

1 **Assessment of microstructure, physical and thermal properties of bitumen** 2 **modified with LDPE/GTR/elastomer ternary blends**

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16 17 **Abstract**

18 LDPE/GTR/elastomer ternary blends with variable LDPE/GTR ratio and constant elastomer content
19 were prepared *via* melt-compounding. Obtained LDPE/GTR/elastomer blends were applied as
20 thermoplastic modifiers into bitumen. Microstructure, physical and thermal properties of the modified
21 bitumen were determined. It was observed that chemical composition of LDPE/GTR/elastomer blends
22 has significant influence on their density and rheological behavior, which are also main factors
23 affecting the dispersion of LDPE/GTR/elastomer blends into bitumen matrix and interfacial
24 interactions between used components. Microstructure and thermal behavior of modified bitumen
25 confirmed that physical interactions between bitumen and LDPE/GTR/elastomer blends are limited
26 with increasing content of GTR. This phenomenon is due to mainly cross-linked structure of GTR and
27 its low flowability. The conducted investigations showed that interfacial interactions between of
28 thermoplastic modifier and bitumen, therefore the conventional and thermal properties of modified
29 bitumen can be improved and easily modified by changing composition of LDPE/GTR/elastomer
30 blends.

31 **Keywords:** ground tire rubber; modified bitumen; recycling; thermoplastic blends; extrusion

1 **1. Introduction**

2 The estimated data demonstrates that more than 17 million tonnes of used car tires are
3 discarded every year worldwide. One of the most important methods of used tires recycling is
4 grinding [1], resulting in ground tire rubber (GTR) particles with desired shape and size.
5 Typically, GTR is used as filler in rubber compounds [2, 3], thermoplastic composites [4, 5],
6 thermoplastic elastomers [6, 7], polyurethanes [8] and epoxy resins [9]. Moreover, GTR can
7 be applied in pyrolysis [10] and reclaiming/devulcanization [11, 12] of waste rubber. Among
8 others applications at industrial scale, use of waste rubber in the construction and building
9 materials should be mentioned. Most of researches in this area are focused on the
10 modifications of cement, concrete [13, 14] and bitumen [15, 16].

11 Application of waste rubber and other polymeric wastes [17-19] as cheap polymeric
12 modifiers of bitumen's enhances their properties and extend their applicability in different
13 branches of industry (e.g. road pavements, roofing applications, sealants, emulsions etc.).
14 Results published by independent research centers over the last decades confirm that the use
15 of GTR as modifier of bitumen improves the elasticity and resistance on permanent
16 deformation of pavements. Road pavements based on bitumen modified with GTR show
17 higher toughness and resistance to climatic factors, which increases their durability as well as
18 keeps the costs of maintenance lower compared to pavements based on unmodified bitumen.
19 Moreover, incorporation of GTR into the bitumen decreases the noise generated by car traffic
20 and manifests the driving comfort and safety through the shortening of braking distance.

21 On the other hand, factors limiting the use of GTR-modified bitumen are higher costs
22 of production arising from energy consumption of the process (long time of mixing at
23 elevated temperatures) and necessity of modification of the devices currently used in the
24 industry. Moreover, because of the cross-linked structure of waste rubber, bitumen modified
25 with GTR shows low stability and high viscosity, which causes difficulties with their storage

1 and further use. Comprehensive literature reviews of the research on the modifications of
2 bitumen with ground tire rubber were recently presented in works of Lo Presti [20] or Shu and
3 Huang [21].

4 Using of reclaimed/devulcanized waste rubber is one of methods of enhancement the
5 stability of GTR-modified bitumen. Singh et al. [22] studied the effect of activated ground tire
6 rubber on properties of bitumen. Activation of GTR was conducted via two-roll milling
7 (strong shear forces) at 210-230°C in 2-3 hours' time. During activation tar oil, elemental
8 sulfur and gilsonite resin were used as reclaiming/devulcanization agents. Activation of GTR
9 by reclaiming/devulcanization or controlled oxidation has beneficial effects on the
10 homogeneity and stability of modified bitumen [23, 24]. Other possibilities to increase
11 stability of GTR-modified bitumen is using of additives (e.g. waxes, plasticizers,
12 thermoplastics), which may improve dispersing of cross-linked rubber particles in bitumen
13 [25, 26].

14 Wang et al. [27, 28] proposed using of polyethylene and reclaimed rubber blends as
15 modifiers of bitumen. Their findings suggest that blending of thermoplastics with reclaimed
16 rubber *via* extrusion improves the storage stability of polyethylene/reclaimed rubber modified
17 bitumen, which was related to dispersion level of modifiers throughout the bitumen. Similar
18 observations were recently reported by Yan et al. [29], who studied the effect of GTR,
19 recycled low density polyethylene and their combinations on the rheological properties of
20 bitumen. In presented state of knowledge there is lack of information about effects of
21 thermoplastics/GTR blends composition and its content in on properties of modified bitumen.
22 These characteristics would be valuable data for evaluation and prediction of the interaction
23 between GTR, thermoplastics and bitumen.

24 In the present work, interfacially modified LDPE/GTR blends with non-polar
25 elastomers were used as bitumen modifiers in order to improve their performance and storage

1 stability. Thermoplastic composites based on LDPE/GTR/elastomer ternary blends were
2 prepared using a co-rotating twin screw extruder. Advantages of extrusion are continuity of
3 the process, short time, high efficiency of mixing and good quality of the obtained products. It
4 is also worth mentioning that during the extrusion process partial reclaiming of GTR is
5 possible [30, 31], which promote the interfacial interaction between polyethylene and
6 bitumen.

7 In order to expand characterization of LDPE/GTR/elastomer blends, during present
8 studies their density and rheological properties were evaluated. The influence of
9 LDPE/GTR/elastomer ternary blends compositions and their content on microstructure,
10 physical and thermal properties of the bitumen 160/220 were investigated. Physical properties
11 of modified bitumens were evaluated by conventional tests (penetration, softening point and
12 penetration index). Microstructure and thermal properties were determined using optical
13 microscopy, dynamic mechanical analysis and thermogravimetric analysis.

14 **2. Experimental**

15 **2.1. Materials**

16 Ground tire rubber (GTR) produced by ambient grinding of used tires (about 50:50
%wt. mix of passenger and truck cars), was obtained from Grupa Recykl S.A. (Poland).

**The
placement
of Figure 1**

Particle size distribution of the used GTR is presented in Figure 1.

19 Low density polyethylene (LDPE) Bralen VA 20-60 (density: 0.91 g/cm^3 ,
20 $\text{MFR}_{190^\circ\text{C}/2,16\text{kg}}$: 20 g/10 min) was received from Slovnaft (Slovakia).

21 During research two types of elastomers: styrene-butadiene block copolymer (SBS) or
22 partially cross-linked butyl rubber, were used as compatibilizer of LDPE/GTR blend. Styrene-
23 butadiene-styrene block copolymer Kraton 1102 (density: 0.94 g/cm^3 , $\text{MFR}_{200^\circ\text{C}/5\text{kg}}$: 8 g/10
24 min) from Kraton Polymers (Germany) is commercially used in industry as modifier of
25 pavement bitumen or as substrate in production of sealants. For comparison, partially cross-

1 linked butyl rubber (IIR) Kalar 5215 (density: 1.07 g/cm³, Mooney viscosity: ML 1+3
2 (127°C): 47-57, filler content: 24.6 %wt.) from Ter Hell & Co (Germany) was applied.
3 Partially cross-linked butyl rubber is commonly used in the manufacture of sealants, caulks,
4 roof coatings, construction adhesives etc. Both type of elastomers are sold as granules, which
5 facilitates their metering for the extrusion process.

6 Bitumen 160/220 from Lotos Asphalt Sp. z o.o. (Poland) was characterized by the
7 penetration at 25°C: 154 (1/10 mm) and softening point temperature: 38.7°C. The type of
8 bitumen was picked based on content of oils and resins fraction, which are higher in
9 comparison to other commercial available bitumen. These low molecular compounds present
10 in bitumen could act like plasticizers, which improve reclaiming process of GTR and
11 dispersion of GTR in the thermoplastic matrix [32].

12 **2.2. Sample preparation**

13 *Step I: Preparation of thermoplastic modifiers*

The placement of Table 1 14 Five types of thermoplastic modifiers were used as bitumen modifiers; their
15 composition is shown in Table 1. LDPE/GTR and LDPE/GTR/elastomer blends were
16 prepared using a co-rotating twin screw extruder, type Leistritz ZSE 27HP (d=27, L/d=44)
17 (Germany). Characteristics of screw configuration is presented in work [33]. During the
18 extrusion barrel temperature was 180°C (80°C in hopper) and rotational speed of screws was
19 300 rpm. All components (LDPE, GTR, elastomer) were gravimetrically dosed directly into
20 hopper with constant throughput (15 kg/h). During these studies gravimetric feeders from
21 Brabender (Germany) were used. **Interfacial interactions between the components in
22 LDPE/GTR/elastomer blends were characterized in details in work [34].**

23 24 *Step II. Modification of bitumen*

25 Bitumen 160/220 was modified with 2, 4, 6 and 12 parts by weight (pbw) of
26 thermoplastic modifier for 100 parts of bitumen. Bitumen modification was performed at

1 180°C, using T 25 digital Ultra-Turrax® rotor-stator homogenizer from IKA (Germany).
2 Rotational speed of rotor was 15000 rpm. Bitumen modification was conducted until desired
3 homogeneity of material was obtained (around 30 minutes).

4 5 **2.3. Measurements**

6 Melt flow index of thermoplastic compositions was determined at 190°C, with load of
7 2.16, 5 and 10 kg, according to ISO 1133, using Mflow plastometer from Zwick. Tungsten
8 carbide capillary die having length of 8.000 ±0.025 mm and diameter of 2.095±0.005 was
9 applied for the measurements. Considering the average size of GTR particles shown in Figure
10 1, die diameter was about five times larger than the GTR particles.

11 Based on the methodology described by Jakubowska et al. [35] rheological
12 characteristics of obtained thermoplastic compositions were determined. Viscosity of melt
13 (η_w) was calculated based on formula (1):

$$14 \quad \eta_w = \frac{\tau_w}{\dot{\gamma}_w} \quad (1)$$

15 where: τ_w - shear stress (Pa), $\dot{\gamma}_w$ - shear rate after correction (s⁻¹)

16 Shear stress were calculated according to formula (2):

$$17 \quad \tau_w = \frac{\Delta p \cdot R_c}{2 \cdot L_c} \quad (2)$$

18 where: Δp - pressure drop (Pa), R_c - radius of capillary (m), L_c - length of capillary (m)

19 Weissenberg–Rabinowitsch corrected shear rate ($\dot{\gamma}_w$) was calculated based on formula (3):

$$20 \quad \dot{\gamma}_w = \frac{3n+1}{4n} \cdot \dot{\gamma}_a \quad (3)$$

21 where n is slope in linear equation of straight line described as (4):

$$22 \quad \log(\tau_w) = f(\log(\dot{\gamma}_a)) \quad (4)$$

23 Apparent shear rate was determined according to formula (5):

$$24 \quad \dot{\gamma}_a = \frac{4 \cdot Q}{\pi \cdot R_c^3} = \frac{4}{\pi \cdot R_c^3} \cdot \frac{m}{t\rho} \quad (5)$$

1 where: Q - the volume flow rate (m^3/s), m - mass of sample (kg), t - time of measurement (s),
2 ρ - density of sample (kg/m^3)

3 Penetration measurements for analyzed samples were conducted according to PN-EN
4 1426 in 25°C . Softening point temperature of materials was determined with Ring and Ball
5 method, according to PN-EN 1427. Penetration index (PI) was calculated in accordance to
6 formulas (6) and (7):

$$7 \quad \text{PI} = \frac{20(1 - 25A)}{1 + 50A} \quad (6)$$

$$8 \quad A = \frac{\log \text{penT}_{25^\circ\text{C}} - \log 800}{T_{\text{softening}} - T_{25^\circ\text{C}}} \quad (7)$$

10 The microstructure of modified bitumen was characterized using confocal microscope
11 Horiba LabRAM ARAMIS. For sample preparation, a small quantity of bitumen was applied
12 onto a glass slide, then the bitumen was heated to about 180°C and a second glass slide was
13 placed onto the sample. Prepared sample was cooled to room temperature. During cooling
14 constant load was put on sample, which allowed obtaining thin film of bitumen. After a short
15 period of cooling, the morphology of samples was estimated.

