sub>2</sub> 3.17:1 wt/wt mixture. Data based on the swelling method show that lignins do not interact with the elastomer matrix to as great an extent as Sillitin/Titanox filler mixture, a finding which is in good agreement with the former DSC and NMR results.

**Keywords:** Swelling; adhesion; lignin; polyurethane sealant.

### 1. INTRODUCTION

Previously it was shown that polyurethane (PU)-based sealants, when blended with Kraft lignin, have tensile properties superior to those of the unblended elastomer [1]. Such sealants were tested in a detailed programme where lignin–sealant polyblends with up to 20 parts by weight (pbw) lignin were supplied to substrates such as aluminum, mortar, and wood, and subjected to different weathering conditions. The results of tensile tests showed that, generally, lignin acts as a reinforcing agent which adds rigidity to the elastomer matrix, as indicated by the increase in the modulus of blended sealants with the addition of lignin.

The results of these studies also showed that lignin when incorporated in such polymeric systems acts as a reinforcing filler in the two-phase polymeric particulate system. Evidence of phase separation was obtained through studies of the morphology of a PU-based sealant modified with lignin using scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) [2]. The latter technique indicated that the two polymers are immiscible. Similar conclusions were drawn from studies using solid-state high-resolution <sup>13</sup>C-NMR [13].

In this study swelling tests were used to determine the number average molecular weight between crosslinks ( $M_{c,s}$ ) of various elastomer formulations and to assess the

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degree of interaction between the various particulate fillers including different types of lignin and the elastomeric matrix.

## 2. EXPERIMENTAL

### 2.1. Materials

For the control PU formulation the following components were used: isocyanate prepolymer, polyol prepolymer, catalyst and solvent, molecular sieve, plasticizer, antioxidant, and filler.

Tables 1 and 2 present the prepolymers, used in this research project. The catalyst was a mixture of lead octoate (24% Pb) and calcium octate (5% Ca), and the solvent was a naphthalene derivative (Solvesso 100, Esso Canada). The molecular sieve was compounded from an alkali alumino-silicate dispersed in castor oil (50% by weight) (Baylith L paste, Bayer Canada) having a density of 1.25 g/cm<sup>3</sup> and a water absorption capacity of 10% (wt).

**Table 1.**

Physical and chemical properties of isocyanate prepolymers

Structure	Trade name	NCO content (%)	Density (at 20 °C) (g/cm <sup>3</sup> )	Viscosity (at 20 °C) (mPa s)	EW <sup>a</sup> (g)	<i>f</i> <sup>b</sup>	<i>M<sub>n</sub></i> (g/mol)
MDI <sup>c</sup> polyisocyanate prepolymer	Desmodur VL <sup>d</sup>	30	1.22	130	160	—	—
MDI <sup>c</sup> polyisocyanate prepolymer	Mondur XP 743 <sup>d</sup>	8	1.16	3000	525	2	1050
TDI <sup>e</sup> diisocyanate prepolymer	Desmodur E 14 <sup>d</sup>	3.5	1.05	8500	1200	2	2400

<sup>a</sup>EW = Equivalent weight.

<sup>b</sup>*f* = Functionality.

<sup>c</sup>MDI = 4,4'-diphenyl methane diisocyanate.

<sup>e</sup>TDI = Toluene diisocyanate.

<sup>d</sup>TDI = Produced by Bayer Co. Canada.

**Table 2.**

Physical and chemical properties of polyol prepolymers

Structure	Trade name	OH content (%)	Density (at 20 °C) (g/cm <sup>3</sup> )	Viscosity (at 20 °C) (mPa s)	EW (g)	<i>f</i>	<i>M<sub>n</sub></i> (g/mol)
Branched polyether	Desmophen 550U <sup>a</sup>	11.5	1.01	600	148	—	—
Branched polyglycol having ether and ester groups	Desmophen 1140 <sup>a</sup>	8	1.04	1400	215	—	—
Branched polyglycol having ether and ester groups	Desmophen 1920D	5	1.01	3500	340	—	—
Branched dispersoid grade polyether	Desmophen 1920D	0.85	1.08	3300	2000	3	6000

EW = Equivalent weight; *f* = functionality; *M<sub>n</sub>* = molecular weight (number average).

