REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
23-08-2003	Final Technical Report	July 1, 2002 – August 31, 2003

4. TITLE AND SUBTITLE

Development of Nanocomposite Reinforced Polymeric Materials to be Used for Racks for Retorting Polymeric Trays

5a. CONTRACT NUMBER

SP0103-02-D-0003/0001

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Sue, Hung-Jue

5d. PROJECT NUMBER

STP 2007

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Texas Engineering Experimental Station
301 Wisenbaker Engineering
Research Center
College Station, TX 77843-3577

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Defense Logistics Agency
8725 John J. Kingsman Rd
Fort Belvoir, VA 22060-6221

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Distribution Statement A. Approved for public release. Distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The Combat Rations Network (CORANET) is a Defense Logistic Agency (DLA) sponsored manufacturing technology program to improve the quality, reduce the cost, and increase the productivity of operational rations while increasing DLA's surge capability in the area of military rations. This report summarizes activity under Short Term Project 2007. The ultimate goal of this project was to develop a material to improve the performance and cost effectiveness of polymeric trays used for retorting Polytray rations. Initially, many candidate materials were gathered based on recommendation and research. Materials selection was limited to Polypropylene-based systems due to cost constraints and their prior proven performance during CORANET I and STP 1016. Studies were also performed on the current rack material as a control and reference point for comparative analysis. This narrowed selection of candidate materials was then subjected to laboratory testing. Tests included ASTM D638 Tensile, ASTM D256 Izod impact resistance, and scratch resistance (in-house developed standard which is under review by ASTM and ISO committees). All materials were tested as-new, and after exposure to the retort environment for extended periods of time. It was concluded that the PP Accpro

15. SUBJECT TERMS

Combat Rations, Military Rations, Retort Racks, Manufacturing Technology Program, Defense Logistics Agency, Polymeric Trays, Polypropylene, Food Processing

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Hung-Jue Sue
U	U	U	U	28	19b. TELEPHONE NUMBER *(Include area code)* 979-845-5024

DEFENSE LOGISTICS AGENCY
COMBAT RATION NETWORK FOR TECHNOLOGY IMPLEMENTATION-II
(CORANET II)

"CORANET Partnership"

Contract Number	**SP0103-02-D-0003**
Contractor	**Texas A&M University**
Delivery Order #	**0001**
Delivery Order Title	**CORANET Partnership**
CDRL #	**A004**
CDRL Title	**Final Project Report, STP 2007**
Reporting Period	**July 1, 2002 – August 31, 2003**
Report Date	**August 22, 2003**
Name of PI/Contact	**Hung-Jue Sue**
E-mail	**hjsue@tamu.edu**
Phone	979-845-5024
Fax	979-862-3989
Address	Polymer Technology Center Department of Mechanical Engineering Texas A&M University College Station, TX 77843-3123

Sponsored by:
DEFENSE LOGISTICS AGENCY
8725 John J. Kingman Road
RT. Belvoir, VA 22060-6221

Contractor:
Texas Engineering Experimental Station
301 Wisenbaker Engineering
Research Center
College Station, TX 77843-3577

Final Report: STP 2007

Development of Nanocomposite Reinforced Polymeric Materials to be Used for Racks for Retorting Polymeric Trays

Table of Contents

Objectives

The ultimate goal of this project is to develop a material to improve the performance and cost effectiveness of polymeric trays used for retorting Polytray rations. To that end, the following sub-objectives are specified:

(1) Determine the required physical and mechanical properties for a polymeric rack to perform satisfactory functions.

(2) Select a proper low cost polymeric material system with properties that meets all the requirement(s) stated in (1).

(3) Use the identified material to produce a trail batch of racks with the goal of reducing defects and extending the lifetime of the current retort rack.

(4) Test the trial racks in an industrial setting to evaluate the performance of the new material.

Background

The Polymeric Tray, or Polytray, is becoming an increasingly important component of the combat rations groups. In a manner similar to MRE pouches, Polytrays are loaded onto plastic trays and processed in a steam retort. The retort environment is very harsh and results in rapid deterioration of racks. Rack deterioration results in excessive costs (replacing damaged racks and product) as well as decreased efficiency due to downtime and replacement issues. Therefore, there is a strong need to create a better polytray retort rack. While it may be possible to alter rack geometry, the material that a rack is made from is of the utmost importance. No matter what advantages the geometry of a rack might offer, those benefits are unattainable unless the material can survive the retort environment.

The use of inorganic fillers has been a common practice in the plastics industry to improve the mechanical properties of thermoplastics, such as heat distortion temperature, hardness, toughness, stiffness, etc. The effectiveness of filler on the mechanical and physical properties of the composites depends strongly on its shape, particle size, aggregate size, surface characteristics and degree of dispersion.

This is of particular interest to the design of polymeric retort racks because the strength requirements of the racks preclude the use of pure (neat) polymers. Therefore, one must identify a filling material that will provide the required mechanical properties yet can survive the retort environment.

Glass fibers are among the most common inorganic filler materials used in strengthening polymers. However, glass fibers are susceptible to moisture-induced degradation; certain chemical components of the fibers dissolve in moisture. This rate of deterioration will increase if the water has an extreme pH (either basic or acidic), has mineral content, or in a high temperature environment. Therefore, glass fiber materials are usually not suitable for marine or retort applications.

Glass fibers, due to their "large" size compared with other filler materials, do not flow well during the injection molding process. Consequently, irregular dispersion of filler and voids are common when molding complex parts from glass-fiber laden resins. These problems are another reason to avoid glass fibers in polytray rack applications.

Our preliminary research has indicated that the nano-$CaCO_3$ particles (30-70 nm) and micro-talc particles (1-2 um), after proper surface treatment, are effective in improving both modulus and Izod impact strength of PP. It is highly conceivable that polymer nanocomposites, such as PP/$CaCO_3$, and advanced microcomposites, such as PP/talc can be utilized for polytray retort rack applications.

These materials are commercially available. If the materials can be shown to provide significant benefit, retort racks using these materials can be readily produced with no new capital.

Conclusions

Some of the operating conditions of retort rack polymers can be defined easily in concrete terms. The polymer (or system) must have a melting point in excess of 140 °C, and must be non-toxic. The material must be stable under a steam environment at 40 psi of pressure. The material must endure this environment without degradation for an extended period of time. The material must be formable by injection molding. Finally, the material should cost less than $1.50/lb in order to make cost effective racks.

Further specifications are prohibitively difficult to pre-quantify, but are very important nonetheless. The material must be non-brittle, and must be stiff enough to support the Polytrays. The material should also be resistant to scratching and surface degradation. The performance of rack materials in this area can be evaluated comparatively, i.e., with respect to the current glass fiber-reinforced PP, hereafter referred to as the "reference" material.

Therefore, the ideal rack material must meet the concrete requirements stated above, and would possess values of Young's modulus, and impact energy higher then that of the current material. It should demonstrate a higher resistance to scratch damage, and should have "better" durability when mechanically gouged or scratched or stressed under retort conditions.

Initially, many candidate materials were gathered based on recommendation and research. Materials selection was limited to Polypropylene-based systems due to cost constraints and their prior proven performance during CORANET I and STP 1016. Studies were also performed on the current rack material as a control and reference point for comparative analysis.

This narrowed selection of candidate materials was then subjected to laboratory testing. Tests included ASTM D638 Tensile, ASTM D256 Izod impact resistance, and scratch resistance (in-house developed standard which is under review by ASTM and ISO

committees). All materials were tested as new, and after exposure to the retort environment for extended periods of time. Additional testing (such as 3-point bending) was carried out in some cases to verify modulus and strength data generated during tensile experiments. We considered studying water quality and packaging material interaction, but these were studied in STP 1016 and were found to have negligible effect. Specimen damage and morphology were studied using optical microscopy and scanning electron microscopy as well.

Mechanical testing revealed that essentially all the candidate systems offered superior performance when compared to the reference material. The improvements due to talc (R-talc, Luzenac) systems proved to be especially good. Therefore, additional R-talc formulations were prepared and studied further.