17 Dynamic mechanical analysis was performed using DMA Q800 TA Instruments
18 apparatus. Samples cut to the dimensions of $40 \times 10 \times 2$ mm were loaded with a variable
19 sinusoidal deformation force in the single cantilever bending mode at the frequency of 1 Hz
20 under the temperature rising rate of $4^\circ\text{C}/\text{min}$ within the temperature range between
21 -40 and 40°C .

22 Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 apparatus.
23 Samples (ca. 5 mg) were placed in a corundum dish. Measurements were conducted in
24 a nitrogen atmosphere for the temperature range 25 - 550°C at a heating rate of $20^\circ\text{C}/\text{min}$.

25

26

3. Results and discussion

3.1. Density and melt viscosity of LDPE/GTR/elastomer blends

Density values of studied thermoplastic modifiers are shown in Table 1. This parameter gives some information about storage stability of modified bitumen during hot storage, which is related with significant changing of bitumen`s density during heating: from ~1.02 at 25°C to ~0.91 at 190°C [36]. It was observed that thermoplastic modifiers filled with 50 %wt. of GTR possess slightly higher density than samples containing 50 % wt. LDPE. Moreover, in comparison to styrene-butadiene-styrene block copolymer, using of butyl rubber as compatibilizer affects on increase of thermoplastic modifiers density, which is related with presence of inorganic filler in this type of elastomer (please see Materials section). Presented results suggest that, during hot storage stability test, in samples with 50 % wt. of GTR, the GTR sediments to bottom, in contrary in samples with 50 % wt. of LDPE, the LDPE migrates on top of modified bitumen.

The placement of Figure 2

The effect of LDPE/GTR/elastomer formulation on the characteristics of melt viscosity is presented in Figure 2. LDPE/GTR at ratio of 50:50 was used as reference sample. It was noticed, that replacement of LDPE or GTR with elastomer increased melt viscosity of obtained thermoplastic compositions. The exception was sample LDPE/GTR/SBS 50:25:25, which possess melt viscosity similar to reference sample (LDPE/GTR 50:50). This phenomenon suggests good compatibility of linear styrene-butadiene-styrene block copolymer with polyethylene matrix. Under tested conditions melt viscosity of LDPE/GTR/IIR 25:50:25 at low shear stress (2.16 kg load) could not be determined, which is due to high filler content in used IIR.

As could be expected, samples containing 50 %wt. of GTR showed higher melt viscosity than samples comprising 50 %wt. of LDPE, which is related with mainly cross-linked structure of ground tire rubber, decreasing it`s flowability. LDPE/GTR/elastomer melt

1 viscosity decreased with increasing shear rate. This behavior is characteristic for filled
2 composites and confirm shear thinning phenomenon. Similar conclusions for PP/GTR and
3 PP/GTR/(EPDM or EPR) blends were described recently by Prut et al. [37] and Lima et al.
4 [38] respectively.

5

6 **3.2. Physical properties of bitumen modified with LDPE/GTR/elastomer blends**

The results of penetration and softening point of modified bitumen are presented in

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of Figure 3

Figure 3. Addition of prepared thermoplastic modifiers has significant influence on physical
9 properties of modified bitumens. It was observed that using of higher content of modifier
10 caused decrease of penetration and proportionally increased the softening temperature of
11 obtained bitumen. The ratio of LDPE/GTR obviously influences the conventional properties
12 of bitumen. The highest content (75 % wt.) of LDPE and elastomer (SBS, IIR) led to lower
13 values of penetration and higher softening point in comparison to samples with
14 LDPE/GTR/elastomer in proportion 25:50:25 (only 50 % wt. of thermoplastic matrix). This
15 result suggests higher interfacial interaction between thermoplastic components (LDPE,
16 elastomer) and bitumen, than between bitumen and ground tire rubber, which is due to cross-
17 linked structure of GTR. Three-dimensional cross-linked structure of the GTR limits its
18 dissolution and dispersion in the bitumen phase, which corresponded with the results of
19 penetration and softening point. Moreover, it was noticed that addition of 12 pbw
20 LDPE/GTR/IIR 50:25:25 modifier cause deterioration of physical parameters of such
21 modified bitumen in comparison to modification with thermoplastic blends of composition
22 LDPE/GTR 50:50 or LDPE/GTR/SBS 50:25:25. This phenomenon suggests decrease of
23 solubility of this type of modifier in bitumen, which may be related with limited interfacial
24 interactions between IIR elastomer and other components (GTR, LDPE and bitumen).

The
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of Figure 4

Penetration index (PI) describes bitumen temperature susceptibility at relatively small
range of temperatures. Penetration index values are presented in Figure 4. Temperature

1 susceptibility is defined as the change in the consistency parameter as a function of
2 temperature. It is well known, that low value of PI parameter corresponds with higher
3 temperature susceptibility of bitumen. It was observed that higher content of modifiers in
4 bitumen 160/220 increases penetration index values. These results suggest that the modified
5 bitumen is more resistant to low temperature cracking and permanent deformation [39].

6

7 **3.3. Microstructure of bitumen modified with LDPE/GTR/elastomer blend**

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of Figure 5

Figure 5 presents microstructure of pure bitumen 160/220 and bitumen 160/220 with
12 pbw modifier content. It was noticed that using of 12 pbw LDPE/GTR/elastomer blend as
10 modifier did not affect on bitumen/polymer phase inversion. Continuous (dominant) phase
11 was bitumen and dispersed phase was LDPE/GTR/elastomer blend. Presented results indicate
12 that the ratio of LDPE to GTR has significant effect on dispersion of modifier in bitumen. It
13 was observed that lower content of GTR affects on better dispersion of thermoplastic phase
14 (LDPE and elastomer phase). It was noticed that better dispersion of thermoplastic modifier in
15 bitumen phase was observed for LDPE/GTR/SBS modifier, as presented in Figures 5C and
16 5E. Better dispersion of this modifier is due to lower melt viscosity of LDPE/GTR/SBS
17 modifier (see Figure 2). For comparison, morphology of bitumen with 12 pbw
18 LDPE/GTR/IIR modifier shows aggregates of thermoplastic phase (Figures 5D and 5F). This
19 phenomenon is related with cross-linked structure of GTR and different compatibility
20 between used components. The largest thermoplastic phase agglomerates were presented in
21 bitumen modified with using LDPE/GTR/IIR 25:50:25, which is due to poor compatibility
22 between butyl rubber and styrene-butadiene rubber, butadiene rubber or natural rubber (main
23 components of car tires) [40] and only partial compatibility with polyethylene matrix [41]. In
24 comparison to slightly cross-linked butyl rubber (IIR), using of styrene-butadiene-styrene
25 (SBS) block copolymer as modifier of LDPE/GTR blend reduces the melt viscosity and

1 improves interfacial interactions between LDPE matrix and ground tire rubber [30, 42]. This
2 phenomenon has dominant influence on interactions between bitumen and
3 LDPE/GTR/elastomer blends. Based on presented results further studies were limited to
4 LDPE/GTR and LDPE/GTR/SBS blends.

5

6 **3.4. Dynamic mechanical analysis of bitumen modified with** 7 **LDPE/GTR/elastomer blends**

8 As could be noticed in previous paragraph (see [Figure 3](#)), pure bitumen and bitumen
9 modified with 2 pbw of thermoplastic composition are characterized by very low softening
10 point ($\sim 40^{\circ}\text{C}$), which could cause small size deformation during placement of samples to
11 DMA apparatus. It is well known that inaccuracies in dimension of samples cause remarkable
12 deviations of storage and loss modulus values. Therefore, to prevent mistakes during analysis
13 of DMA results, dimension independent loss tangent ($\tan\delta$) values were evaluated. The results
14 of dynamic mechanical analysis are shown in [Figure 6](#).

15 According to literature [43, 44], the temperature at maximum value of the loss tangent
16 ($\tan\delta$) is related to the change in colloidal structure of bitumen due to collapse of the structure
17 formed by asphaltene phase, immersed in a maltene phase. It was observed that higher content
18 of LDPE/GTR/elastomer blend used as thermoplastic modifier causes shift of the maximum
19 value of the loss tangent ($\tan\delta$) to higher temperatures. This indicates that the modified
20 bitumen becomes harder, which correspond also with the results of bitumen penetration (see
21 [Figure 3](#)). This phenomenon is related to the interfacial interactions between the polymer
22 modifier (LDPE/GTR/elastomer blend) and the saturate oils, which causes change in the
23 maltene phase and stabilized asphaltene phase. Furthermore, short-term aging (e.g. oxidation,
24 volatilization of low molecular compounds, etc.) during bitumen modification causes partial
25 transformation of the maltene phase into the asphaltene phase, which could also affect the

1 maximum value of the loss tangent ($\tan \delta$). It was noticed that addition of thermoplastic
2 modifiers not only shifts the position of the $\tan \delta$ peak towards higher temperatures, but also
3 lowers the peak magnitude. These results confirm the changes in the stiffness of the modified
4 bitumen due to increasing viscosity of bitumen during modification with thermoplastic
5 modifiers, which is related to partial swelling of used modifiers [45]. Bitumen modification
6 conducted at elevated temperature with non-polar low-molecular weight compounds causes
7 swelling of LDPE and non-polar elastomer, while aromatic compound should interact with
8 GTR due to polarity of used components.

The
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of Table 2

9 The transition temperature associated with the loss tangent peak ($\tan \delta$ maximum) and
values of $\tan \delta$ at -30°C are presented in Table 2. As mentioned above, the transition
10 temperature at $\tan \delta$ maximum is related to the change in the colloidal structure of bitumen. It
11 could be surprising that thermoplastic modifier composition had a small impact on transition
12 temperature at $\tan \delta$ maximum determined for modified bitumen. This phenomenon confirms
13 weak interactions between bitumen phase and ground tire rubber, due to the cross-linked
14 structure of GTR. These results correspond also with increasing values of penetration and
15 softening point determined for modified bitumen. Furthermore, it was noticed that the
16 presence of SBS in LDPE/GTR blends causes decrease of transition temperature at $\tan \delta$
17 maximum, comparing to LDPE/GTR blend. This observation suggests stronger interactions
18 between bitumen phase and SBS copolymer, which affect also on thermal properties
19 presented in next section (see Figure 7).

21 The results of $\tan \delta$ at -30°C provides information about mechanical response of road
22 pavement in winter conditions. It was observed that higher content of thermoplastic modifier
23 in bitumen caused higher losses comparing to pure bitumen, which indicate their lower
24 stiffness and enhanced flexibility at low temperature [43]. An exception was the bitumen
25 sample modified with 12 pbw LDPE/GTR 50:50 due to the highest content of polyethylene

1 phase. According to the literature, application of polyethylene as bitumen modifier improves
2 high-temperature performance of bitumen and at the same time deteriorate its low-
3 temperature properties [46, 47].