<sup>a</sup>all products are those produced by the Bayer Corporation, Canada.

Data from Bayer Technical Publication No. LS 44399e (4.83 ed.), Bayer A.G., L.S. Group, Leverkusen, Germany, 1983.

An alkyl phenol sulphonic ester (Mesamoll, Bayer Canada) having a density of  $1.03 \text{ g/cm}^3$  and a viscosity of 95–125 mPas and butyl phthalate (Santicizer, Bayer Canada) with a density of  $1.11 \text{ g/cm}^3$  and a viscosity of 2.12 mPas were used as plasticizers. 2,2-Methylene-bis(4-methyl-6-tert.-butylphenol) (Vulcanox BKF, Bayer Canada) was the antioxidant.

The molecular sieve acts as a sponge to absorb excess moisture from hydrophilic polyols and from the surface of fillers. Free surface moisture is the cause of bubble formation in elastomers due to the reaction of water with isocyanates which produces  $\text{CO}_2$ . Bubble formation, although not itself detrimental to the overall strength of the resulting elastomer, is not considered advantageous from the point of view of forming products with predetermined properties.

In some cases, inorganic fillers were replaced by Kraft lignin to obtain polyblends of PU–lignin. The following types of Kraft lignin were used: Tomlinite (TO), Indulin AT (AT), and Eucalin (EU).

## 2.2. Procedure

**2.2.1. Compounding formulations. Unfilled PU:** The hygroscopic nature of the isocyanate and polyol prepolymers necessitated that precautions be taken with respect to the storage of materials and the level of moisture present while blending the components. For this purpose, a double-size glove box was used in which all moisture-sensitive chemicals were stored and formulations were prepared. A two-step procedure was used to ensure a dry atmosphere in the chamber; a positive pressure was maintained using dry nitrogen (purged of moisture by passage through a packed column of desiccant), so that the moisture-laden air could not enter, and a bed of desiccant was placed in the bottom of the chamber to absorb any traces of moisture present in the nitrogen atmosphere.

Various unfilled formulations were prepared in order to study the change in thermal and mechanical properties as a function of three parameters: the stoichiometric ratio (SR), the plasticizer content (PC), and the Baylith paste–polyol ratio (BPR).

The stoichiometric ratio refers to the molar ratio of active components, namely, the ratio of active isocyanate to hydroxyl groups. The plasticizer content is measured in relation to the amount of polymeric components [polyether, toluene-2,4-diisocyanate (TDI) and Baylith paste] in the formulation on a wt% basis. The polyol ratio refers to the molar ratio of hydroxyl groups provided by the Baylith paste (which contains 50 wt% castor oil) to that provided by the primary polyol.

Formulations were blended by weighing individual components and stirring these manually for 3 min after each component had been added. The order of mixing of these components was as follows: (i) polyol prepolymer, (ii) Baylith paste, (iii) plasticizer, (iv) isocyanate prepolymer, (v) catalyst and solvent. Blended formulations were then poured into the various moulds. The cast elastomers were permitted to cure in the glove box at room temperature for at least 24 h, depending on the rate of cure of the system, after which they were allowed to complete their curing process in standard laboratory conditions ( $25^\circ\text{C}$  and 50% relative humidity). The curing process was monitored on a regular basis using hardness tests.

**Filled PU:** The use of fillers results mainly from the requirement for certain physical properties. With suitable fillers, the modulus of elasticity can be increased over a greater temperature range; stability and heat distortion can be increased; and the thermal expansion coefficient can be decreased.