It was concluded that the BP Accpro 9346 + 25% Luzenac R-talc by weight is the best for its overall performance and cost benefits. This material was used to mold racks for the Phase II trial.

Final analysis of used trial racks supports our conclusion that Accpro 9346+R-talc is a superior material for polytray rack applications. The Accpro 9346+R-talc based racks exhibit 100% performance satisfaction, even after 25 weeks of heavy use at the SOPACKO facility.

Recommendations

A fiberglass-based material should not be used for retort racks because of its tendency to fail after retort environment exposure.

A high crystallinity grade PP (polypropylene) that is specifically intended for high temperature applications should be used as the base material. We recommend BP Chemical ACCPRO 9346 (formerly Amoco). This is a commercially available product.

Surface-modified Talc (R7-talc) should be used as filler. Talc from Luzenac America demonstrated excellent performance. Talc should be used in concentrations ranging from 25 to 35 percent by weight. Higher talc concentrations are useful when extremely high stiffness is desired, but the talc concentration should not be increased beyond what is necessary in order to prevent brittleness.

Procedure

Samples of candidate materials were obtained from their respective manufacturers (Accpro 9346 PP from BP Chemical and R7-talc from Luzenac America). A new "reference" rack sample was obtained from SOPACKO Foods. This rack, produced by Stock America, was chosen as a basis of comparison. Rutgers University supplied another sample of the new material used by ALLPAX. All samples were machined into ASTM standard bars for Tensile and Izod-impact tests. Scratch testing was carried out on 10mm x 3mm x 100mm flat bars. Three-point bend/sag testing was conducted on 3mm x 3mm x 100 mm rectangular bars. "New" specimens were tested as molded.

Material testing was carried out both on "new" samples and samples exposed to simulated retort conditions. The benchtop retort (designed and constructed for CORANET use during STP 1016) at TAMU was used for exposure simulation. This instrument uses PID digital and analog controls to maintain the treatment chamber at predetermined temperature and pressure settings. "Exposed" samples were exposed to conditions of 125 degrees C and 35 psi of saturated steam spray. Tap water was used for retort conditions. This water was found to be chemically similar to plant water during our work on STP# 1016.

Each candidate material underwent tensile, impact, and scratch-resistance testing both as "new" and after service simulation. Initial testing revealed the basic properties of the material, while extended exposure testing demonstrates the material's behavior and performance change over time. As well, specimens were examined microscopically in order to study the affects of service exposure and scratching on the material surface quality.

Tensile testing was conducted using an Instron series-II universal test fixture operated by a Sintech computer interface. Raw strain and force data was gathered using an RS-232 serial interface. All linear measurements (for strain calculation) were made using a

Mitutoyo DigiMatic slide caliper and recorded to three decimal places. Data analysis was performed using Microsoft Excel.

Impact testing was carried out using a TMI computerized impact test machine configured to output raw impact energy digitally. These values were normalized based on surface area of the fracture region. All linear measurements (for area calculation) were made using a Mitutoyo DigiMatic slide caliper and recorded to three decimal places.

Cross-sectional scratch-resistance and surface crack resistance analysis were performed optically. The specimens were sectioned and embedded in epoxy. The mounted samples were then prepared using an Abramin polishing machine. The polished specimens were examined and photographed using an Olympus BX-60 optical microscope equipped with a digital image capture system and variable polarizer.

Further scratch and surface analysis was performed using a Jeol JSM-6400 Scanning Electron Microscope in order to obtain a topdown (surface) view of the specimen. Samples were vacuum-dried and sputter coated with Au-Pd in order to provide a conductive surface required for the microscope to function. SEM images were captured digitally and the images were post processed in Adobe PhotoShop.

Scratch resistance quantification was performed on our Scratch Analyzer, which is capable of resolving data to the centi-newton scale.

Three-point-bend (sag) study was performed in a Blue M environmental chamber. Measurements were made using a Mitutoyo dial indicator. Environmental conditions were 125 degrees C, saturated steam at atmospheric pressure. Deadweight load was maintained throughout the test period with no immersion.

Final study of the post-trial rack samples was performed using a Zeiss stereomicroscope. Photographs were taken using a Nikon camera and Kodak TMAX ASA100 film.

Results and Discussion

Initial research and manufacturer-provided specifications allowed effective initial screening of candidate materials. Most potential polymer solutions were eliminated from consideration early on due to excessive cost issues. Final polymer evaluation and selection were determined by laboratory testing.

The initial phase of the work-study focused on identifying the mechanical characteristics and problem areas of the reference material, used in current polytray retort racks. The problem areas are several: The mechanical properties (strength and impact resistance/toughness) drop off sharply after exposure [Figs. 1-5]. As well, the rack material has poor adhesion between filler (i.e., glass fibers) and resin, which weakens the material and results in varying properties throughout the rack [Fig. 7a]. As well, air inclusions were commonplace.

Every fiberglass-based material tested in this project (two commercial products as well as the reference material and the ALLPAX-Rutgers material) demonstrated initially satisfactory properties, yet suffered from a significant drop in material properties after prolonged exposure to the retort environment. This behavior can be clearly observed on charts of tensile strength [Fig 3], surface durability [Fig 4], and sag [Fig 5]. As well, microscopy can clearly show the breakdown of the fiberglass materials [Fig 6,7]. This lead us to conclude that fiberglass-filled materials are a poor choice for use in the retort environment.

Environmental testing is crucial because a rack will fail—regardless of geometry—if the material it is made from cannot survive the operating environment.

Our initial work focused on using nano- and micro-composites based on PP (polypropylene). Our experience with these materials in STP 1016 indicated that newly developed thermostabilized PP (such as BP Chemical 9346) was particularly well suited

for Retort use. Initial candidates included various nano- and micro-composites made using BP 9346.

Mechanical testing demonstrated that all candidate materials possess superior tensile strength and impact resistance to the current (reference) material [Fig. 1]. The R7-talc systems offered the highest stiffness while nanocomposite PP offers the greatest impact resistance. It is interesting to note that while increasing the amount of R7-talc in those systems improves stiffness in a nearly linear fashion, impact resistance is not affected to as large a degree.

Scratch-resistance studies were used to evaluate the durability of the candidate materials. This is of vital importance because we believe that the failure of the reference material initiates at the rack surface. Scratch testing can directly quantify the surface durability of each material [Fig. 6].

The reference material demonstrated poor resistance to scratching and surface wear, requiring a relatively low applied load in order to achieve significant surface damage [Fig. 2]. It was discovered that adding large amounts of R7-talc to neat PP decreases scratch resistance, yet lower concentrations had no noticeable effect. On a microscopic scale, all candidate materials show a far greater resistance to significant damage.

Optical microscopy and SEM analysis shows that while the reference material has a rough surface [Fig. 7a] with protruding fibers and clearly visible de-bonding, all candidate materials present a smooth surface with no significant damage or deterioration, despite exposure. This means that racks molded from any of the candidate materials will have smoother, safer surfaces. As well, the lack of significantly sized crevices, cracks, or other stress risers indicates that these materials will be more durable, since there are fewer opportunities for failure to initiate.

In this case, we are faced with a situation in which all of the candidate materials are superior to the reference material [Figs. 1 and 2]. It is a matter of selecting which

material is optimal. While the nanocomposite system offers greatly enhanced impact resistance, the R7-talc system offers a better combination of good impact resistance and increased stiffness. The 25% concentration achieves excellent strength properties, while further optimizing impact resistance and balanced processability. Therefore, we recommended that the 25% R7-talc system be used in Phase II of the project.

Our Phase II trial consisted of two full retort loads of racks. Racks were molded on the government mold by Stock America. Thus, the trial racks were geometrically identical to the reference racks currently used by industry. Racks were used daily for a twenty-five week period. Trial data indicated that the recommended material (BP 9346 + 25% Luzenac R-Talc) did indeed perform extremely well, with no rack failures noted. This was described by SOPACKO Personnel as "significantly better" than their experience with the reference racks [Table 2].