5 3.5. Thermal properties of bitumen modified with LDPE/GTR/elastomer blends

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Figure 7

Thermogravimetric analysis of pure bitumen, LDPE, GTR, SBS and their blends was
conducted in nitrogen atmosphere and obtained results are presented in Table 3. $T_{-2\%}$, $T_{-5\%}$,
 $T_{-10\%}$ and $T_{-50\%}$ represent temperatures for which the samples have lost the indexed amount of
9 their initial mass, respectively. T_{max} is temperature at which the rate of thermal decomposition
10 of the sample is at its peak, as estimated from the derivative thermogravimetry (DTG).
11 Additionally, the char residue at 550°C is given. For better illustration of thermal behavior of
12 selected samples obtained results are presented as TGA curves in the [Figure 7](#).

13 It was observed that, regardless of thermoplastic modifier type and its content used
14 during bitumen modification, bitumen modified with LDPE/GTR/elastomer blend showed
15 lower thermal stability in comparison to pure bitumen. This phenomenon is related with two
16 main factors. First of them is obviously lower thermal stability of used thermoplastic
17 modifiers. Second factor affecting on thermal stability of modified bitumen are interfacial
18 interactions between bitumen and LDPE/GTR/elastomer, due to swelling/plasticization of
19 thermoplastic matrix (LDPE, elastomer) and partial reclaiming/devulcanization of GTR. It
20 was noticed that bitumen modified with LDPE/GTR and LDPE/GTR/elastomer blends were
21 characterized by lower char residue values in comparison to pure bitumen or pure
22 thermoplastic modifiers. This effect was observed especially in case of bitumen modified with
23 12 pbw LDPE/SBS/GTR blend in ratio 50:25:25 % wt.. It should be mentioned, that this
24 sample was characterized by the highest content of thermoplastic matrix. Presented TGA
25 results suggest swelling, plasticization and partial solubility of thermoplastic matrix (LDPE,

1 SBS), which cause higher mobility of polymer chains in bitumen. Similar observations were
2 described by Zhang et al. [48], who used bitumen as compatibilizer during processing of
3 thermoplastic elastomers containing GTR.

4 Furthermore, elevated temperature and high shear forces applied during modification
5 of bitumen cause swelling and partial reclaiming/devulcanization of GTR, which
6 simultaneously release the low molecular weight compounds [49]. Higher content of low
7 molecular weight products generated during thermo-mechanical degradation of GTR
8 contributed to higher mass loss at lower temperatures before reaching the highest rate of
9 thermal decomposition and to lower content of char residue at 550°C.

10 For better characterization of interfacial interactions between bitumen and
11 LDPE/GTR/elastomer blends, theoretical and experimental values of weight loss determined
12 for modified bitumens have been compared. Theoretical results of weight loss at different
13 temperatures were calculated from the data for pure bitumen and pure blends components
14 (LDPE, GTR, SBS) assuming the additivity principle and lack of interactions. Calculated
15 theoretical results are compared with experimental thermal degradation measurements, as
16 presented in the Table 4. It was observed that experimental results of weight loss at different
17 temperatures were generally higher than calculated values. This indicates better compatibility
18 between the bitumen and GTR particles. Swelling and partial reclaiming/devulcanization of
19 GTR particles during bitumen modification, cause components exchange between bitumen
20 phase and GTR phase, which facilitated release of the volatile rubber degradation products to
21 bitumen phase and diffusion of some bitumen compounds into GTR phase [50, 51].

22 Furthermore, it was noticed that at 300°C, experimental values of weight loss were
23 lower than calculated theoretical values only for bitumen modified with LDPE/GTR/SBS in
24 ratio 25:50:25 % wt. At higher content (12 pbw) of modifier LDPE/GTR/SBS 25:50:25 % wt.
25 this effect was observed also at 350°C. These results suggest weak interfacial interactions

1 between bitumen and LDPE/GTR/SBS in ratio 25:50:25 % wt. in comparison to other used
2 modifiers (LDPE/GTR 50:50 % wt. and LDPE/GTR/SBS 50:25:25 % wt.). This phenomenon
3 may be related with the higher melt viscosity of modifier LDPE/GTR/SBS 25:50:25 % wt.
4 (see [Figure 2](#)). Weak interfacial interactions between bitumen and LDPE/GTR/SBS 25:50:25
5 % wt. were also confirmed by measurements of penetration and softening point. Based on
6 presented above assumptions schematic diagram of physical interactions between bitumen
7 and LDPE/GTR/elastomer blend is presented in [Figure 8](#).

8

9 **4. Conclusions**

10 Application of LDPE/GTR/elastomer blends as potential bitumen modifiers was
11 evaluated. LDPE/GTR/elastomer blends were prepared *via* melt compounding using a co-
12 rotating twin screw extruder. It was found that LDPE/GTR ratio and type of used elastomer
13 have significant influence on density and rheological properties of obtained blends.
14 LDPE/GTR/SBS blends was characterized by significantly lower density and melt viscosity
15 in comparison to LDPE/GTR/IIR blends. Chemical composition, density and rheological
16 properties of LDPE/GTR/elastomer are also crucial factors affecting on processing and
17 storage stability of modified bitumen, which is related with dispersion of thermoplastic
18 modifier into bitumen matrix and interfacial interactions between these components.

19 [Maximum \$\tan\delta\$ value](#) of modified bitumen shifted to higher temperatures comparing to
20 [pure](#) bitumen in result of swelling of the LDPE/GTR/elastomer blend and physical
21 interactions on phase boundary. The [maximum loss tangent value](#) shift was predominantly
22 influenced by the LDPE/GTR/elastomer blend content and only slightly by its composition.
23 [Furthermore, dynamic mechanical analysis confirmed that addition of thermoplastic modifiers](#)
24 [to bitumen improves stiffness and enhances the flexibility at low temperature.](#)

1 Thermal stability of the modified bitumen was lower comparing to pure bitumen due
2 to interaction between bitumen phase and LDPE/GTR/elastomer phase. This phenomenon
3 was related with plasticization of thermoplastic matrix (LDPE, elastomer) and partial
4 reclaiming/devulcanization of GTR. It was found that interfacial interactions between
5 bitumen and LDPE/GTR/elastomer blends are limited with increasing content of GTR, which
6 is due to its mainly cross-linked structure and its limited flowability. The conducted
7 investigations indicate that bitumen performances can be improved by addition of
8 LDPE/GTR/elastomer blends.

9

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1 **Tables captions**

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26

Table 1. Composition of thermoplastic modifiers

Composition				Density at 25°C (g/cm ³)	Density at 190°C* (g/cm ³)	MFI _{190°C/2.16kg}
LDPE	GTR	SBS	IIR			
50	50	-	-	1.002±0.006	0.887±0.001	4.68±0.14
50	25	25	-	0.952±0.014	0.851±0.013	5.83±0.04
50	25	-	25	0.970±0.001	0.874±0.018	3.83±0.17
25	50	25	-	1.013±0.006	0.919±0.002	1.84±0.06
25	50	-	25	1.053±0.005	0.941±0.023	-

*determined as MFR/MVR from MFI measurements

Table 2. Comparison of temperature at maximum tangent and tanδ at -30°C determined for modified bitumen

Sample composition	Transition temperature at tanδ max (°C)	Damping factor (tanδ) at -30°C
Bitumen 160/220	23.8	0.056
Bitumen 160/220 + 2 pbw LDPE/GTR 50:50	33.3	0.093
Bitumen 160/220 + 12 pbw LDPE/GTR 50:50	37.7	0.058
Bitumen 160/220 + 2 pbw LDPE/GTR/SBS 50:25:25	27.5	0.063
Bitumen 160/220 + 12 pbw LDPE/GTR/SBS 50:25:25	35.0	0.109
Bitumen 160/220 + 2 pbw LDPE/GTR/SBS 25:50:25	30.7	0.072
Bitumen 160/220 + 12 pbw LDPE/GTR/SBS 25:50:25	34.2	0.089

Table 3. Decomposition temperatures as function of weight losses, different maximum peak and char residue determined for neat components and modified bitumen

Sample composition	T _{-2%} (°C)	T _{-5%} (°C)	T _{-10%} (°C)	T _{-50%} (°C)	Char residue at 550°C (%)	T _{max} (°C)
Bitumen 160/220	371.4	402.0	424.0	471.4	18.1	472.5
LDPE	425.1	441.8	452.2	477.7	0.03	480.2
GTR	255.7	302.6	348.1	453.1	41.6	388.8/435.2
SBS	313.3	391.2	414.5	463.9	0.3	471.2
LDPE/GTR 50:50	307.9	358.7	384.0	479.9	18.3	486.8
LDPE/GTR/SBS 50:25:25	361.5	388.8	411.8	476.1	9.0	486.2
LDPE/GTR/SBS 25:50:25	314.7	362.2	386.7	472.6	19.6	484.1
Bitumen 160/220 + 2 pbw LDPE/GTR 50:50	354.0	383.5	405.9	461.2	14.2	464.7
Bitumen 160/220 + 12 pbw LDPE/GTR 50:50	347.3	382.0	407.0	466.1	13.9	471.3
Bitumen 160/220 + 2 pbw LDPE/GTR/SBS 50:25:25	363.7	394.8	418.2	468.4	14.2	472.9
Bitumen 160/220 + 12 pbw LDPE/GTR/SBS 50:25:25	344.1	375.7	399.2	459.6	6.7	469.7
Bitumen 160/220 + 2 pbw LDPE/GTR/SBS 25:50:25	362.0	389.5	411.8	464.2	13.4	467.1
Bitumen 160/220 + 12 pbw LDPE/GTR/SBS 25:50:25	359.1	389.4	412.3	467.6	14.9	466.3

Table 4. Comparison between theoretical and experimental results of weight loss at different temperatures determined by TGA

Sample composition		Weight loss (%)				
		300°C	350°C	400°C	450°C	500°C
Bitumen 160/220	theo.	-	-	-	-	-
	exp.	0.32	1.18	4.79	25.06	77.68
LDPE	theo.	-	-	-	-	-
	exp.	0.09	0.19	0.68	8.51	95.84
GTR	theo.	-	-	-	-	-
	exp.	5.24	10.78	29.74	49.29	58.51
SBS	theo.	-	-	-	-	-
	exp.	1.66	2.23	6.48	30.18	98.40
Bitumen 160/220 + 2 pbw LDPE/GTR 50:50	theo.	0.37	1.26	4.99	25.14	77.67
	exp.	0.40	1.91	8.53	37.53	83.31
Bitumen 160/220 + 12 pbw LDPE/GTR 50:50	theo.	0.57	1.64	5.91	25.47	77.63
	exp.	0.72	2.23	8.37	32.83	82.59
Bitumen 160/220 + 2 pbw LDPE/GTR/SBS 50:25:25	theo.	0.35	1.22	4.88	25.04	77.87
	exp.	0.40	1.45	5.93	28.59	81.86
Bitumen 160/220 + 12 pbw LDPE/GTR/SBS 50:25:25	theo.	0.48	1.41	5.28	24.96	78.69
	exp.	0.71	2.64	10.47	39.59	90.36
Bitumen 160/220 + 2 pbw LDPE/GTR/SBS 25:50:25	theo.	0.37	1.27	5.02	25.24	77.68
	exp.	0.35	1.60	7.26	33.62	83.73
Bitumen 160/220 + 12 pbw LDPE/GTR/SBS 25:50:25	theo.	0.75	1.98	6.84	27.14	76.69
	exp.	0.50	1.67	7.03	30.25	81.34