**Table 3.**

Physical properties of inorganic particulate fillers

Type	Trade name	Specific gravity	Specific surface area (m <sup>2</sup> /g)	Average particle size (μm)	Oil absorption (g/100 g)	$\phi_m^a$
Ground silica <sup>b</sup>	Sil-co-Sil #400	2.65	0.6	7.4	33	0.52
Silica/kaolin <sup>c</sup> (Al silicate)	Sillitin Z86	2.60	12	1.35	45–55	0.42
Titanium dioxide <sup>d</sup>	Titanox 2101	4.00	10	0.3	25	0.48

Chemical analysis of inorganic fillers

Filler type	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	LOI <sup>e</sup>
Ground silica	99.8	0.015	0.047	0.013	< 0.01	0.01	0.09
Al silicate (ST)	80.5	0.7	12.5	0.7	0.5	0.5	3.6
Titanium dioxide	—	—	—	92	—	—	8

<sup>a</sup> $\phi_m$  = Maximum packing factor.<sup>b</sup>Ottawa Industrial Sand Co., Ottawa, Canada.<sup>c</sup>Hoffman Mineral, Franz Hoffman & Sehne KG, Neuburg/Donau, Germany.<sup>d</sup>NL Chem Canada Inc., Montreal, Canada.<sup>e</sup>LOI = Loss on ignition.**Table 4.**

Physical characteristics of organic particulate fillers

Filler type	Name	Specific gravity	Specific surface area (m <sup>2</sup> /g)	Average particle size (μm)	pH	Oil absorption (g/100 g)	$\phi_m^a$
Kraft lignin–eucalyptus wood	Eukalin <sup>b</sup> (EU)	1.379	—	10.5 <sup>c</sup>	9–10	40	0.63
Kraft lignin–softwood	Indulin AT <sup>d</sup> (AT)	1.238	1.5	8	6.5	85	0.471
Kraft lignin–hardwood	Tomlinite <sup>e</sup> (TO)	1.295	0.7	16	6	74	0.49

<sup>a</sup>Maximum packing factor.<sup>b</sup>Empresa Nacional de Celulosas, S.Q., Madrid, Spain.<sup>c</sup>Estimated visually from photomicrographs of EU particles.<sup>d</sup>Westvaco, Chemical Division, Charleston, SC, USA.<sup>e</sup>Domtar Corporation, Cornwall, Ontario, Canada.

The various particulate fillers used in this study are given in Tables 3 and 4, which also list the respective properties relevant to the formulation of elastomeric sealants.

The preparation of filled formulations required two additional steps in comparison with the formulation procedure used for preparing unfilled specimens. The particulate matter was dried in a forced air oven at 105 °C for 24 h and then allowed to cool to room temperature in a desiccator. The dried matter was then dispersed in the plasticizer in appropriate proportions, using a high-speed disk dispenser operating at 5000–6000 rpm. The dispersion process continued until a uniform paste was obtained.

The amount of fillers used when compounding the various specimens was varied from 5 to 15% v/v. The mixing order for filled formulations was the same as that for

unfilled ones with the exception that the dispersed phase was added, whereas in the case of unfilled formulations plasticizer was required.

### 2.3. Characterization of fillers

Fillers were characterized in terms of particle size and size distribution, maximum packing fraction, oil absorption, and specific gravity. An estimate of the various size filler types was established from a series of colour and monochrome photomicrographs taken with an Olympus model BHM reflected bright-field incident light microscope, using magnifications of 50 $\times$ , 100 $\times$ , and 500 $\times$ . The particle sizes were measured directly from the photomicrographs. The particle size distribution of particulate fillers was determined in accordance with ASTM D3360 and ASTM D422. The method uses the sedimentation technique as a means of obtaining a particle size distribution curve.

Fillers, when incorporated in a rubbery matrix, always increase the modulus of the composite and the extent of the increase is essentially dependent on the packing characteristics of the filler particles [4]. The packing characteristics of a filler may be determined using the methods described by Patton [5], in which the packing factor is related to the absorption of wetting liquid by a filler in the following manner:

$$\phi_m = \frac{\frac{100}{\delta_f}}{\frac{OA}{0.935} + \frac{100}{\delta_f}},$$

where  $\phi_m$  is the maximum packing factor, OA is the oil absorption (g/100 g), and  $\delta_f$  is the density of filler (g/cm<sup>3</sup>).

The technique described in ASTM D281, referred to as the spatula rubout method, is commonly used to determine the value of OA of a given filler. In this method, the weight of linseed oil taken up by a given weight of dried filler, in sufficient quantity to form a required paste, provides a value of OA.