During the Phase II study, we performed additional laboratory testing concerning the long-term exposure of rack materials. In particular, we focused on the issue of rack sag as raised during a CORANET Workshop.

A group of specimens was prepared, including laboratory samples of 25% R-talc, "trial" samples (cut from Phase II test racks), reference samples, and samples of the new ALLPAX material provided by Rutgers University. Samples were exposed for up to 288 hours in retort conditions.

This testing revealed that the trial rack material performed nearly identical to the laboratory samples [Figs. 1 and 5]. This is to be expected. Furthermore, the data indicates that sag is not a problem with the PP + R-talc system. Most interesting of all, however, is the clear demonstration of the unusual degradation properties of fiberglass-filled materials [Figs. 3-5]. This supports our initial conclusion that fiberglass-based materials are a poor choice for retort applications.

After the conclusion of the 25-week trial period, used rack specimens were shipped to our laboratory for final evaluation. An optical microscopy study was performed in order to compare the condition of a trial rack with a reference rack. We selected three points of comparison: a central intersection point [Fig. 8], a corner [Fig. 9], and a narrow ridge {Fig. 10]. Comparison of these surfaces clearly demonstrates the ability of the new material to endure in the retort environment when the reference material cannot. All fiberglass surfaces—especially the high wear corner area—show significant material deterioration. Cracking and debonding of the glass fibers is obvious and can even be seen with the naked eye. Conversely, the trial material shows no damage in these same areas.

Table 1: Cost Analysis of Materials: (estimated cost *per rack*)

•Reference Material	$9.00
•Neat PP	$3.00
•R-talc 25%	$3.10
•R-talc 30%	$3.00
•R-talc 35%	$2.90
•PP-$CaCO_3$ Nanocomposite	$4.00

***Based on $.10/lb compounding fee; excludes molding costs.**

Table 2: Phase II Trial Data

- Total Minor Defects* 2
- Total Major Defects† 0
- Total Failures / Rejects‡ 0

*Minor Defect defined as a scrape, crack, or chip that is visible under close inspection, not immediately obvious, and does not compromise the usability of the rack

†Major Defect defined as a rack damage that is significant enough to be clearly visible, and may require special care or "work around" in order to use the rack.

‡Failure / Reject defined as damage so severe that the rack must be removed from service