Figure 1. Particle size distribution of GTR
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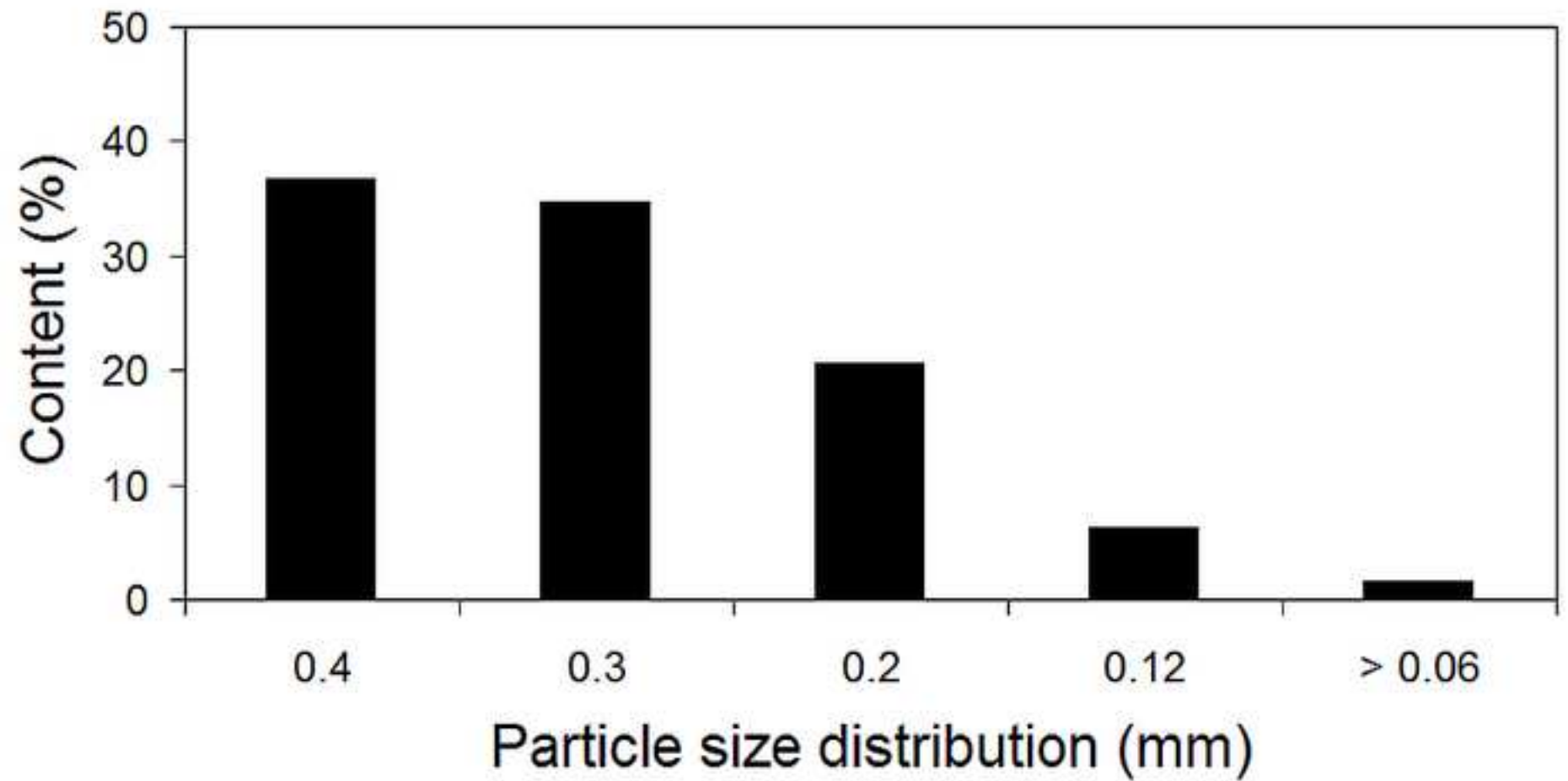


Figure 2. Melt viscosity of LDPE/GTR/elastomer blend measured at [Click here to download high resolution image](#)

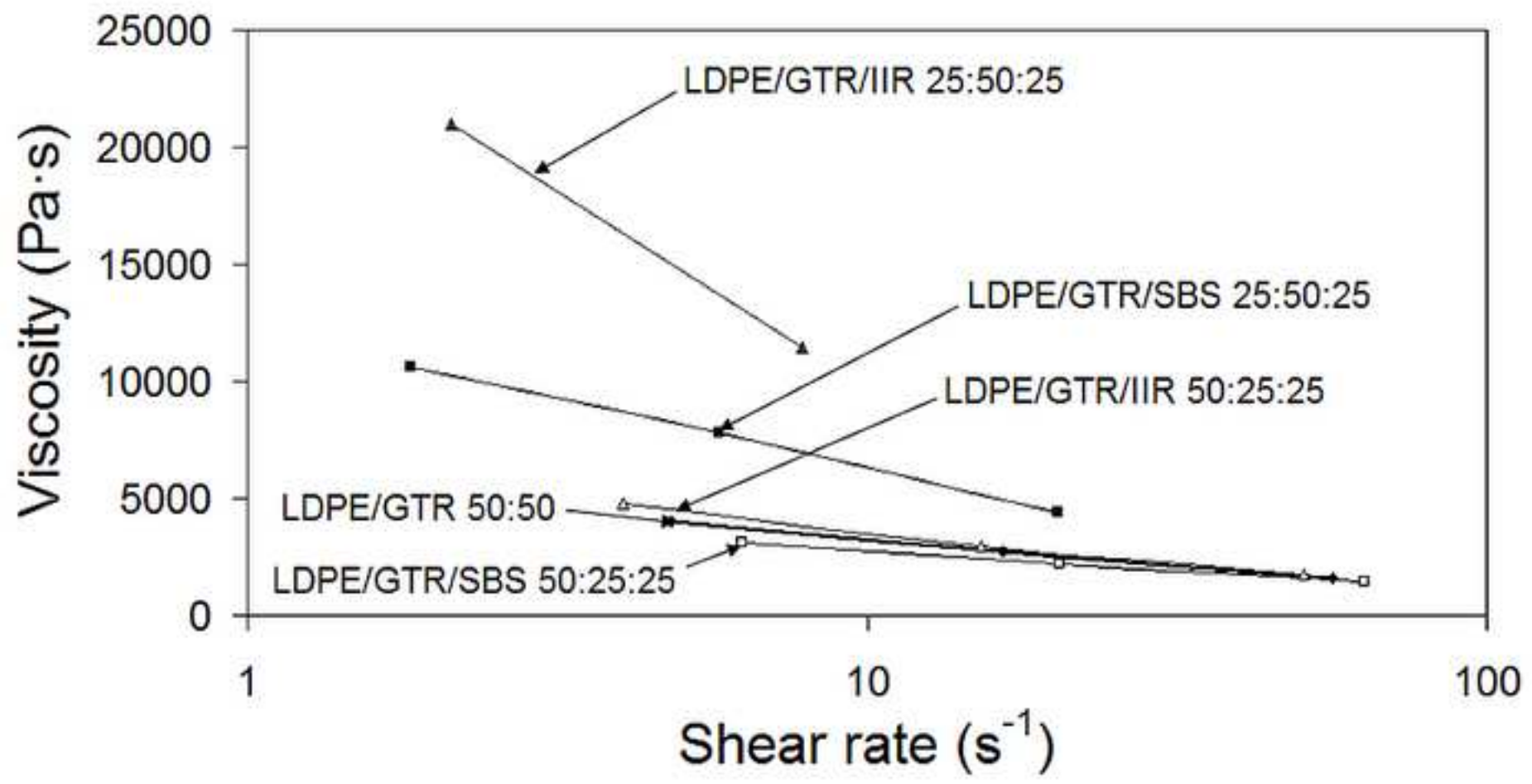


Figure 3. Penetration (at 25 °C) and softening point of bitumen
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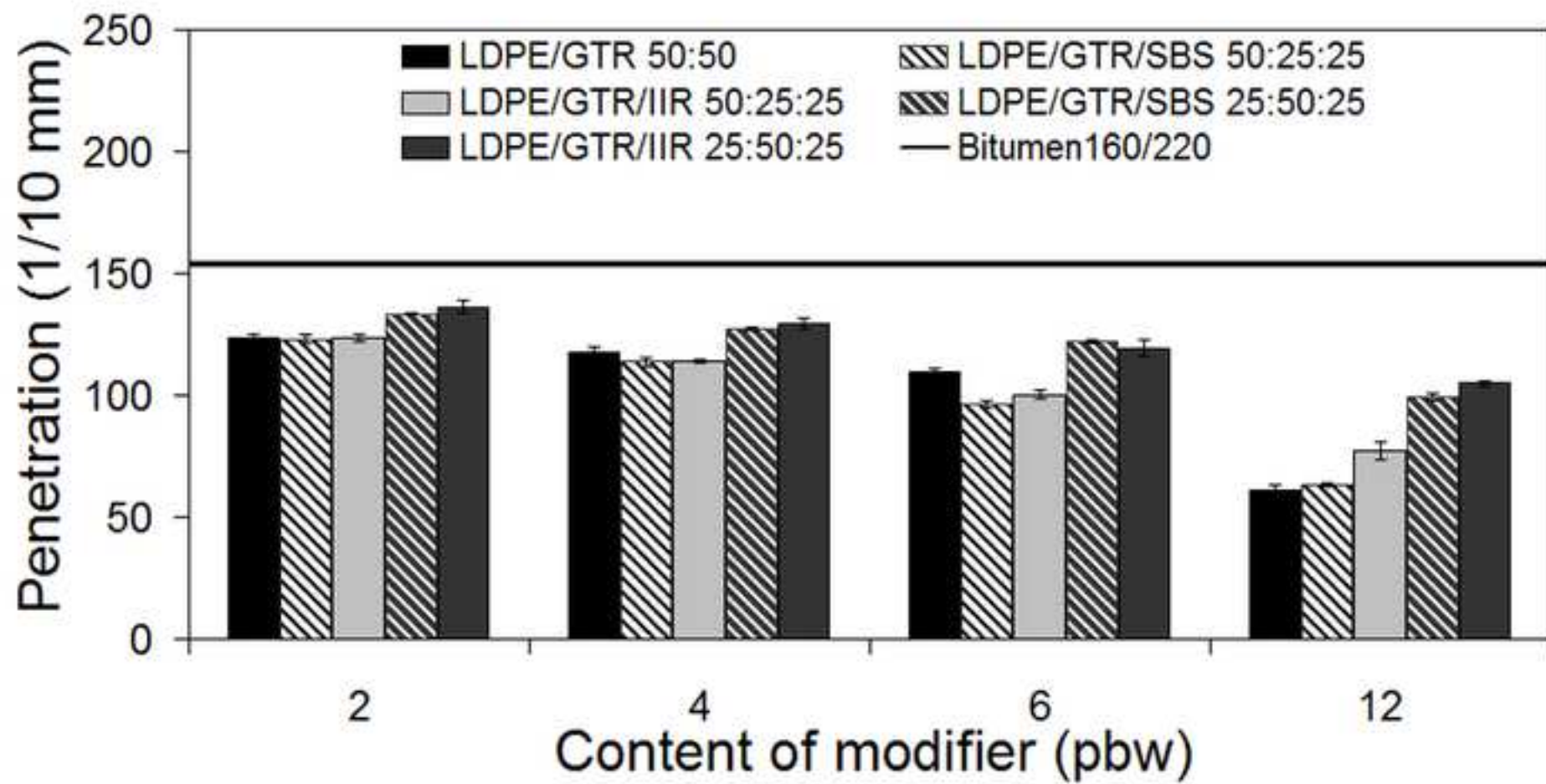