OA values were determined for Sil-co-Sil (silica), Titanox (titanium dioxide), Tomlinite (hardwood Kraft lignin), Indulin AT (softwood Kraft lignin) and Eucalin (eucalyptus Kraft lignin) fillers. These results, together with the corresponding values for the maximum packing fraction, are given in Tables 3 and 4. They are based on an average calculated from at least ten determinations. Included in these tables are the results (average data of at least six determinations) of the specific gravity established according to ASTM D153.

### 2.4. Swelling tests

Swelling tests were used to determine the number average molecular weight between crosslinks ( $M_{c,s}$ ) of the elastomer obtained with different formulations and to assess the degree of interaction between the various particulate fillers and the elastomeric matrix.

It is known that a three-dimensional network of polymer chains will swell in the presence of a non-reactive solvent, in which the long chain portions (soft segments) are extended in proportion to the amount of solvent present in the polymer [6–8]. An elastic retractive force opposes the swelling such that after a limited time of immersion in the solvent (e.g. 5–10 days), the swelling reaches an equilibrium point (i.e. equilibrium between the attractive forces and those causing swelling is attained). The

theory developed by Flory and Rehner [8] indicates that the molecular weight between crosslinks is inversely proportional to the elastic forces at equilibrium. This may be expressed as

$$\frac{\delta}{M_{c,s}} = \frac{\phi_{p,s}^{1/3} \sigma}{RT(\alpha - \alpha^{-2})},$$

where  $\delta$  is the density (g/cm<sup>3</sup>);  $M_{c,s}$  is the number average molecular weight between crosslinks (g/mol);  $\phi_{p,s}$  is the volume fraction of polymer in the swollen sample;  $\sigma$  is the force per unit area (of the unswollen sample) required to deform the sample to the deformation ratio,  $\alpha$  (MPa);  $\alpha$  is the deformation ratio ( $= dh/h_0$ );  $h_0$  is the height of the unswollen disk (cm);  $R$  is the universal gas constant (82 057 cm g/K mol); and  $T$  is the absolute temperature (K).

The method adopted by Damusis *et al.* [9], based on the work undertaken by Cluff *et al.* [10], was used to determine the elastic properties of the swollen polymer. Cylindrical disks [height = 12.5 mm (0.5"); diameter = 32 mm (1.25")] were swollen in toluene until equilibrium was attained, after which they were subjected to compression load–deflection measurements while immersed in solvent. An Instron Universal Testing machine operating at a crosshead speed of 0.1 mm/min was used to obtain the load–deformation curve. The slope of the linear portion along the curve was used to evaluate the number of effective network chains per unit volume,  $\nu_e/V$ , based on the equation

$$\frac{\nu_e}{V} = \frac{h_0 S}{3a_0 RT} = \frac{\delta}{M_{c,s}},$$

where  $\nu_e/V$  is the number of effective network chains per unit volume;  $h_0$  is the height of the unswollen disk (cm),  $S$  is the slope of compression load–deflection curve (g/cm),  $a_0$  is the cross-sectional area of the disk (cm<sup>2</sup>),  $R$  is the universal gas constant (82 057 cm g/K mol),  $T$  is the absolute temperature (K),  $\delta$  is the density of the polymer (g/cm<sup>3</sup>), and  $M_{c,s}$  is the number average molecular weight between crosslinks (g/mol).

An average value of the slope obtained from three specimens was used to calculate the required data. For the different formulations used in this study, the slope of the compression load–deflection curves varied in the range of 4.73–8.32 kg/mm.

The swelling for a large number of elastomers containing reinforced fillers has been found to obey an equation of the form [11]

$$\frac{\nu_{ro}}{\nu_r} = 1 - \frac{\phi_f}{1 - \phi_f} [3C(1 - \nu_{ro}^{1/3}) + \nu_{ro} - 1],$$

where  $\nu_{ro}$  is  $\nu_r$  of the unfilled elastomer;  $\nu_r$  is the volume fraction of elastomer in the swollen specimen;  $\phi_f$  is the volume fraction of filler in the filled elastomer; and  $C$  is a constant, which is characteristic of the filler (but independent of the polymer, solvent, or degree of crosslinking).