Fig. 1: Property Comparison of Rack Materials

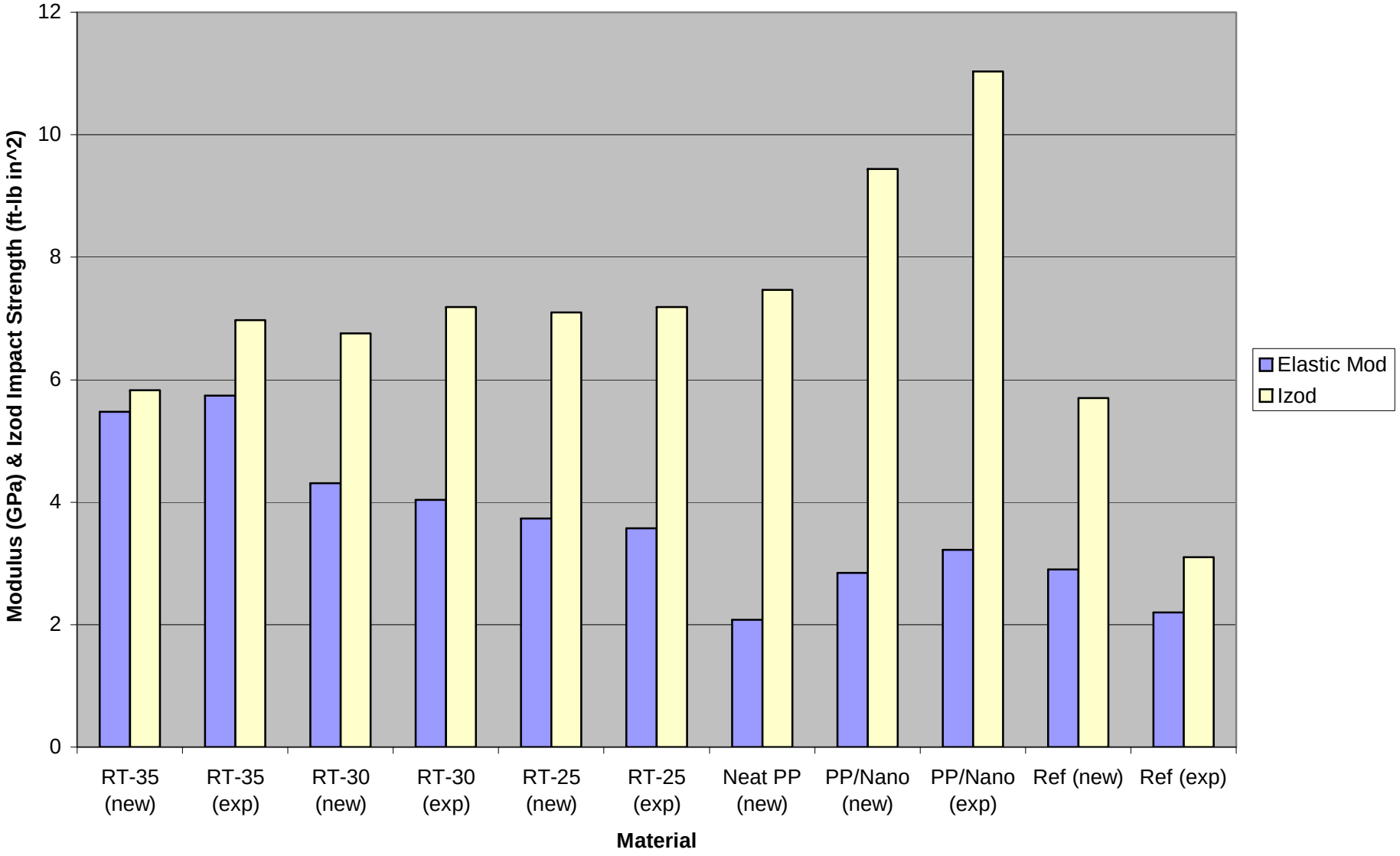


Fig. 2: Material Property Comparison

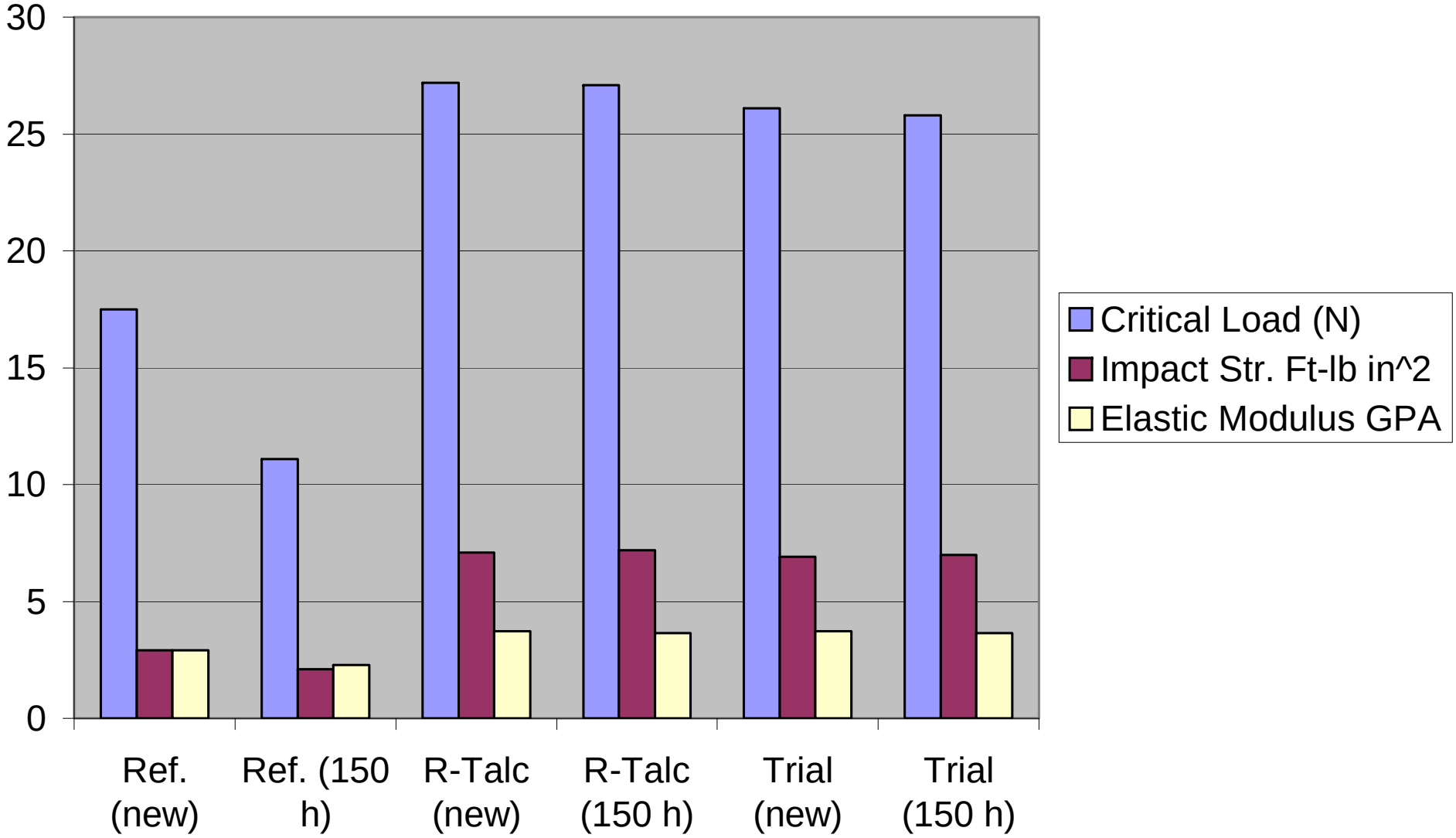


Fig. 3: Effect of Retort Exposure on Tensile Strength of Rack Materials

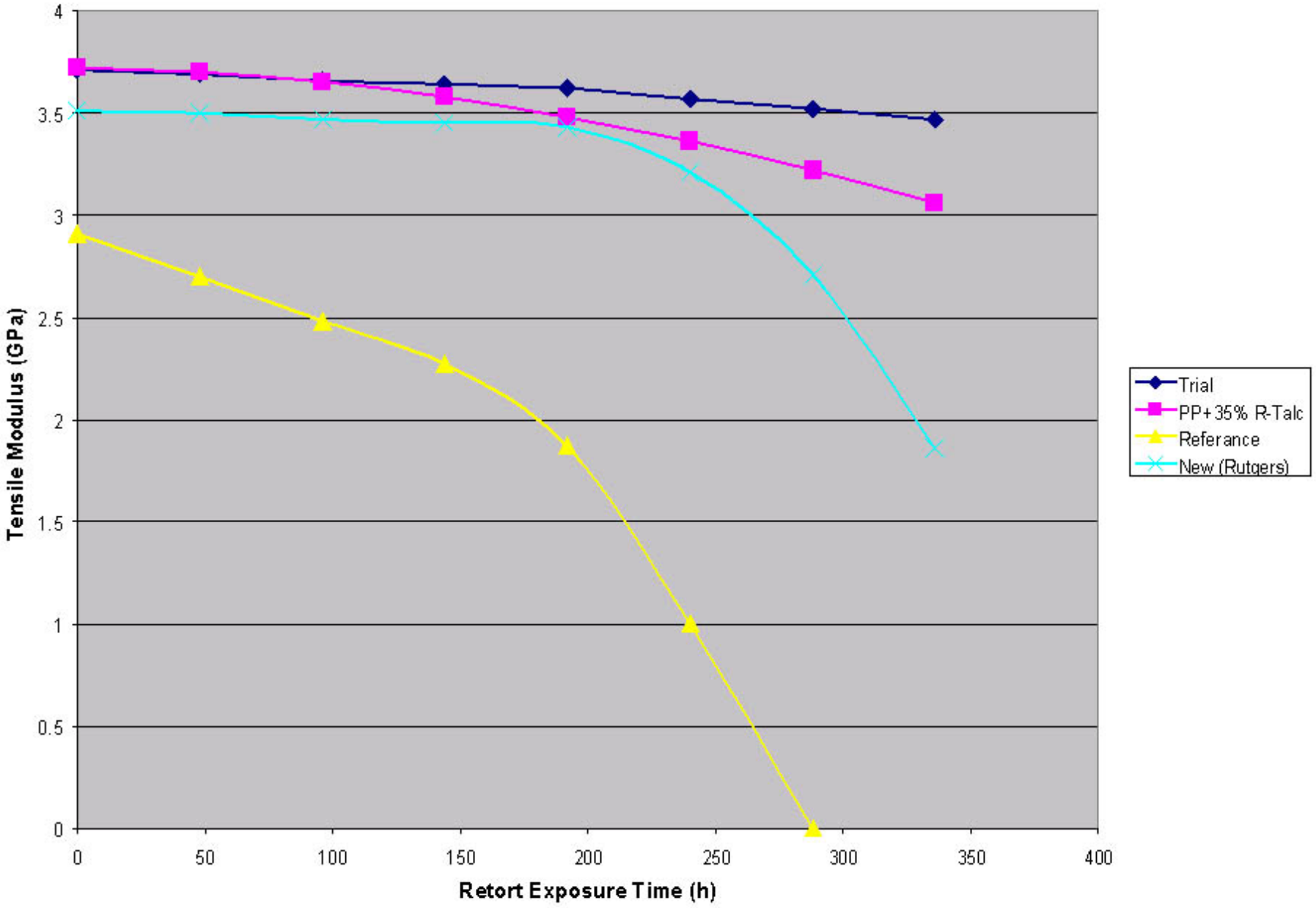


Fig. 4: Effect of Retort Exposure on Surface Durability of Rack Materials