Figure 3. Penetration (at 25 °C) and softening point of bitumen
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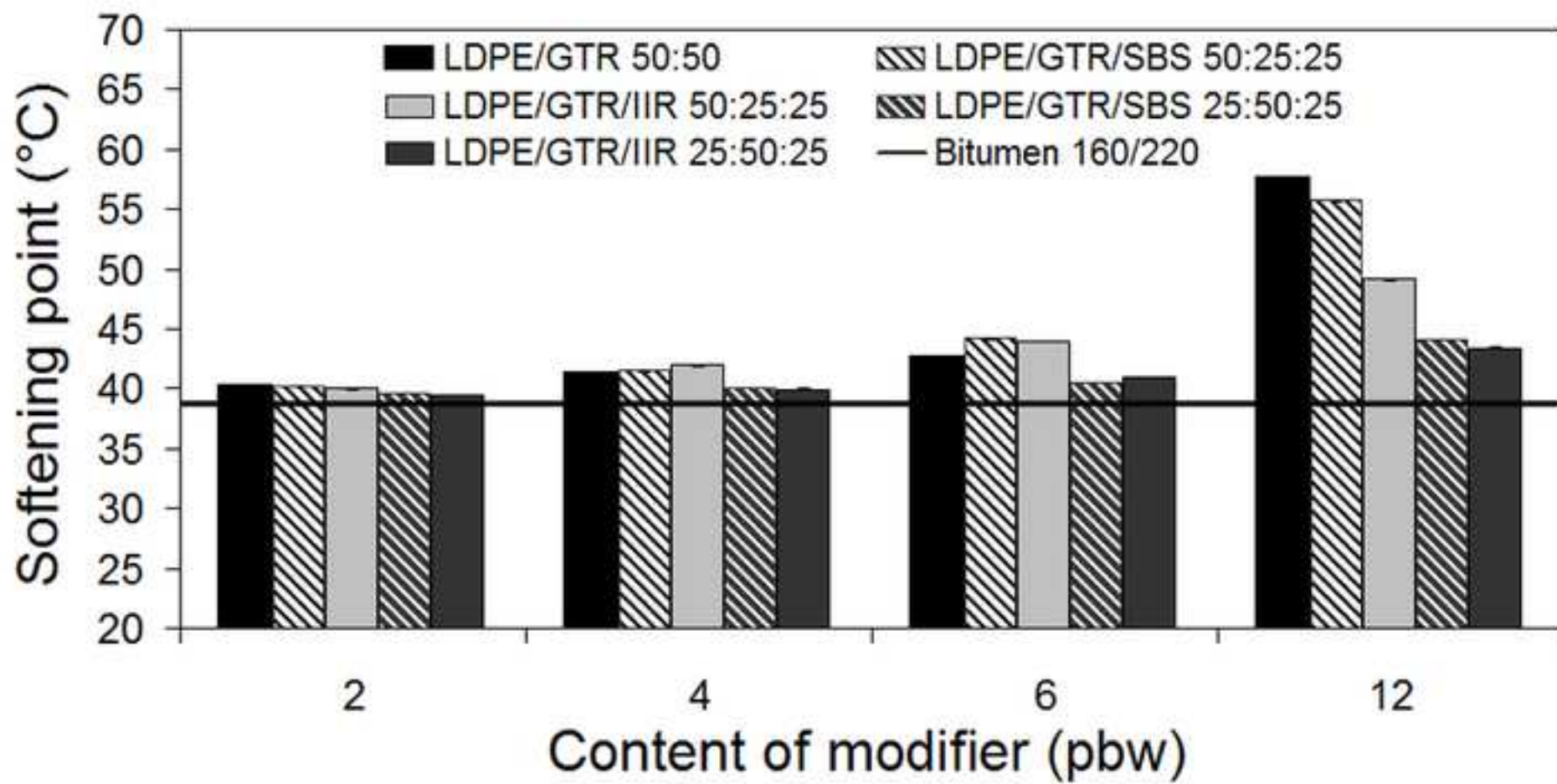


Figure 4. Penetration index (PI) of bitumen modified with LDPE/G
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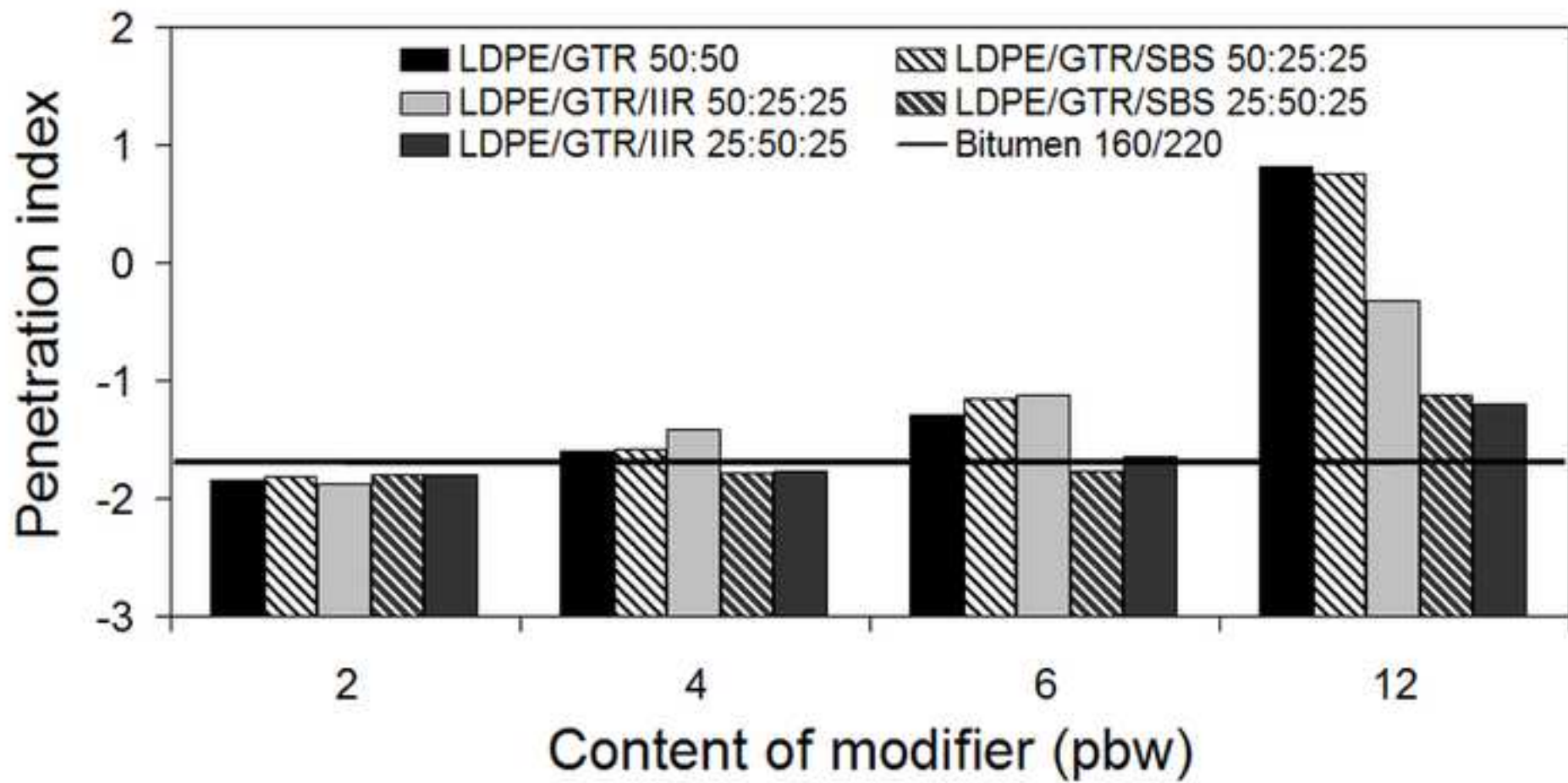


Figure 5. Microstructure of: A - bitumen 160/220; bitumen with 1
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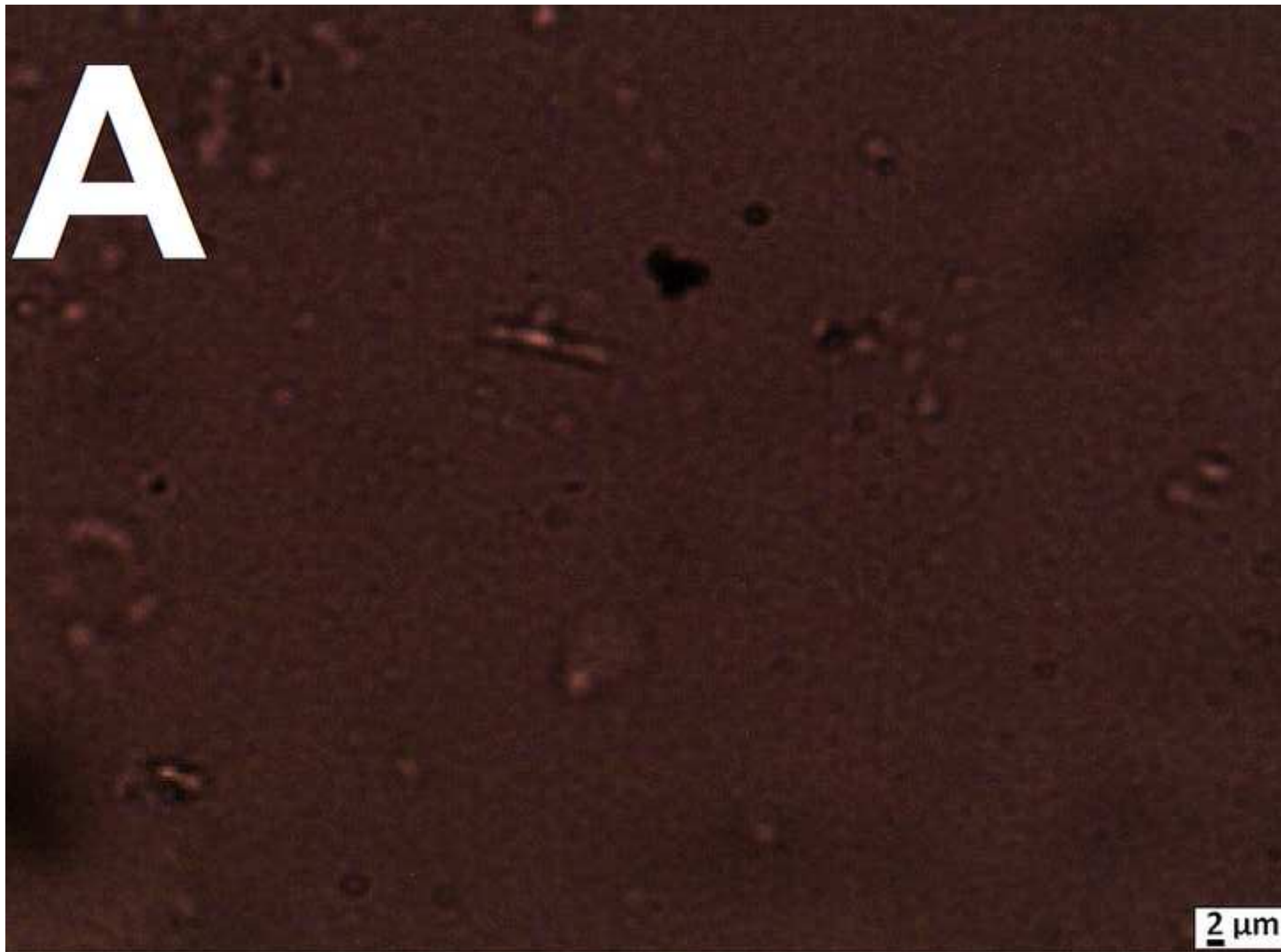