The data suggest that the restrictions in swelling depend, to a fair degree of approximation, only on the filler and the extent to which an otherwise identical unfilled elastomer will swell. This further suggests that the restriction of swelling depends only on the fact that a firm bond between the elastomer and filler is established, and does not depend on the number and strength of the individual linkages.

### 3. RESULTS AND DISCUSSION

The particle size distribution curves for fillers used in this study are given in Fig. 1. The curves for silica, Tomlinite, and Indulin AT were obtained using the sedimentation technique. The particle size distribution for both the Titanox and Sillitin Z86 fillers were obtained from the literature [12, 13]. The curve describing the particle size distribution for the Titanox–Sillitin Z86 mixture was calculated based on the particle size distribution curves of each component taking into consideration the weight ratio of components in the mixture (Titanox: Sillitin: 7 g: 22.2 g).

Based on these particle size distribution curves, the average equivalent spherical diameter for each filler series is equal to the particle diameter at the midpoint of the distribution (i.e. at 50% finer than) (Table 5).

An estimate of the specific surface area can be made based on the particle size distribution curve according to the method developed by Gates and described by Ferrigno [4]. The area beneath the curve represents the specific surface area. Hence the specific surface area is given by

$$SA = \frac{Q}{\delta_f} \left( \sum \frac{dW}{X_m} \right),$$

where SA is the specific surface area ( $\text{m}^2/\text{g}$ ),  $Q$  is a proportionality constant,  $dW$  is the weight increment (g),  $\delta_f$  is the density of the filler ( $\text{g}/\text{cm}^3$ ), and  $X_m$  is the average particle size ( $\mu\text{m}$ ).

The proportionality constant is applied because the computational values are based on the areas of equivalent spheres and hence a correction must be made to take into

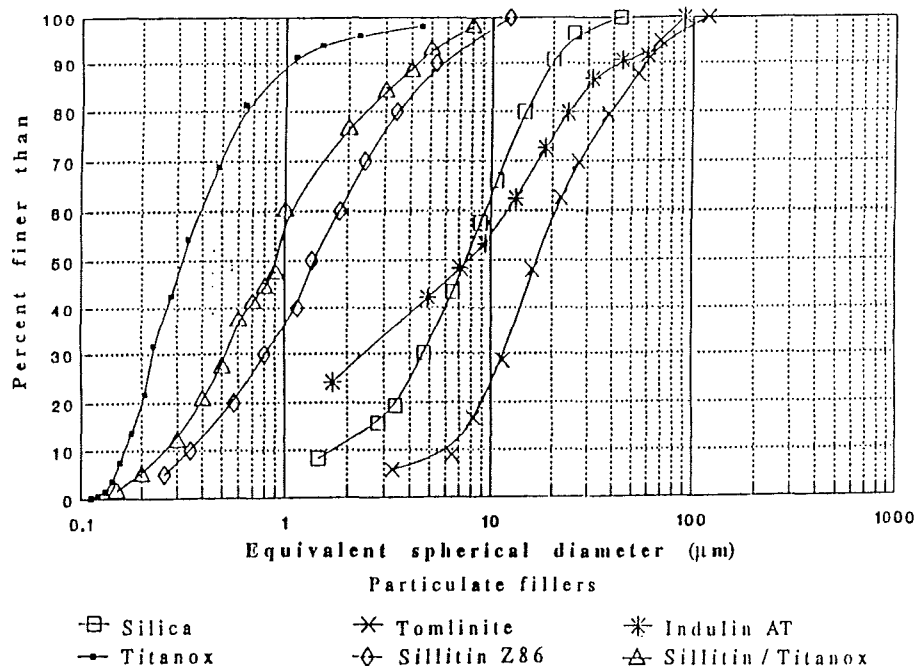


Figure 1. Particle size distribution curves for various fillers used in this study.