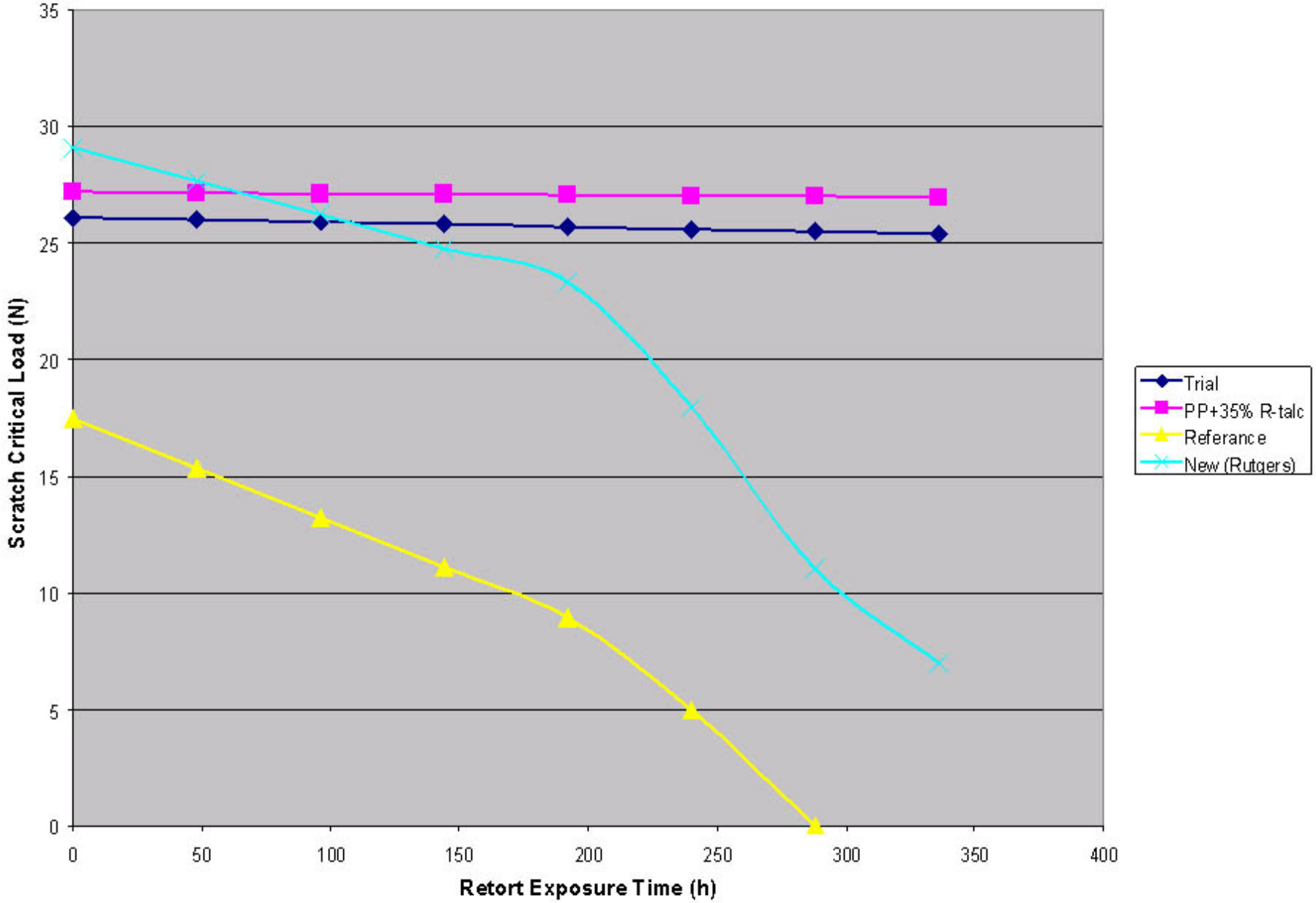


Fig. 5: **Effect of Retort Exposure and Load on Rack Deflection (Sag)**

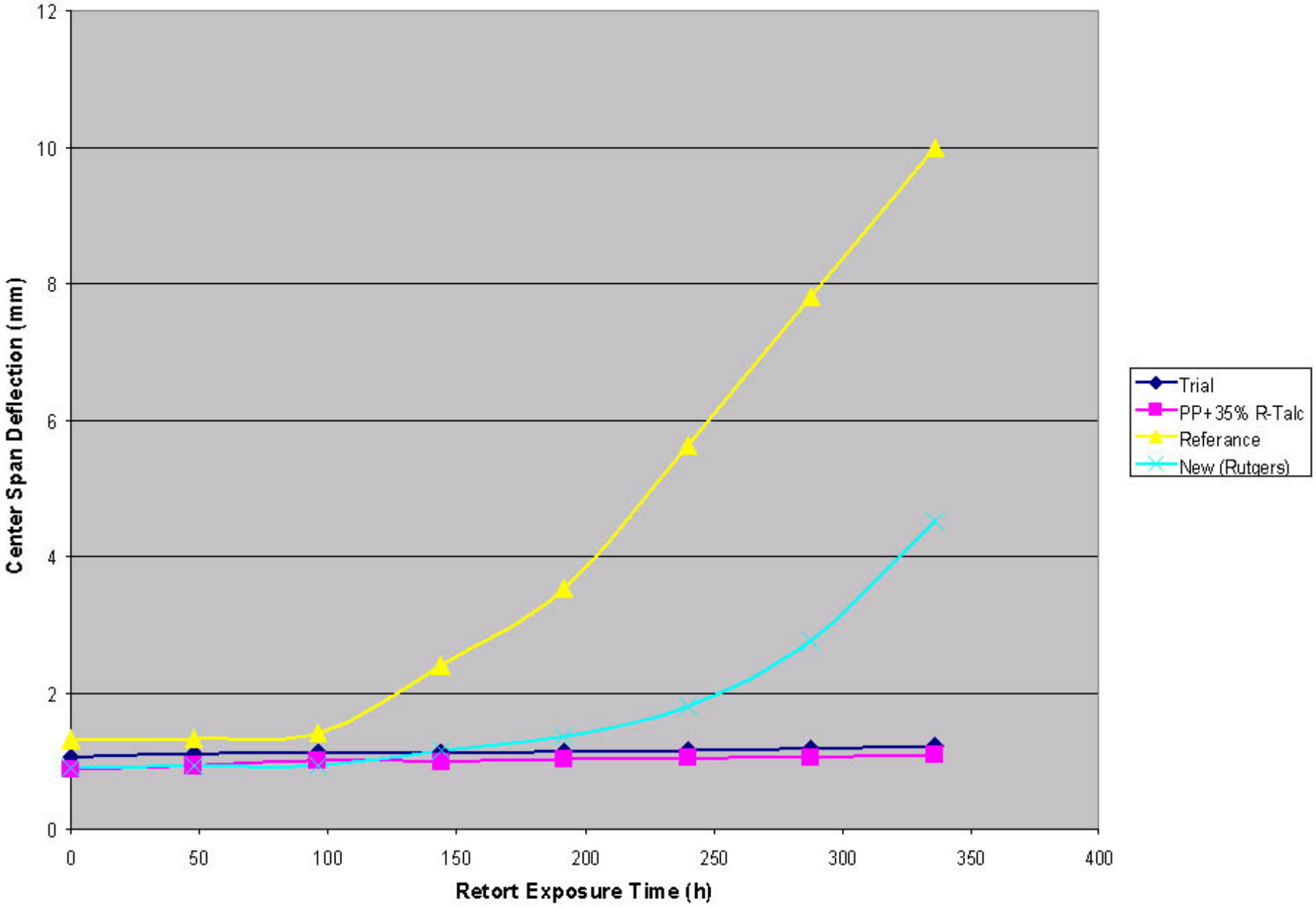
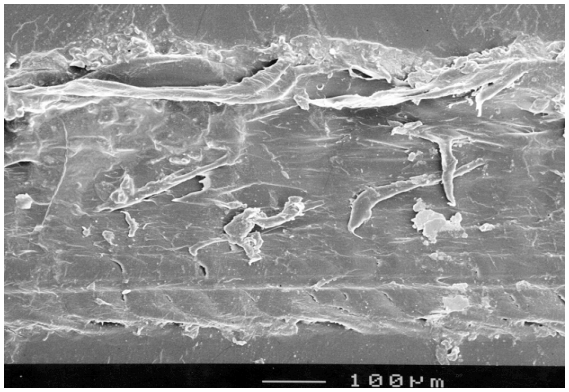
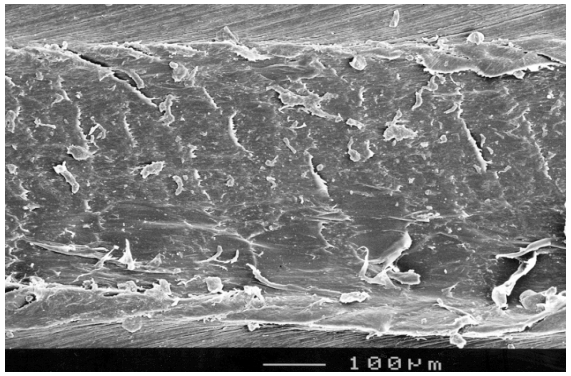


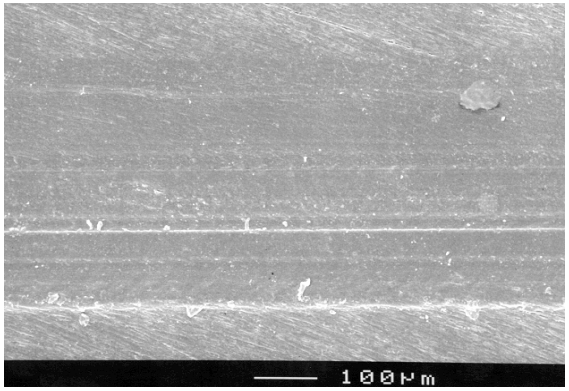
Fig. 6a: Surface Durability Comparison New Material