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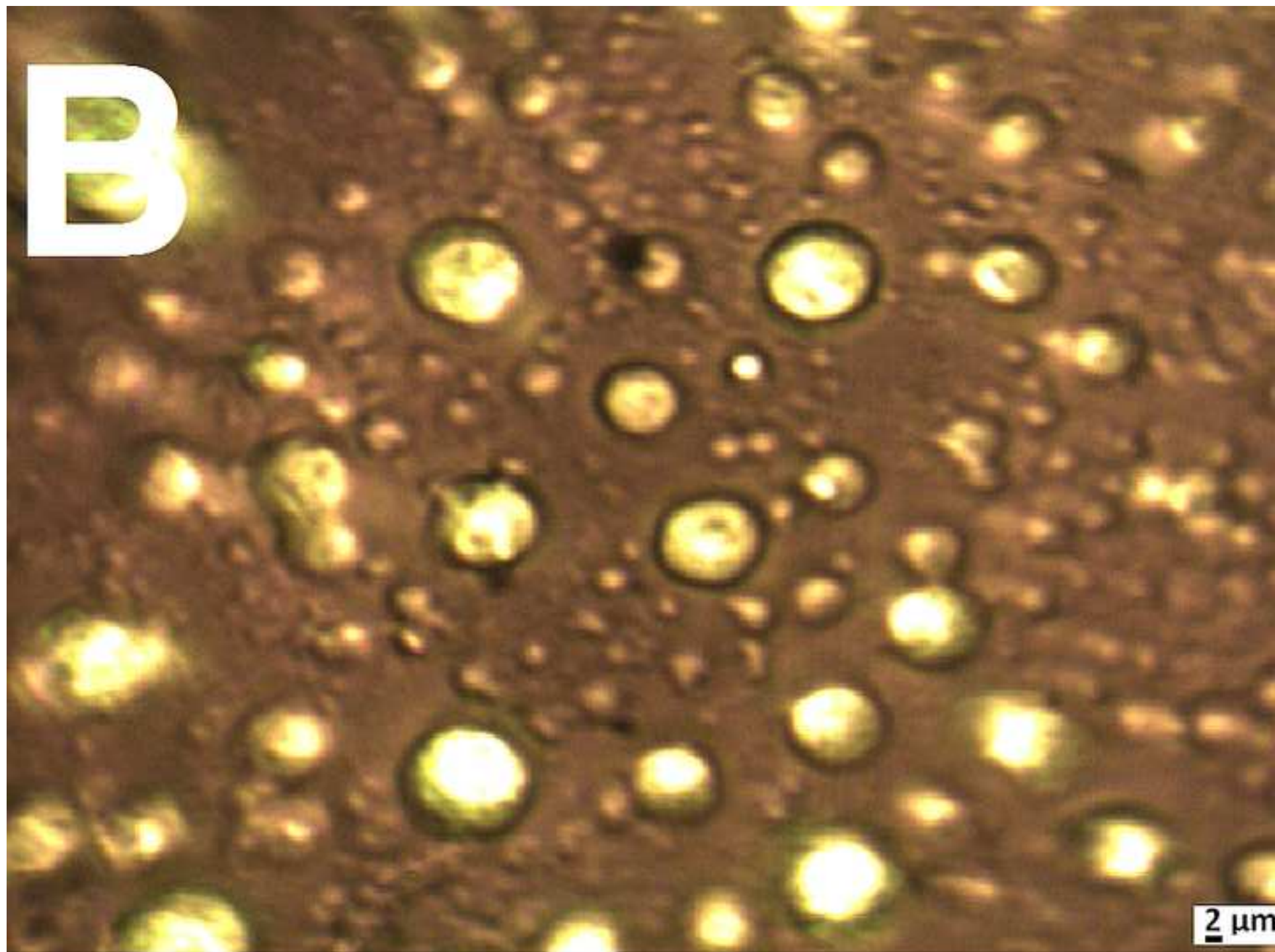


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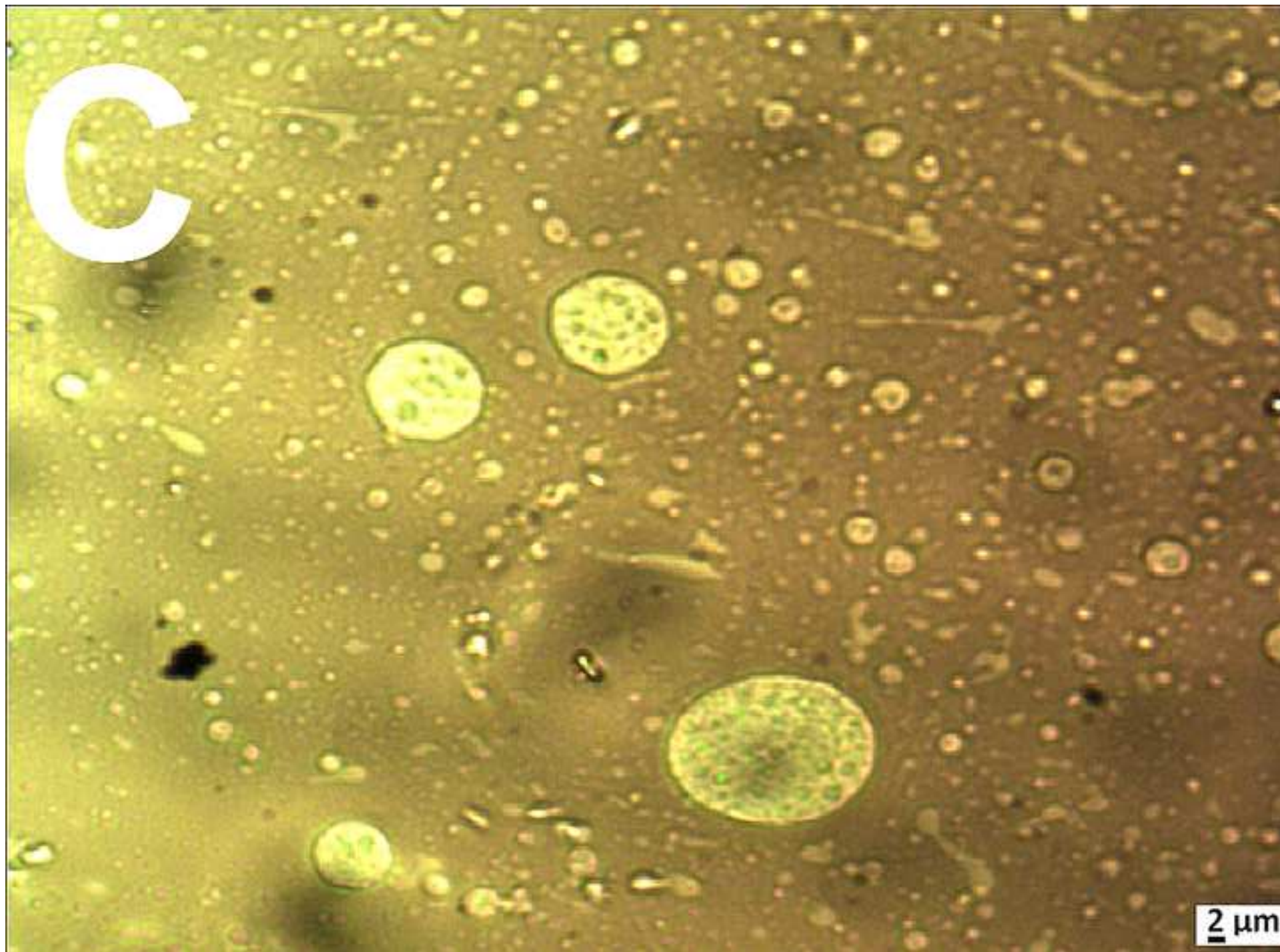


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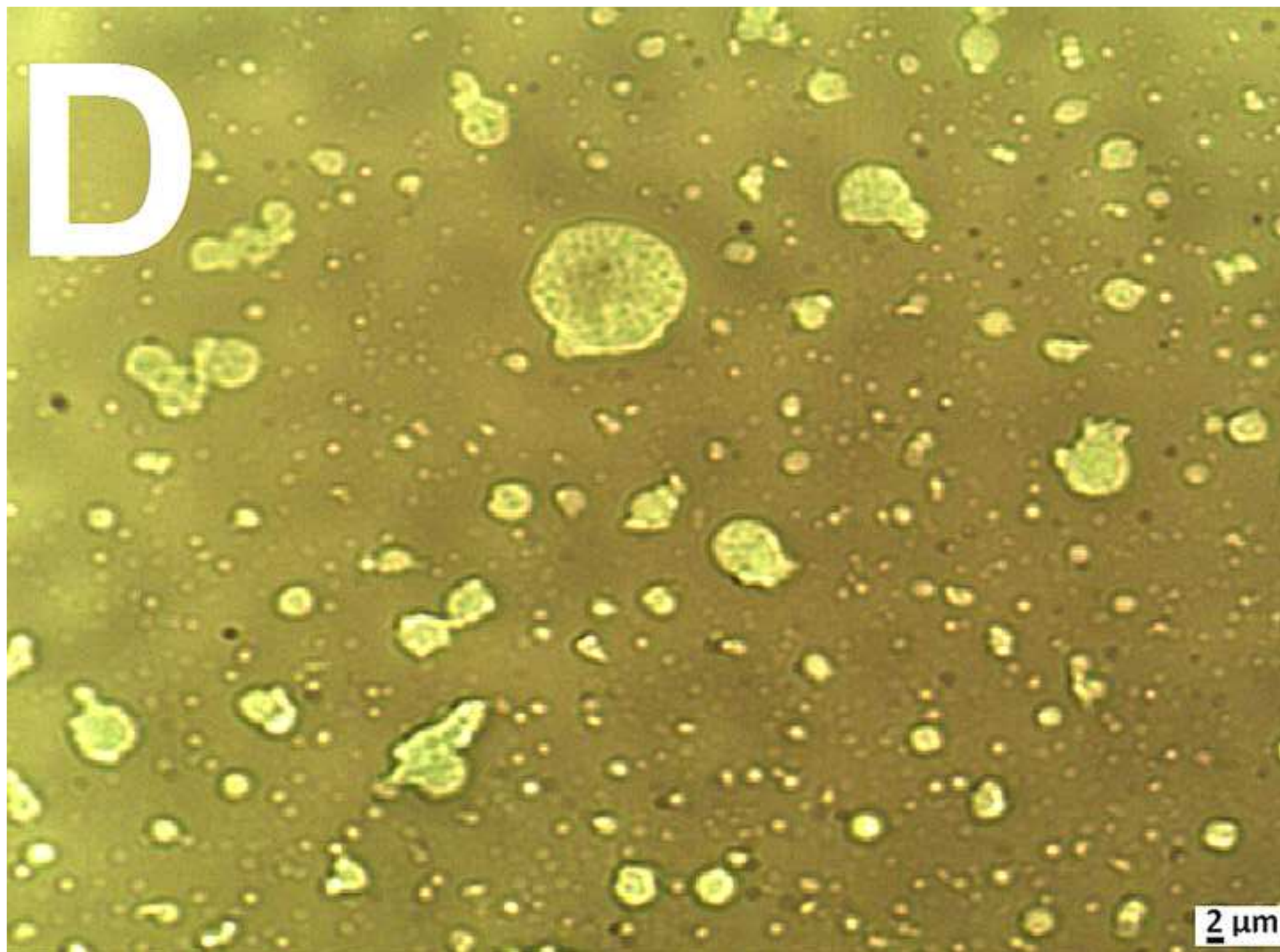