**Table 5.**  
Particle size of fillers as determined by the sedimentation technique

Filler	Average equivalent spherical diameter ( $\mu\text{m}$ )	Specific surface area ( $\text{m}^2/\text{g}$ )	$Q$
Titanox	0.3	10	6
Titanox/Sillitin	0.9	11.7	21
Sillitin	1.35	12	24
Silica	7.4	0.6	6
Indulin AT	8	1.5	9
Tomlinite	16.2	0.7	9

$Q$  = Proportionality constant.

**Table 6.**  
Results from microscopic observation of filler particles

Filler type	Particle shape	Estimated size range ( $\mu\text{m}$ )	Estimated average size ( $\mu\text{m}$ )
Indulin AT	Blocky, angular	2–40	10
Eucalin	Spheroidal	6.5–15	10.5
Tomlinite	Blocky, rounded	2–20	12
Sillitin Z86	Flaky, angular	<1–5	2

account other particle shapes. The assumed value of  $Q$  for each of the fillers, taken from the work of Gates [14], is provided in Table 5.

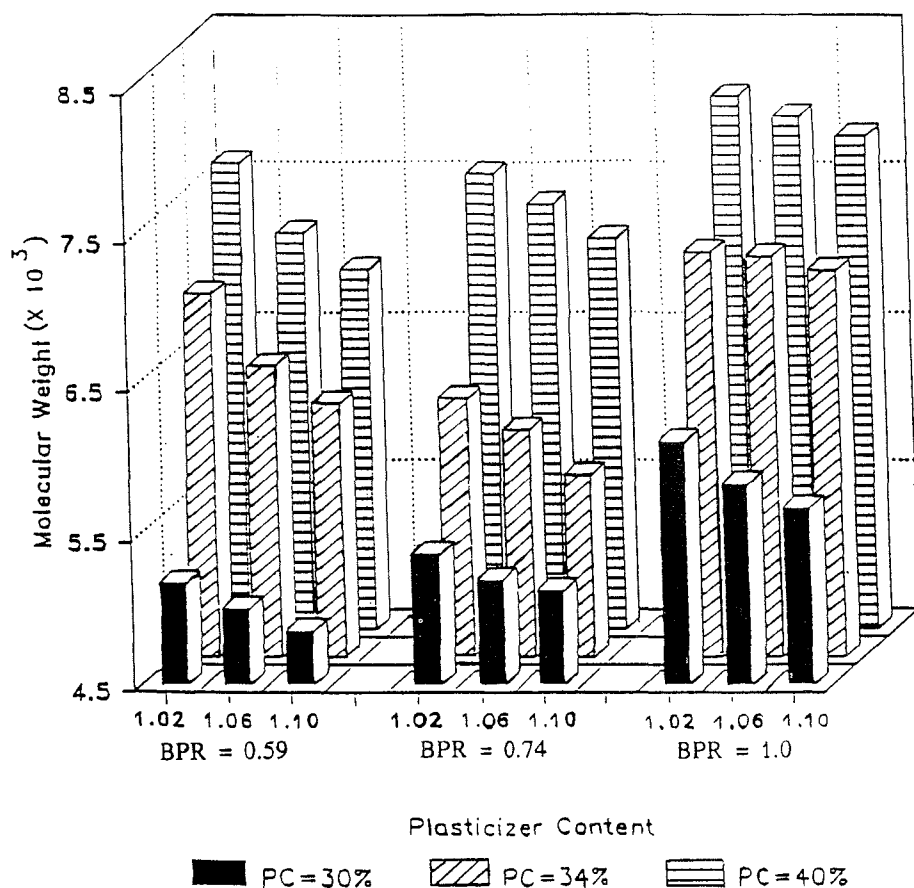
The use of the photomicrographs permits an assessment of the shape and an estimate of the average size and size distribution of the various filler particles. These observations are summarized in Table 6. The observations made from the photomicrographs generally confirm the results obtained from the sedimentation analysis. Furthermore, they permit an estimate to be made of the average particle size and size distribution of Eucalin particles, which were not available during the time that the sedimentation analysis was performed.

### 3.1. Unfilled PU

The dependence of  $M_{c,s}$  of the unfilled formulations on the various chemical parameters is illustrated in Fig. 2. There are three blocks of data arranged in sets of nine data points, each set corresponding to the molecular weights derived for blends having a particular BPR. Within each block, the data are arranged in order of increasing SR and PC. The SR increases from left to right, starting with a value of 1.02 and proceeding to a final value of 1.1, whereas the PC for the various blends increases from front to back of the plot.