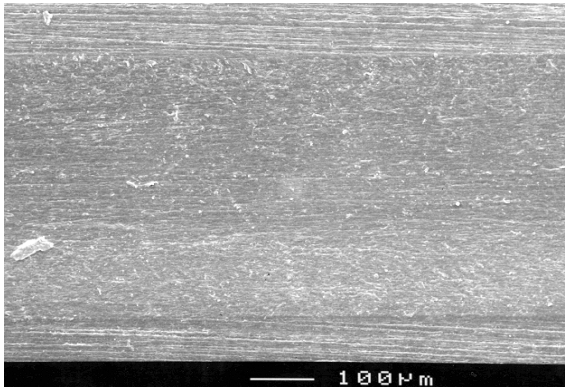
Neat PP



Reference

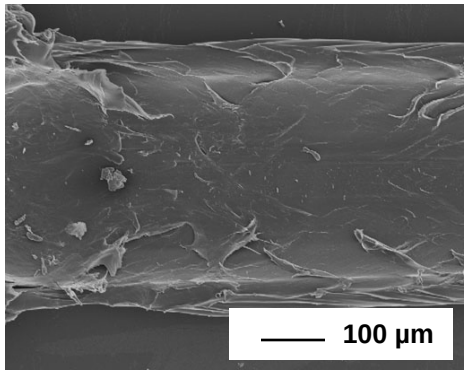


R7-Talc

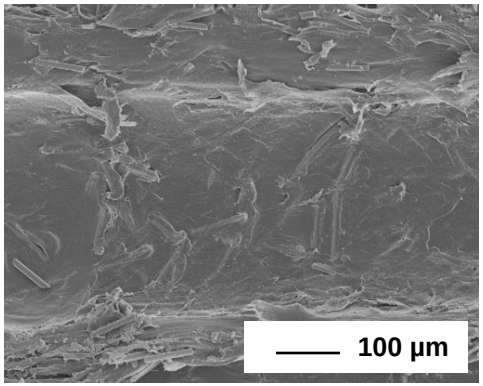


PP/$CaCO_3$

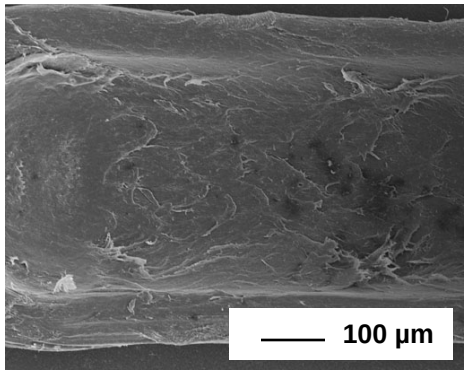
Fig 6b: Surface Durability Comparison Exposed Material