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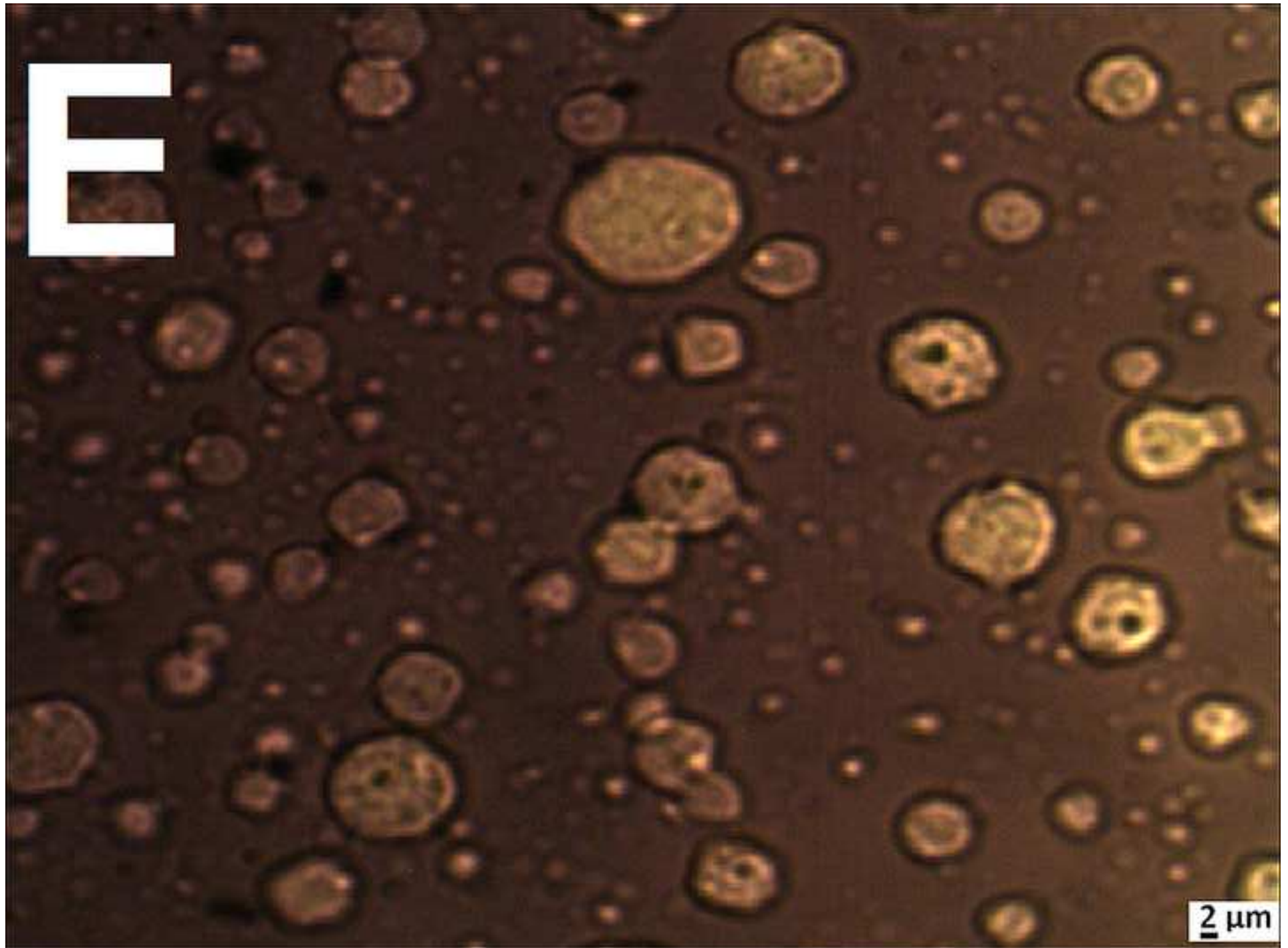


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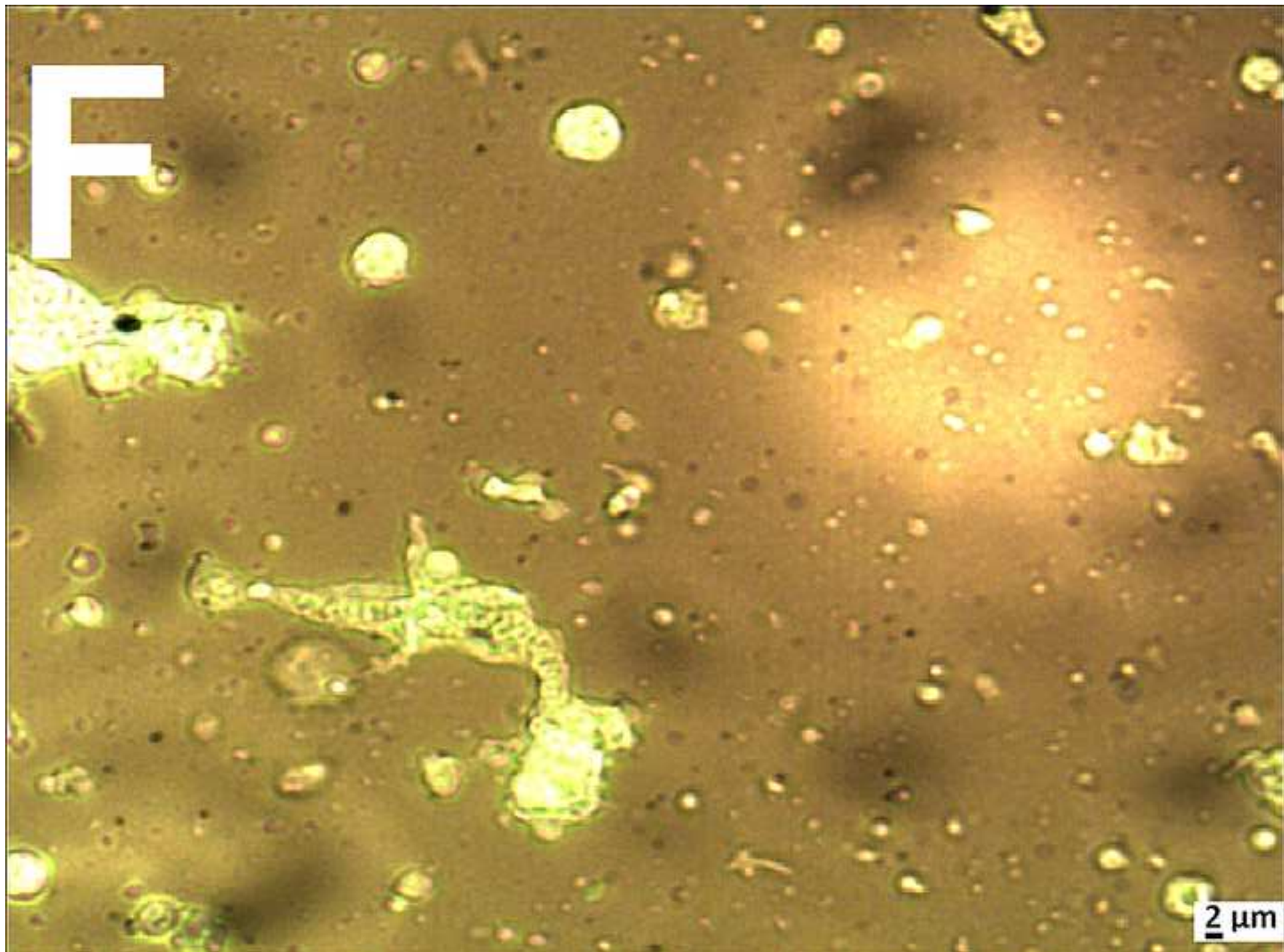


Figure 6. Loss tangent as a function of temperature plotted for
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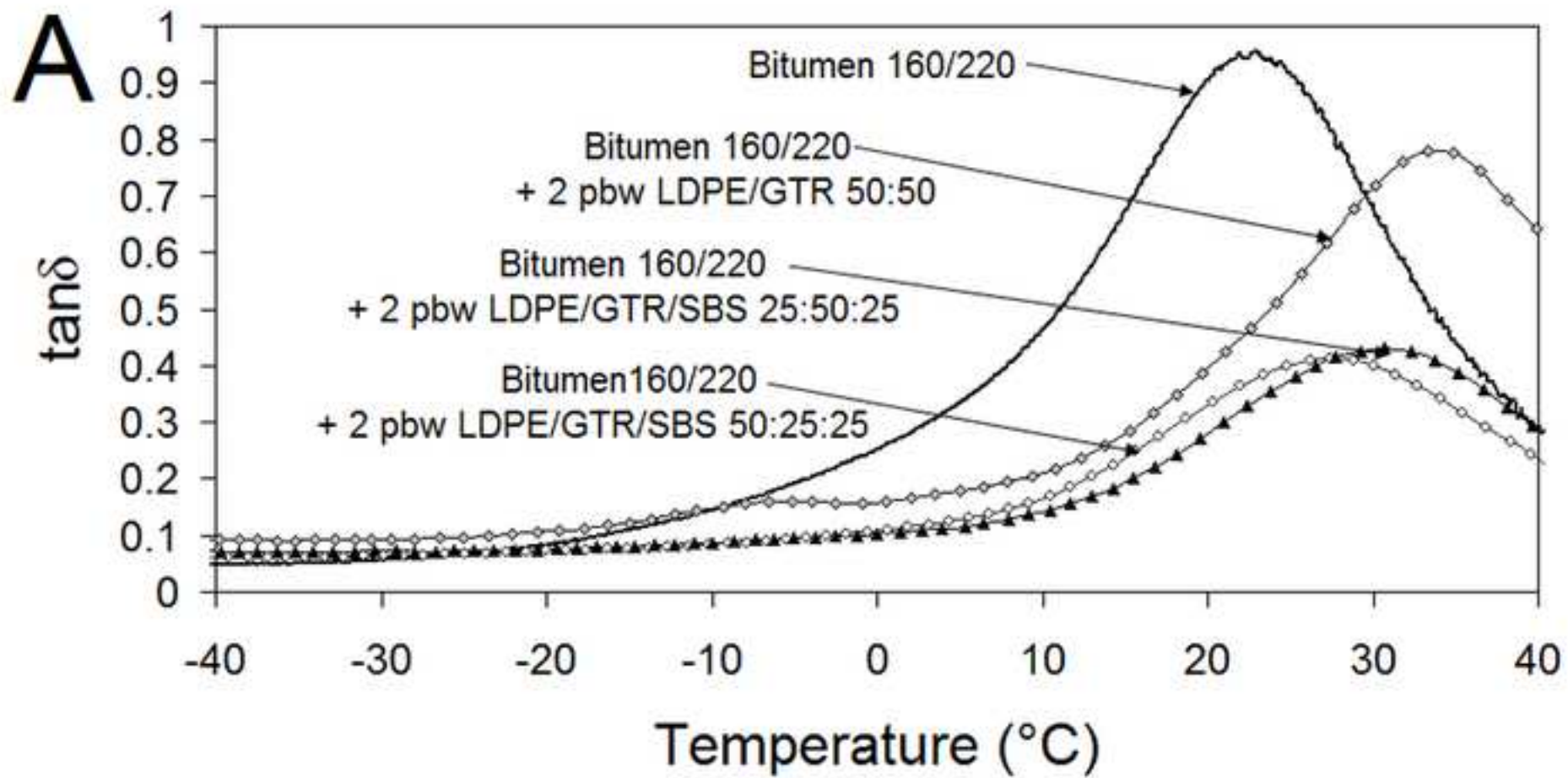