The general trends which can be observed from this figure are as follows:

- (i)  $M_{c,s}$  increases with the addition of both plasticizer and Baylith paste (castor oil); and
- (ii) there is a decrease in  $M_{c,s}$  with a corresponding increase in SR.



**Figure 2.** Number average molecular weight between crosslinks of PU elastomer formulations as a function of SR, BPR and PC.

The addition of plasticizer is known to reduce the  $T_g$  of blends as a result of separating macromolecular chains, decreased interaction between chains, and increased chain mobility [15]. This same effect provides an explanation for the increase in molecular weight between crosslinks with the addition of castor oil.

If it is supposed that the castor oil takes part in the reaction to form a crosslinked network, then there should be a reduction in the molecular weight between crosslinks with the addition of castor oil by virtue of the lower molecular weight between crosslinks in comparison with that of the long-chain polyol prepolymer. Since this is evidently not the case, it is supposed, then, that there is little or no reaction between castor oil and the isocyanate prepolymer, and, further, that the castor oil acts as a diluent in the same manner as the plasticizer.

The decrease in  $M_{c,s}$  with a corresponding increase in SR is due to the formation of supplemental crosslinks with urea groups present in the elastomer chain. As has been noted elsewhere [6], the higher the SR, the greater the number of free isocyanate groups

left for curing with other active groups, allowing the formation of additional crosslinks which occurs, for example, in the formation of biuret groups.

### 3.2. Filled PU

Two possibilities may occur when a filled elastomer is swollen in an appropriate solvent. The interaction between the elastomer and particulate modifier is disturbed by the action of the solvent and the bonds at their interface break down; the elastomer remains fully or partially bound to the surface of the particulate matter, even in the presence of the solvent [16].

If all bonds at the filler–elastomer interface rupture, then around each particle cavities will form which will fill with solvent. In this case, the particles do not influence (i.e. restrict) the swelling behaviour and, consequently, there is an increase in the swelling of the elastomer [16].

**Table 7.**  
Swelling results from filled elastomers

Series	$W_0$ (g)	$W_s$ (g)	$W_{sol}$ (g)	$V_0/V_s$	$\nu_{ro}/\nu_r$
50AT	10.8508	28.1203	17.2695	0.3305	0.927
75AT	11.2572	27.9772	16.7200	0.3459	0.885
100AT	10.9557	26.1566	15.2009	0.3615	0.847
125AT	11.1439	25.6617	14.5178	0.3762	0.814
150AT	11.0222	24.3839	13.3617	0.3932	0.779
50EU	11.0090	29.0187	18.0097	0.3240	0.944
75EU	10.9848	28.2706	17.2800	0.3330	0.920
100EU	11.2793	27.7853	16.5060	0.3493	0.877
125EU	11.0396	26.4696	15.4300	0.3600	0.851
150EU	11.0522	25.8206	14.7684	0.370	0.827
50ST	11.7268	29.4331	17.7613	0.3415	0.897
75ST	12.4172	29.4715	17.0543	0.3639	0.841
100ST	12.6594	28.5415	15.8869	0.3850	0.795
125ST	13.6776	29.2664	15.5888	0.4080	0.750
150ST	13.3376	26.7200	13.3824	0.4391	0.697
50TO	10.9704	28.1305	17.1601	0.3343	0.916
75TO	11.1425	27.3795	16.2370	0.3500	0.874
100TO	11.4434	27.1008	15.6574	0.3647	0.840
125TO	11.3570	25.5638	14.2068	0.3858	0.794
150TO	11.1351	24.3237	13.1886	0.3990	0.768
28C	10.7082	29.7648	19.0566	0.3062	1.0

Specimens were immersed in toluene and permitted to swell, at room temperature, until no significant change in weight was measured. Values provided in the table are the average of three determinations; the value of  $\nu_{ro}$  is derived from formulation 28C.  $\delta_e = 1.1035 \text{ g/cm}^3$ ;  $\delta_{sol} = 0.8669 \text{ g/cm}^3$ .