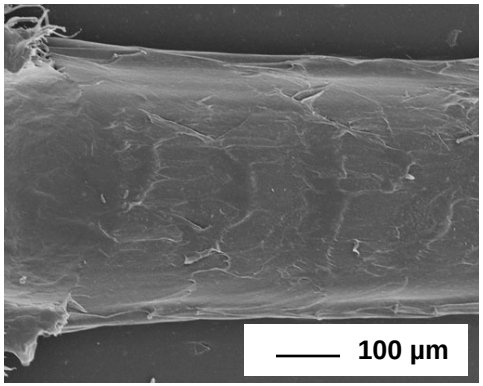
Neat PP



Reference



R7-Talc



PP/$CaCO_3$

Fig. 7a: SEM Analysis of Surface: Reference Sample

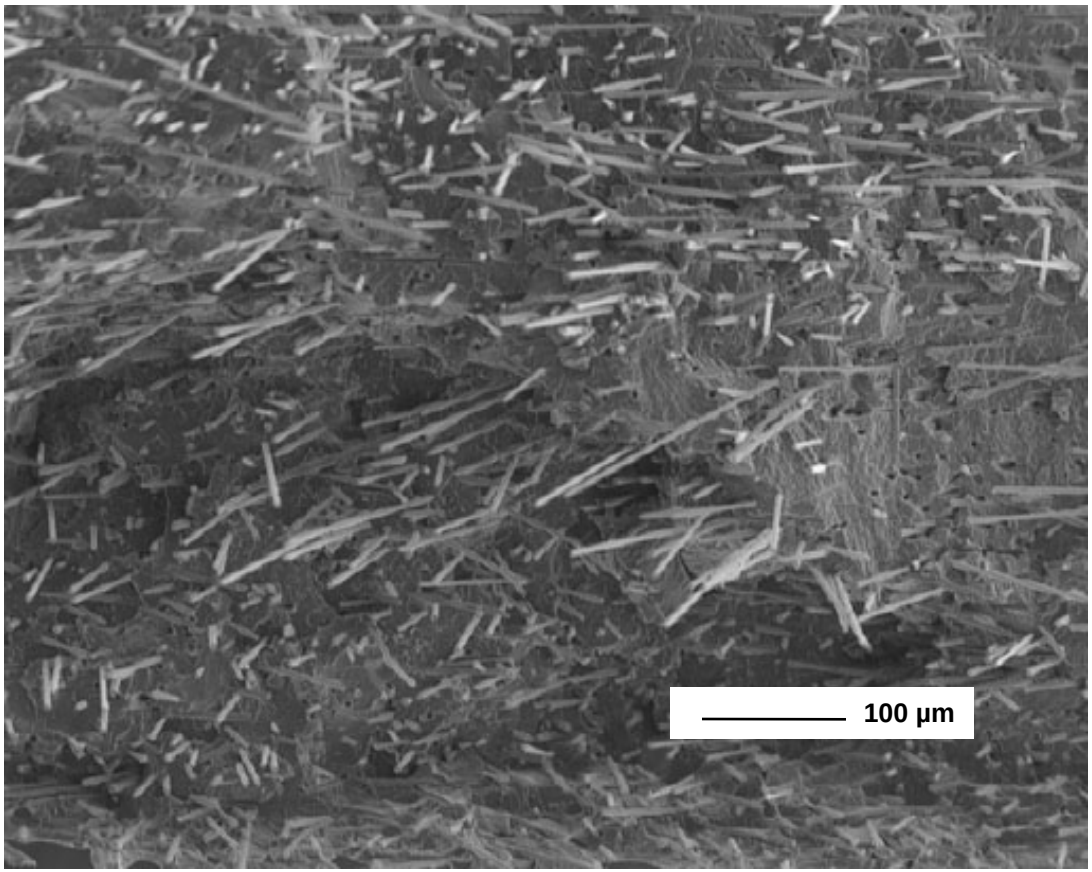


Fig. 7b: SEM Analysis of Surface: R-talc Sample

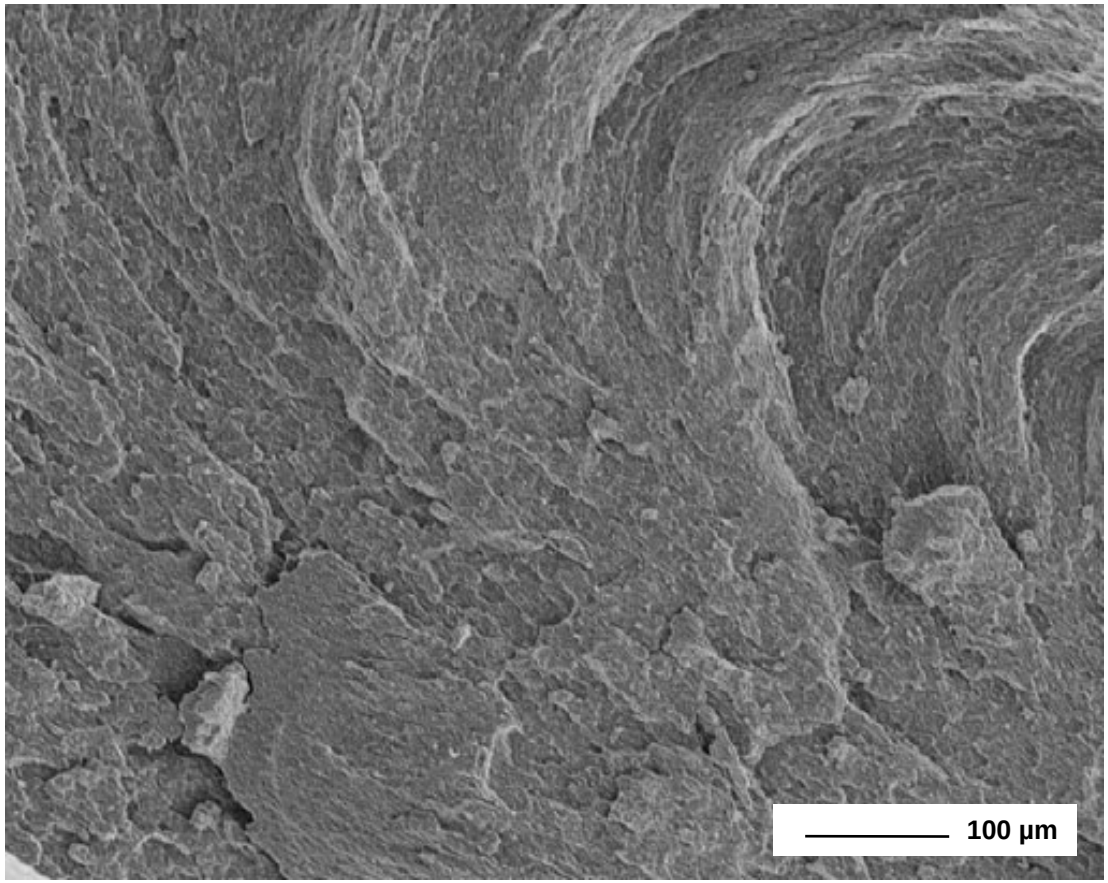
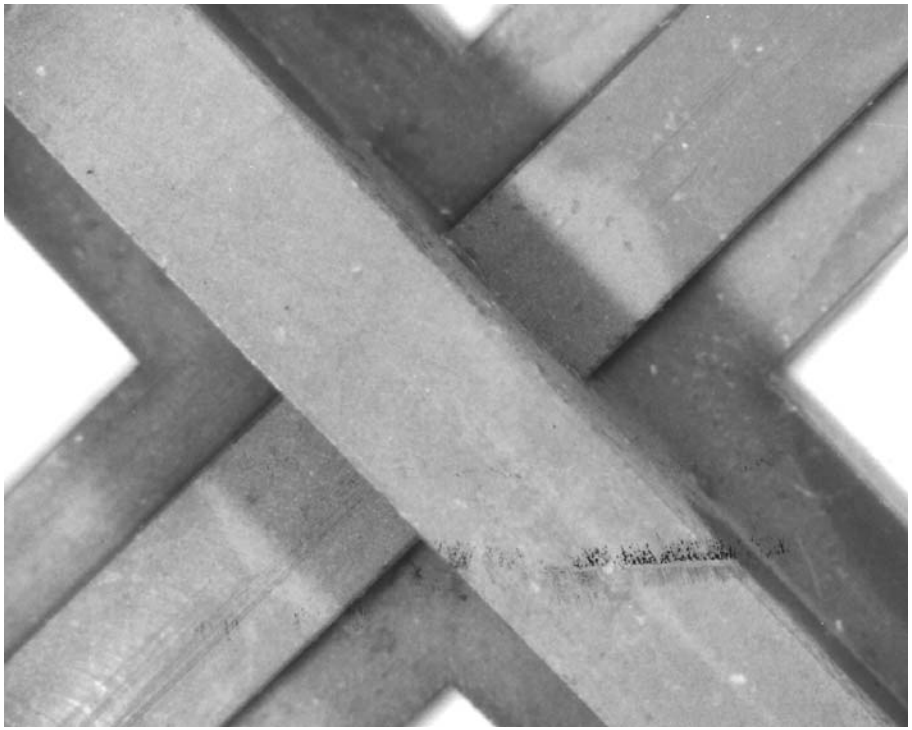
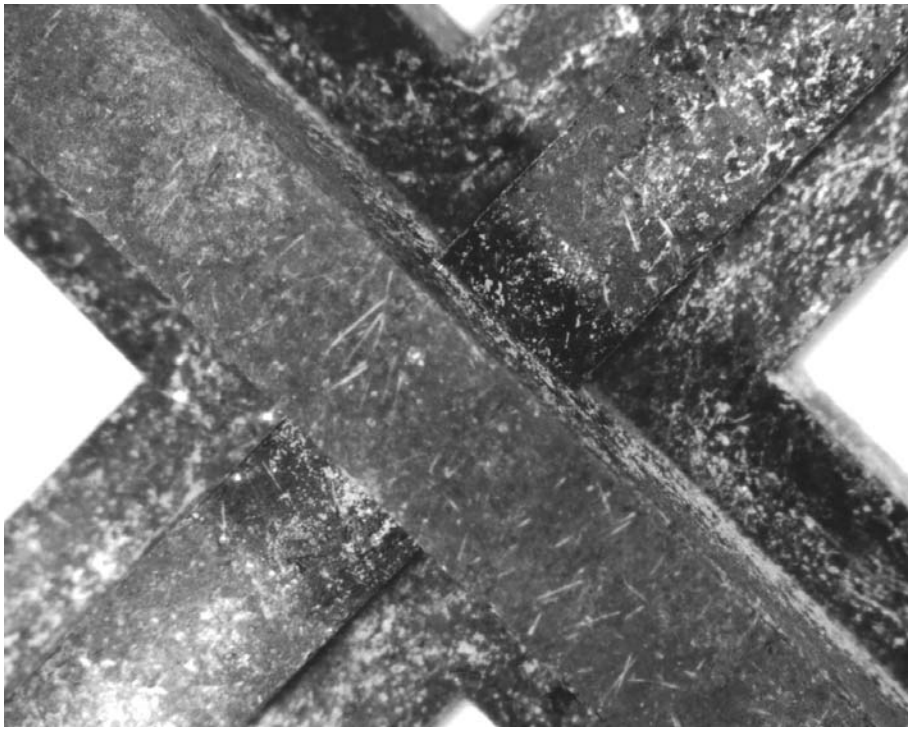


Fig. 8: Stereomicroscope Image of Phase II Trial Racks; Center Detail

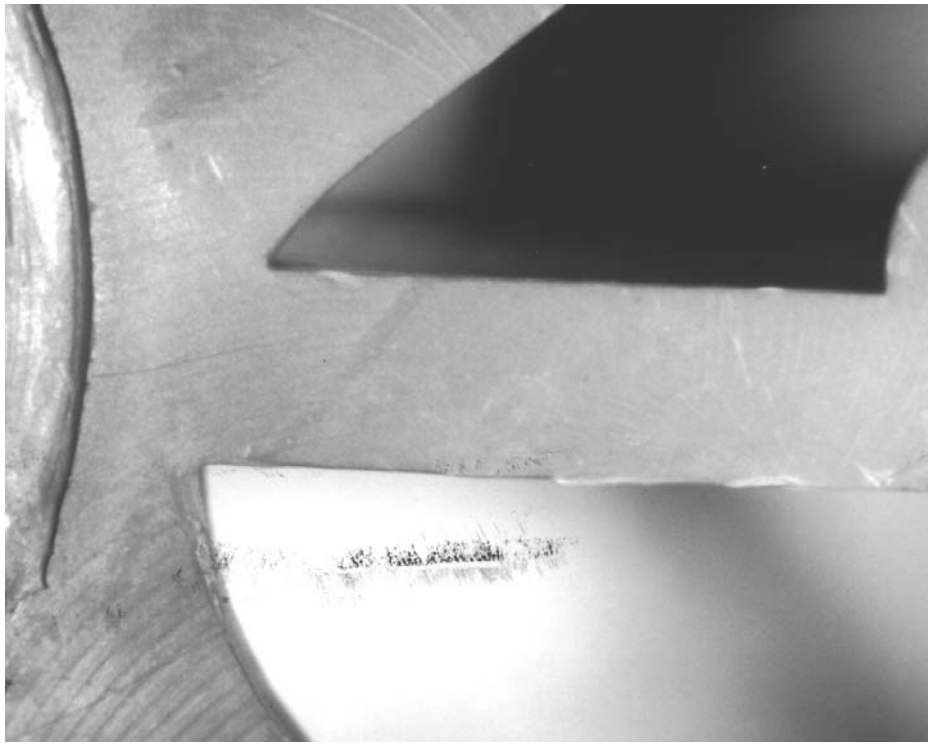


Trial Material
(R7-Talc modified PP)