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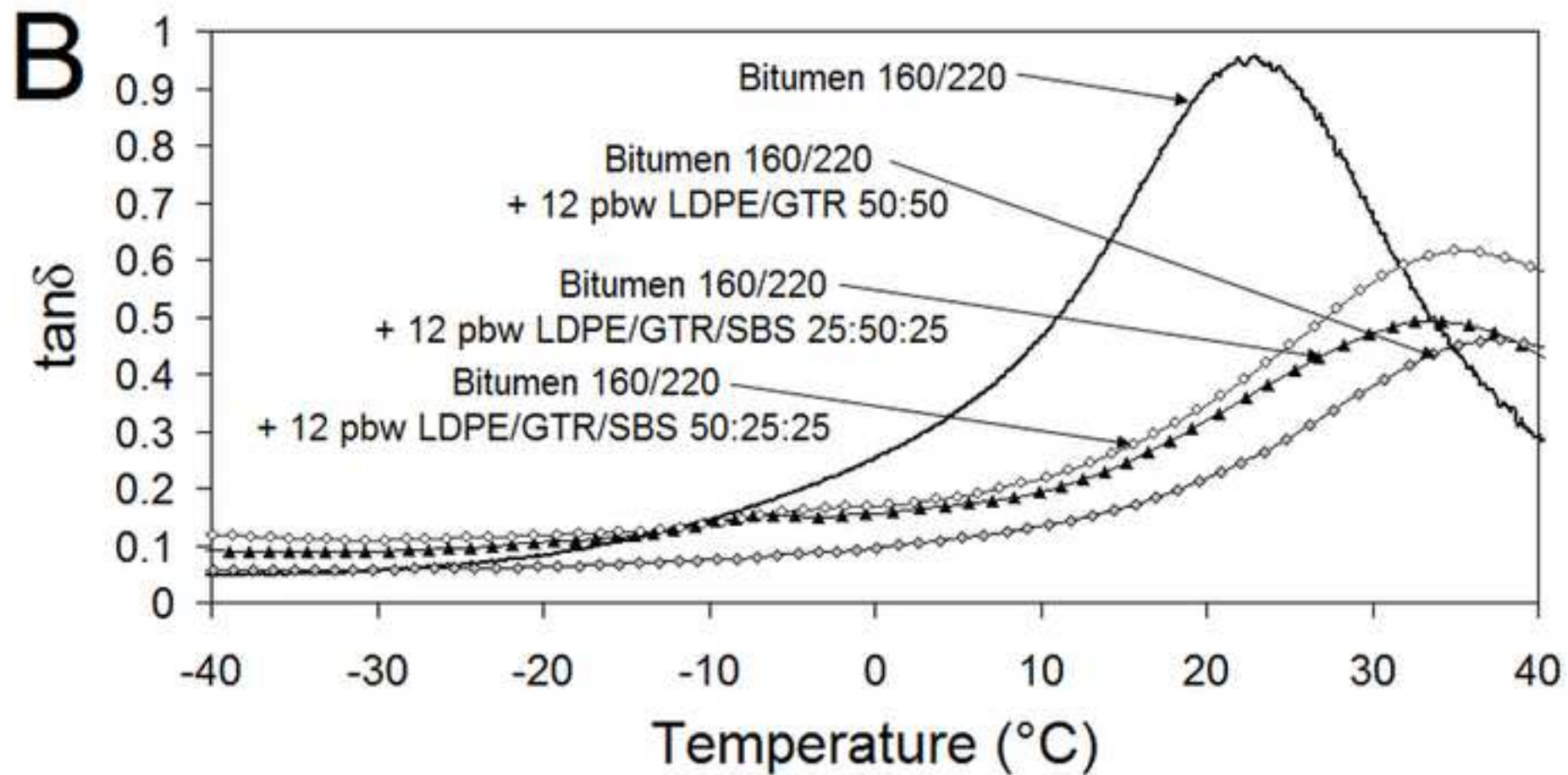


Figure 7. TGA curves determined for used components and selected
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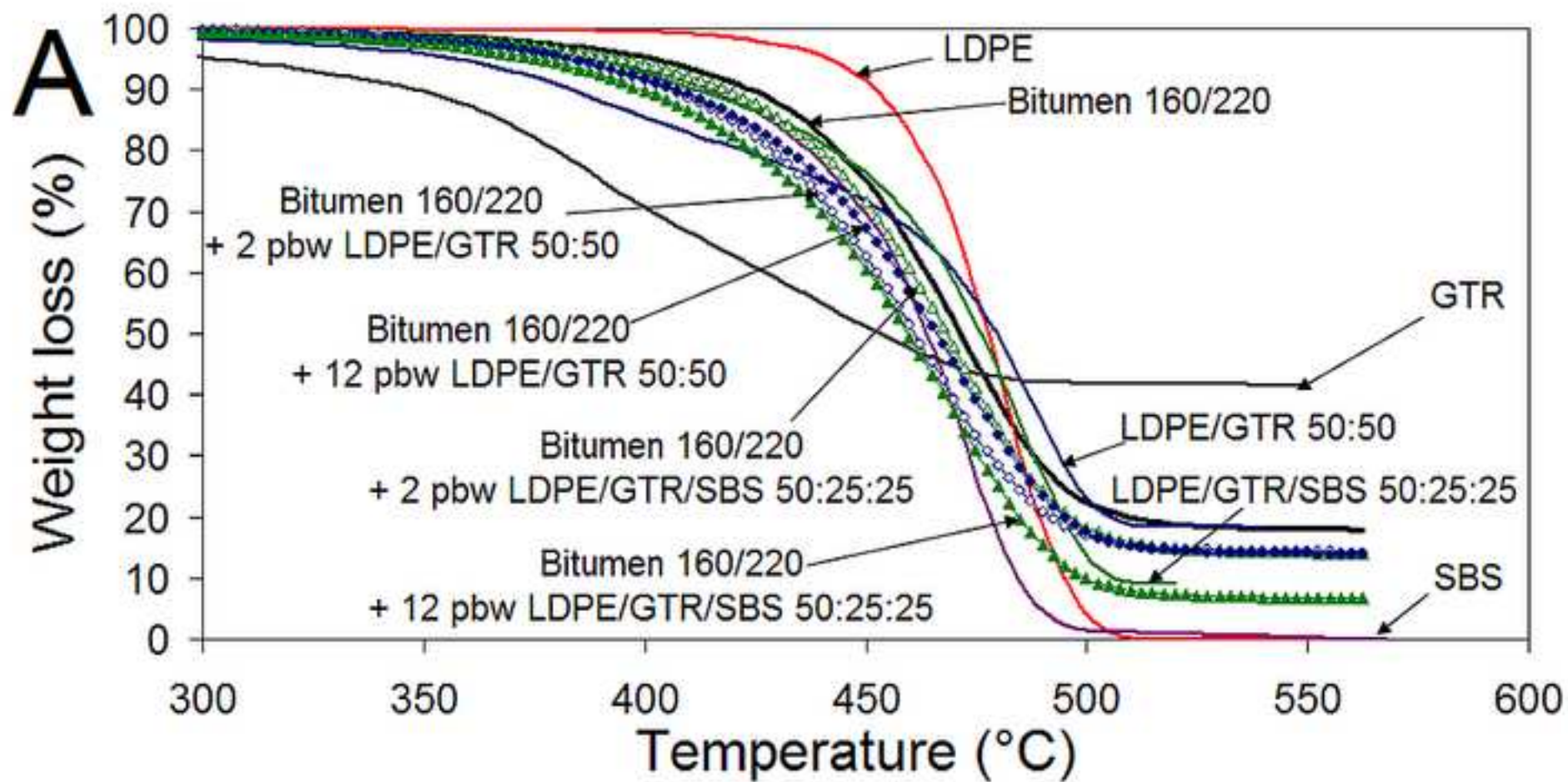


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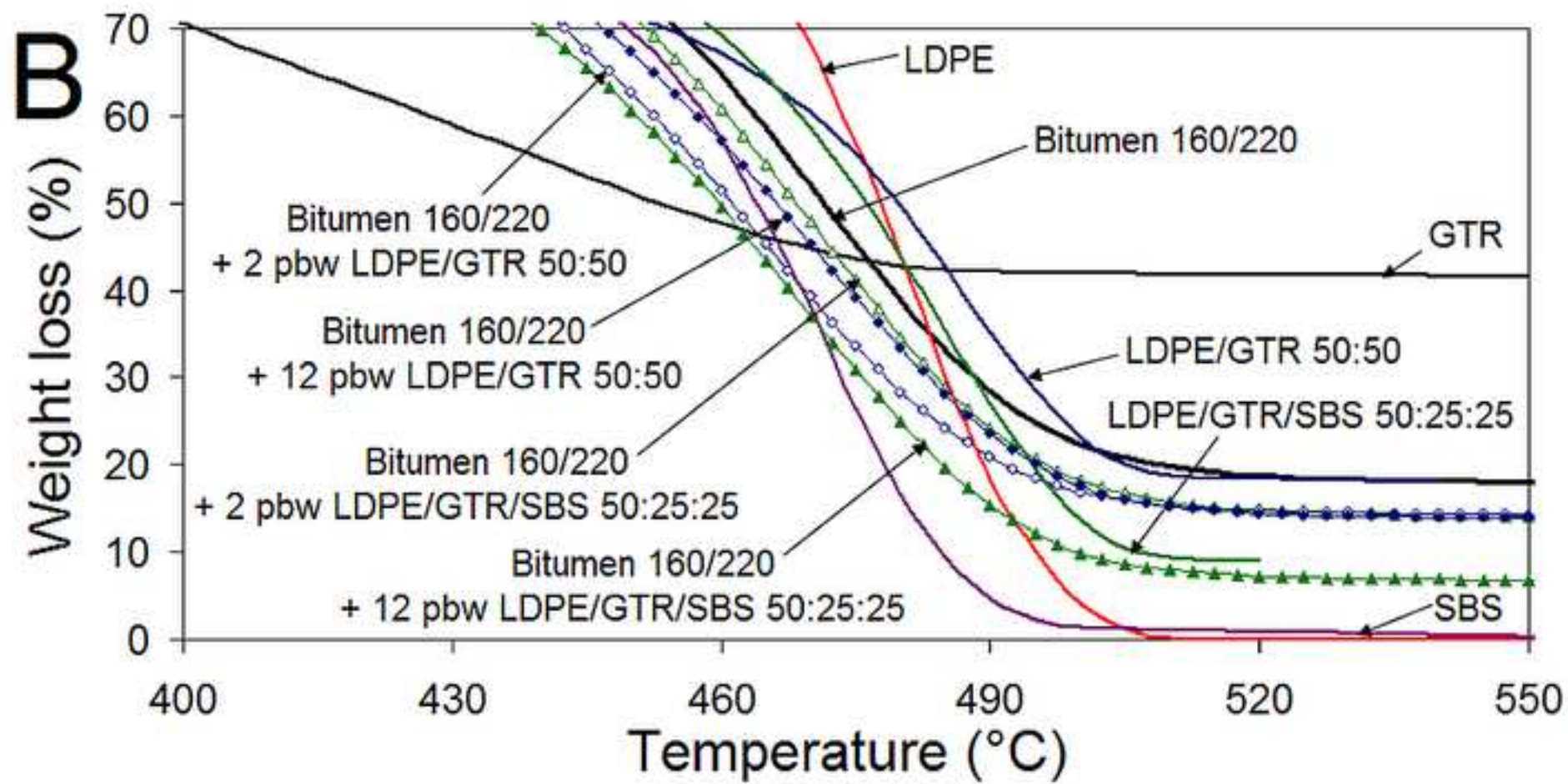


Figure 8. Schematic diagram of physical interactions between bit
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