Numbers in the first column represent % vol. of filler (e.g. 50 is 5.0%; 75 is 7.5%, etc.). 28C = unfilled PU (BPR = 1.0, SR = 1.062).

In the case when all filler–elastomer bonds rupture, the swelling is restricted by the influence of the particles and the behaviour may be characterized by the relation derived by Kraus [11, 17, 18] (previously given) and provided below in a modified form:

$$\frac{\nu_{r_0}}{\nu_r} = 1 - m \left( \frac{\phi_f}{1 - \phi_f} \right), \quad (a)$$

where

$$m = 3C(1 - \nu_{r_0}^{1/3}) + \nu_{r_0} - 1. \quad (b)$$

The value of  $m$  is simply the slope of the line plotted. The swelling results of filled elastomers are given in Table 7. The weight of the solvent absorbed by the specimen,  $W_{sol}$ , is simply the difference between the swollen weight,  $W_s$ , and the initial weight,  $W_0$ . Following these data, it was observed that the amount of solvent absorbed by the different lignin-filled specimens is lower than the amount absorbed by the unfilled specimen (C28). The increase of lignin content led to an increase in the ratio between the polymer volume ( $V_0$ ) and the solvent volume ( $V_s$ ). This observation is valid for all the types of lignin tried. The volume fraction of elastomer in the solvent specimen,  $\nu_r$ , is given by the following relation:

$$\nu_r = \frac{1}{1 + \frac{W_{sol}}{W_0} \cdot \frac{\delta_e}{\delta_{sol}}},$$

where  $\delta_e$  and  $\delta_{sol}$  are the densities of the elastomer and solvent, respectively. The value of  $\nu_{r_0}$  is calculated from the unfilled formulation used for preparing all the modified compounds. If a firm bond is established between the elastomer matrix and the filler, then the degree of swelling will be restrained. The slope of the straight line for each series of points establishes the extent of the restraint, and is related to the coefficient  $C$ , which is a filler characteristic. Lipatov [16] has suggested that this coefficient can be used as a qualitative characteristic of the adhesion of the elastomer to the particulate surface.

The slopes and corresponding ‘adhesion’ coefficients for the four particulate modifier series are given in Table 8. The values indicate that the ‘ST’ series, consisting of a mixture of siliceous clay (Sillitin Z-86) and titanium dioxide (Titanox), provides the

**Table 8.**  
Characteristic particulate filler coefficients based on swelling behaviour

Particulate filler series	$m$	$C$
ST: Sillitin Z-86/Titanox	1.83	2.58
TO: Tomlinite	1.44	2.18
AT: Indulin AT	1.27	2.01
EU: Eucalin	1.09	1.82

Values were calculated using  $\nu_{r_0} = 0.3062$  (volume fraction of elastomer in the swollen unfilled specimen).

$C$  is a constant which is a filler characteristic independent of the polymer, solvent, or degree of crosslinking.

$$m = 3C(1 - \nu_{r_0}^{1/3}) + \nu_{r_0} - 1.$$

greatest restraint to swelling. It is also evident that less restraint is provided by the modifiers of series TO, AT, and EU, given in order of their decreasing contribution. Although the difference between the  $C$  values is not very high, it also results that TO has the higher adhesion to the elastomer.

#### 4. CONCLUSION

The degree of physical interaction between phases was assessed using a technique based on swelling in toluene. Interaction between the polymer and filler, as determined by swelling, is dependent on the type of filler and can be characterized by the degree of restriction to swelling which a filler imparts to the polymer matrix. Lignins are found to restrict less the degree of swelling of PU than that by the siliceous clay, titanium dioxide mixture. Hence, using this method, it is seen that lignins do not interact with the elastomer matrix to as great an extent as the Sillitin/Titanox filler mixture.

#### Acknowledgements

We wish to thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support, and Bayer Canada for providing some of the raw materials. Thanks are also extended to Hüls Canada, Debro Chem Canada, NL Chem Canada, and Hottman Mineral, Germany for various ancillary products.

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