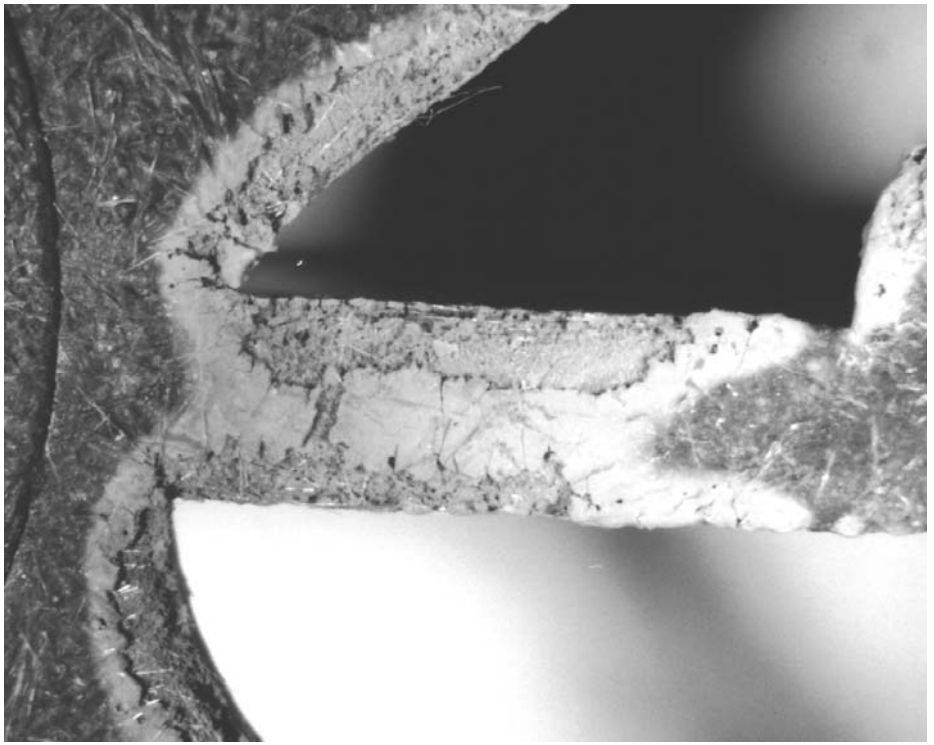


Reference Material
(Glass Fiber modified PP)

Fig. 9: Stereomicroscope Image of Phase II Trial Racks; Corner Detail (high wear area)

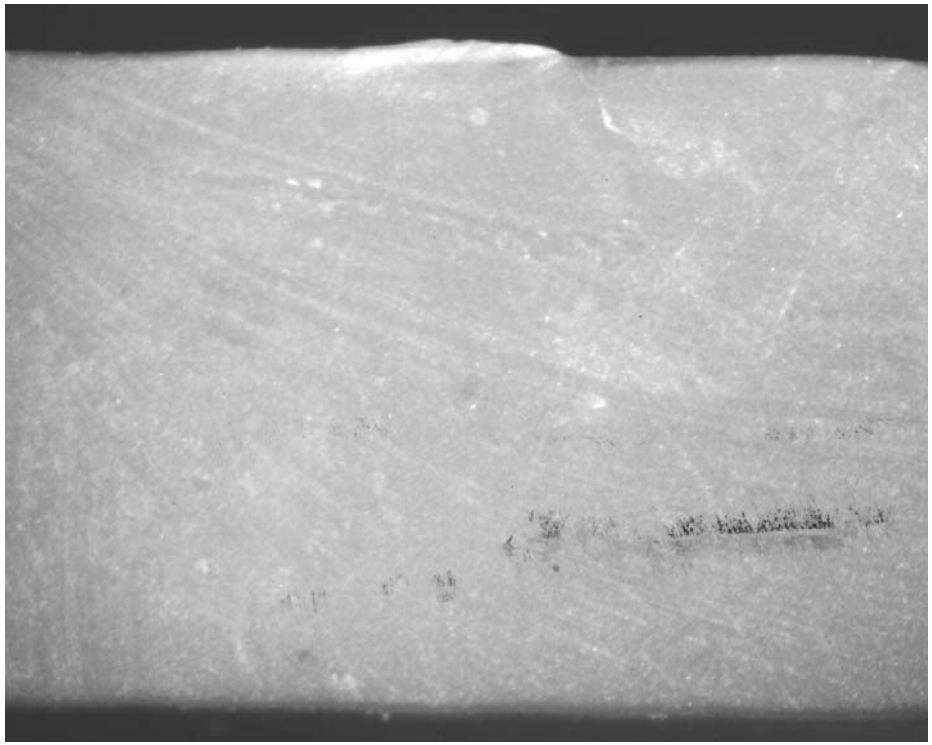


Trial Material
(R7-Talc modified PP)

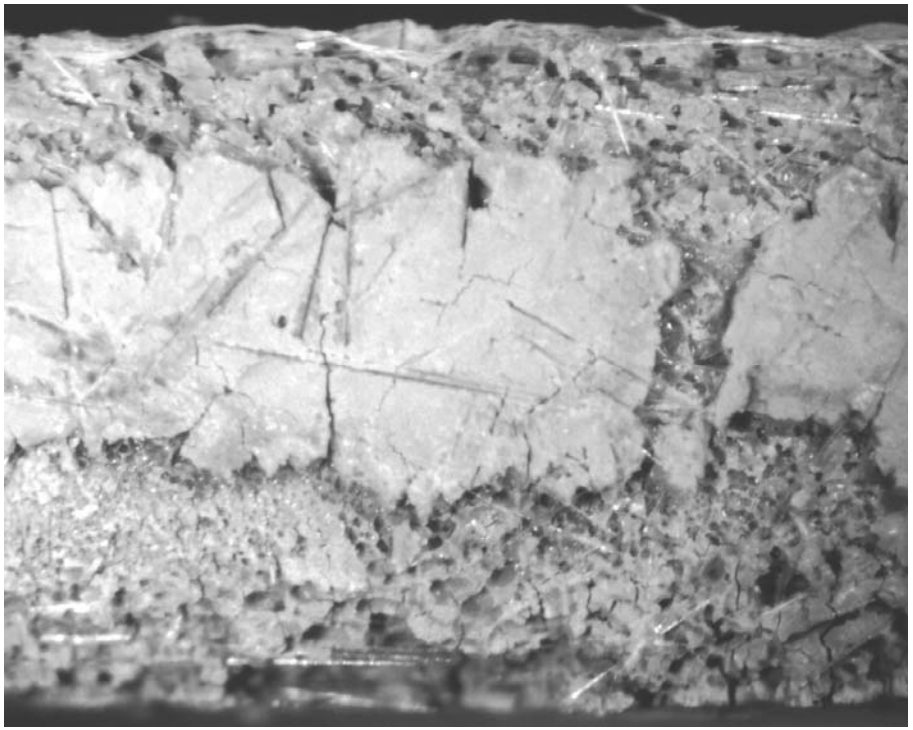


Reference Material
(Glass Fiber modified PP)

Fig. 10: Stereomicroscope Image of Phase II Trial Racks; Wear Close-up



Trial Material
(R-Talc modified PP)



Reference Material
(Glass Fiber modified PP)